THE CHEMICAL IMPACT OF PHYSICAL CONDITIONS IN THE INTERSTELLAR MEDIUM

DISSERTATION

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By

Paul Brandon Rimmer, B.S. Physics Graduate Program in Physics

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Dissertation Committee: Eric Herbst, Co-Adviser Richard Freeman, Co-Adviser John Beacom Gregory Lafyatis Pierre Agostini © Copyright by

Paul Brandon Rimmer

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ABSTRACT

We examine the role cosmic rays, X-rays and ultra-violet (UV) photons play in the chemical evolution of the interstellar medium, and how astrophysical processes like massive star formation can change the fluxes of these energetic particles. We connect star formation rates to interstellar chemistry.

We first explore the basic effects of cosmic-ray and X-ray ionization and UV photodissociation (scaled by a factor, χ) on the chemistry. For cosmic-ray and X-ray ionization, increasing the ionization rates ζ and ζ_X (s⁻¹) enriches the chemistry, up to $\zeta \sim 10^{-14}$ s⁻¹, whereupon molecules and ions are quickly destroyed due to the high electron fraction. Isolated from other effects, the UV field tends to dissociate species much more efficiently than ionizing them, and generally reduces molecular abundances, especially those of complex molecules. The combination of a high $\zeta \sim 10^{-15}$ s⁻¹ and a high UV field ($\chi = 60$) can enhance the production of some molecular species, such as small hydrocarbons.

We investigate the role of cosmic rays and UV photons in the Horsehead Nebula, and determine the impact a column-dependent cosmic ray ionization rate makes on photodissociation region (PDR) chemistry. The column-dependence of ζ is solved using a three-dimensional two-fluid magnetohydrodynamics model, treating the cosmic rays as a fluid governed by the relativistic Boltzmann Transport Equation, and treating the interstellar medium as a second fluid, governed by the standard non-relativistic magnetohydrodynamics equations.

We then utilize a modified version of the Morata-Herbst time-dependent PDR model, incorporating our function for ζ . Our results help solve a chemical mystery concerning high abundances of small hydrocarbons at the edge of the nebula. We discuss predictions the model makes for species currently unobserved in the Horsehead Nebula. Finally, we examine the role of star formation on interstellar astrochemistry in the Orion KL region. We develop a new astrochemical gas-grain PDR model with a time-dependent UV radiation field and X-ray and cosmic ray flux, scaled to the star formation rate and radiative contributions of different spectral-type stars. The results provide an explanation for OH^+ , H_2O^+ and water observations, and H_3O^+ non-detection in the region, as well as make unique predictions for HCO^+ and other molecules. These results allow us to constrain the age of the Orion KL region to $10^5 - 10^6$ years after OB star formation.

To my wife.

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VITA

March 18, 1983	Born - Denver, Colorado, USA
May 2005	B.S. Physics, Magna Cum Laude, Uni-
	versity of Colorado Health Sciences Cen-
	ter in Denver, Colorado, USA
September 2005 - March 2007	Graduate Teaching Assistant at the Ohio
	State University Physics Department in
	Columbus Ohio, USA
March 2007 - Present	Graduate Research Assistant at the Ohio
	State University Physics Department in
	Columbus Ohio, USA

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Chapter 1 INTRODUCTION

θεοὺς μὲν αίτῶ τῶνδ΄ ἀπαλλαγήν πόνων φρουρᾶς ἐτείας μῆκος, ἕν κοιμώμενος στέγαις Άτρειδῶν ἄγκαθεν, κυνὸς δίκην, ἄστρων κάτοιδα νυκτέρων ὀμήγυριν, καὶ τοὺς φέροντας χεῖμα καὶ θέρος βροτοῖς λαμπροὺς δυνάστας, ἐμπρέποντας αἰθ/ερι ἀστέρας, ὅταν φθίνωσιν, ἀντολάς τε τῶν.

- ΑΙΣΧΥΛΟΣ, ΑΓΑΜΕΜΝΩΝ, 1-7¹

Commonplace depictions of Chemistry on earth usually include images of large hexagonal arrangements of carbon saturated with hydrogen. Pressures are measured in Torr, gas and solution are in thermodynamic equilibrium. Reaction times are counted in nanoseconds. These terrestrial interactions, so familiar to most who study them, are in fact rather unique manifestations in our universe.

The vast majority of chemistry in the universe is nothing like this. Carbon is free, or when bound, is tied to oxygen or arranged in lines instead of hexagons. Most carbon is hydrogen-poor, and hydrogen, the most abundant element, is itself free or bound up in pairs. Figure 1.1 re-purposes the periodic table of elements so that the size of each square is proportional to interstellar abundances, showing us how "standard" chemical relationships are transformed in the interstellar medium. In the small fraction of the interstellar environment that has interesting chemistry, reactions often occur outside thermodynamic equilibrium, and are driven by non-thermal processes involving the intro-

¹Eng. Tr. A plea to the gods throughout this years-long watch // Release me from my enduring task // I crouch like a dog upon my lord's high tower // I have learned the secret whispers of the stars // the bright-shining powers blinking in the night // They show the seasons' change unto mankind // and trace the time as they rise and set.

duction of light or high energy particles from violent outside sources.

Density is measured in handfuls of particles per cubic centimeter. Pressures are at the edge of the best laboratory vacuums. Interstellar space is, for the most part, cold and sparse. Because of the low kinetic energies and low densities, collisions occur over a matter of seconds or minutes, and reaction rates are measured by the scale of days or years. Thermodynamic equilibrium is often impossible; steady state, a phase when all chemical abundances are constant in time, is often a convenient fiction, because the time-scale for steady state is on the order of astronomical timescales: typically millions of years or more. The parameters describing the interstellar chemical environment are not constant over such a long period of time.

Understanding this dynamic chemical environment is vital, because it is sensitive to interstellar conditions, time-dependent, and the results of interstellar chemistry can be observed and measured. These results can be compared to laboratory experiments and theoretical chemical models, and may help us understand both the changing environment in which stars form, as well as the chemistry that preceded life's origins. The focus of this thesis will be on aspects of theoretical astrochemistry and related chemical models, but theoretical investigations of this nature, if they are to be meaningful, must be essentially linked to both observation and experiment.

1.1 Astrochemical Modelling

Once atomic and molecular species are observed in various interstellar environments (Section 1.2), and once we have calculated or experimentally determined the ways these species could be formed or destroyed in their environment, we should try to figure out why the abundance is what it is, and how the molecule or atom came to be there. This is where astrochemical models come in. These models take the best information about the physical conditions in the interstellar medium, the most comprehensive rates, and evolve a network of chemical kinetics equations to determine species abundances. The results of a model can be compared to observations, and unique models will ideally make new predictions which can validate or falsify particular chemical or astrophysical theories.

Astrochemical models rely on temperature as a parameter. Though the interstellar medium is



Figure 1.1: Periodic table in the interstellar medium. The size of the square is proportional to standard interstellar elemental abundances. From McCall (2006).

in general far from thermodynamic equilibrium, the great number of particle collisions over astronomical time-scales allows the velocity to come into a Maxwell-Boltzmann distribution, with variations to this distribution too small to significantly affect the chemical kinetics, according to Spitzer (1998), though this claim has been recently challenged (see Black 2010). The distribution of velocities allows us to define a kinetic temperature, although this temperature will not be associated with a typical radiation field, and so atomic levels may be populated according to a separate excitation temperature (see Section 1.2).

Astrochemical modelling began soon after the first molecules were observed, but did not really develop until ion-neutral reactions were included. Hayakawa et al. (1961) developed the first kinetics method applied to the interstellar environment, and McNally (1962) built a small model to predict the observations of CH and CH⁺, assuming formation on the surface of dust grains. Gould (1962) attempted to apply a rate method calculation to the molecular hydrogen problem, with some success. The first robust astrochemical model was developed ten years later by Watson & Salpeter

(1972), but this model did not include ion-neutral reactions, and so many species that would otherwise have been very abundant did not form quickly enough. This problem, and the inaccuracy of the rates utilized, did not result in good agreement between predictions and abundances. Watson & Salpeter (1972) state as much at the end of their paper.

One year later, Herbst & Klemperer (1973) developed a full astrochemical network, incorporating ion-neutral reactions. This important addition led to numerous accurate predictions, and opened the way to many future astrochemical models. In a similar way, the work of Tielens & Hagen (1982) with gas-grain networks resulted in an improved predictive power for larger molecules and surface-dependent species. With the inclusion of a better understanding of the interstellar environment (McKee & Ostriker 1977), van Dishoeck & Black (1986) were able to take chemical observations and use them to infer physical conditions in various clouds. In an important way, this thesis is a continuation of their work. After 1990, there were two dominant gas-phase networks, the Ohio State University Gas-Phase Network developed by Eric Herbst, grown from his original paper (Herbst & Klemperer 1973), and the UMIST Database for Astrochemistry, constructed by Millar et al. (1991).

The first successful application of a gas-phase chemistry that properly incorporated dust extinction (from Draine 1978) and self-shielding is the work of Tielens & Hollenbach (1985). Since then, astrochemical networks have come to include gas-grain reactions with photodesorption and thermal desorption (Garrod et al. 2008), consequences of uncertainty in the rate (Wakelam et al. 2005) and a very wide temperature range, from 10 K to 800 K (Harada et al. 2010). More mathematically involved modelling methods have been incorporated, including modified rate methods (Caselli et al. 1998), Master-Equation or stochastic methods (Stantcheva et al. 2002), moment equations (Barzel & Biham 2007) and microscopic and macroscopic Monte Carlo calculations (discussed in Cuppen & Herbst 2005; Vasyunin et al. 2009). Most of these methods have been developed to better account for surface chemistry. Various physical effects have now been accounted for in detail, such as cosmic rays (Rimmer et al. 2012; Bayet et al. 2010) and X-rays (Meijerink et al. 2012). This thesis will explore the connection between the UV field, cosmic rays and X-rays, all changing in time and depth, and the impact they have on interstellar chemistry.

1.1.1 Rate Method

The standard rate method involves the concept of smooth changes in species abundances over timescales much longer than the reaction times, and at high enough absolute abundances such that there is more than one molecule of a given species available to enter into a reaction.

Imagine all the molecules in a box, and the molecules are moving around, along with light particles and X-rays and cosmic rays and grains of dust. At any given time from t to t + dt, there is a probability that one particular species, A, with number density (represented with brackets only in this section), [A], will be destroyed by being struck with a light particle. There is also a probability it will collide with another species, say species B, and react. Or it may be that species C and D interact to form an A.

All of these effects can be be accounted for by a differential equation, and the probabilities over dt are accounted for by rate coefficients. Formation reactions for species A can be accounted for with the rate coefficients k_f^A ; destruction reactions with the coefficients k_d^A . It is important to note that a formation rate coefficient for A may be a destruction coefficient for B, etc.

Rate coefficients that account for first-order processes $(k_{f,0}^A)$ have units of s⁻¹. These coefficients represent interactions between chemical species and light, dust grains or something else not coupled to the chemistry. Rate coefficients that account for second-order processes represent interactions between species, say *A* and *B* for $k_{f,1}^{AB}$, and have units of cm³ s⁻¹. Third order processes, which we do not incorporate, represent three-body collisions, very uncommon even in the denser regions of the interstellar medium. The rate coefficients have units of cm⁶ s⁻¹ and would be noted here as $k_{f,2}^{ABC}$.

A standard rate equation is of the form:

$$\frac{d[A]}{dt} = k_{f,0}^{A}[B] + k_{f,1}^{CD}[C][D] - k_{d,0}^{A}[A] - k_{d,1}^{AE}[A][E].$$
(1.1)

There exists an equation like this for every species, [A], [B], ..., and the system of equations must be solved simultaneously. Often the way that this system is solved is by treating it as a steady state system. Presumably, if you leave the system to evolve for a long enough time, it will stabilize, and the destruction and formation rates will achieve a balance. This effectively involves setting all of the differentials to zero, i.e. d[A]/dt = 0. The equation above can be solved for [A] as:

$$[A] = \frac{k_{f,0}^{A}[B] + k_{f,1}^{CD}[C][D]}{k_{d,0}^{A} + k_{d,1}^{AE}[E]}.$$
(1.2)

If there are as many equations are there are unknowns, and if there are only first order and second order rate coefficients, then the problem can be solved by placing all the different values into a $n \times n$ matrix **M**, where the diagonal entries are negative and involve destruction reactions and the off-diagonal entries involve formation reactions. For example, the 1,1 entry has all the destruction processes for A ($-(k_{d,0}^A + k_{d,1}^{AE}[E])$) and the rest of the rows in the first column have the formation processes for A: the 1,2 entry is formation involving species $B(k_{f,0}^A)$; the 1,3 is formation involving species $C(k_{f,1}^{CD}[D])$, and so on; it is important to make sure reactions are not double-counted by this method. The system of equations can be put into the form of this matrix equation:

$$\mathbf{M}|S\rangle = |0\rangle,\tag{1.3}$$

where $|S\rangle$ is a column-vector with elements [A], [B][C], ..., and $|0\rangle$ is a column-vector with only zero-values. Note that this equation contains no information about the initial conditions of the system, and so the steady-state solution is independent of initial conditions. By this definition, few codes are genuinely steady-state models. The Meudon PDR code, for example, applies initial abundances to the solution, and so has some sort of initial conditions, even though it is time-independent. In many cases, initial abundances are applied to time-dependent calculations that are evolved until they achieve steady state. This is because solving the series of differential equations is interestingly often faster than solving Equation (1.3).

An algorithm has been developed to solve the kinetics as a system of coupled differential equations with completely defined initial conditions, and has been optimized for this and related problems. The algorithm is called the Gear algorithm, after Gear (1971). This algorithm is somewhat involved, and the technical level of its components will require that we skip over details here. In brief overview, if the differential equations are not stiff, the algorithm will solve these equations by placing them in the form $d/dt|S\rangle = |f(|S\rangle, t)\rangle$, where $|f(|S\rangle, t)\rangle$ contains the rate equations, and is of a form very similar to $\mathbf{M}|S\rangle$. The algorithm determines the Jacobian, $J = \partial f/\partial |S\rangle$. Because the chemical kinetics assume conservation of the elemental abundances over time, the eigenvalue of the differential will be negative, and so the dynamic equation involving the Jacobian:

$$\frac{\partial f}{\partial |S\rangle} |S\rangle = \lambda(|S(0)\rangle) |S\rangle, \tag{1.4}$$

will always yield a stable solution. The Eigenvalue λ is solved by determining the Jacobian and then applying the initial values for $|S\rangle$, $|S(0)\rangle$, taking the determinant, and finally solving for λ from the polynomial.

The computational efficiency of the Gear Algorithm is best described as preternatural. It is eerily fast, much faster than the steady-state calculations under most conditions. It can be quickly applied to the complex system of the gas-grain network, involving over a thousand coupled differential equations, and will yield a solution in a matter of minutes. The system can be evolved out to many times the characteristic time-scale for the problem. A typical characteristic time is 10^9 seconds, so the algorithm can quickly determine the chemistry at times $\geq 10^8$ years. For the gas-phase models, the Gear solution eventually falls into the steady-state solution. When surface reactions are included, the system may never settle into steady state. There is nothing requiring it to do so. In our case, we often change the parameters applied to the Gear algorithm, sometimes rapidly, and this can create problems for the algorithm. In the future, someone needs to recalculate accuracies in the Gear algorithm, to find out what effect rapidly changing parameters has on the method.

1.1.2 Estimating Rates

There are different kinds of rates incorporated into the kinetics equations. We have already, in Section 1.1.1 discussed first order, second order and third order processes. First order processes are incorporated in the kinetics equation as a way to couple physics and chemistry within the astronomical environment, and therefore will be discussed below, in Section 1.3. Third order processes are entirely neglected in our models. Therefore we will be concentrating here only on second-order processes. The discussion in this section closely follows Draine (2011).

The rates we discuss in this section deal with two-body interactions, and there are a variety of ways two bodies can interact. They may collide without reacting, or may swap electrons without changing their chemistry. The rates for these sorts of interactions are neglected, because they do not impact the chemistry, but rates for collisions like this can be important when distinguishing

between ortho and para nuclear-electron spin coupling, a very important investigation into the interstellar medium (Uy et al. 1997, for example). Other reactions we consider do change the chemistry. We divide the reactions into groups. The different reactions reviewed below are charge-exchange reactions, ion-neutral reactions, neutral-neutral reactions, electron recombination reactions and radiative association reactions.

Charge exchange reactions are of the form:

$$A^+ + B \to A + B^+. \tag{1.5}$$

The rates for this reaction are determined by comparing the two potential surfaces (one for $A^+ + B$ and another for $B^+ + A$). Though semi-classical methods can be applied to solve for reaction rates in this regime, often the rates are determined quantum mechanically (see Stancil et al. 1999). The rates, if conditions are favorable, tend to be on the order of 10^{-8} cm³ s⁻¹ (see, for example Draine 2011).

Ion-neutral reactions often dominate gas-phase astrochemistry, despite the low abundance of ions. This is because of the high reaction rates. Ion-neutral reactions are of the form:

$$A^+ + B \to C^+ + D. \tag{1.6}$$

Note the similarity between Reaction (1.6) and Reaction (1.5). If C = B and D = A, then the two reactions are identical. Therefore, intuitively, we might expect these reactions to be within an order of magnitude to the charge-exchange, or 10^{-8} cm³ s⁻¹, and in many cases we would not be too far off. The rates for these reactions can be calculated quantum mechanically, or they can be estimated by considering the problem semi-classically. The ion will come close to the neutral species, and induce a dipole (r^{-3} term) with polarizability α . The ion contains the coulomb term of r^{-2} , resulting in a force term of r^{-5} , or a potential of the form:

$$U(r) = -\frac{1}{2} \frac{\alpha Z^2 e^2}{r^4}.$$
 (1.7)

We can develop a cross-section $\sigma = \pi b^2$, where *b* is a parameter achieved by comparing the kinetic energy $T = 1/2\mu v^2$ (μ is the reduced mass) with the potential energy from Equation 1.7. Setting

U(b) = -T/4 and solving for b, we find that the cross-section is:

$$\sigma = 2\pi Z e \left(\frac{\alpha}{\mu v^2}\right)^{1/2}.$$
(1.8)

Rate coefficients can be estimated by the formula:

$$k = \langle \sigma \upsilon \rangle, \tag{1.9}$$

and σ for ion-neutral reactions is proportionate to 1/v, so the rate is independent of v, and therefore independent of temperature. It is approximately the Langevin rate:

$$k = 2\pi Z e \left(\frac{\alpha}{\mu}\right)^{1/2},\tag{1.10}$$

and is typically of order 10^{-9} cm³ s⁻¹. The fact that the reaction, if without barrier, is independent of temperature, is interesting, and is one of the reasons ion-neutral reactions are so powerful in the interstellar environment.

Often neutral-neutral reactions will become much less rapid at lower temperatures, while ionneutral reaction rates remain constant over change in temperature. Of course, the temperature independence is somewhat a fiction, because the ion induces a dipole in the neutral species and this affects the rate. There are also unaccounted-for quantum effects. The trajectory of reaction that we consider has the ion passing through the origin of the neutral species, and this cannot be the case. Careful consideration of these effects will sometimes apply a weak temperature dependence of $T^{-1/2}$ to the rates.

Neutral-neutral collisions are of the form:

$$A + B \to C + D \tag{1.11}$$

and induce dipoles in both species, and so have an attractive potential $U(r) \propto r^{-6}$. This is often treated as the Lennard-Jones Potential. The potential has proportionality constants, α_{LJ} and the radius, r_{\min} at which:

$$\left(\frac{dU}{dr}\right)_{r_{\min}} = 0. \tag{1.12}$$

The potential has a repulsive term $\propto r^{-12}$, and appears as:

$$U(r) = 4\alpha_{LJ} \left[\left(\frac{r_{\min}}{r} \right)^{12} - \left(\frac{r_{\min}}{r} \right)^{6} \right], \tag{1.13}$$

where α_{LJ} is determined quantum mechanically, or via various semi-classical approximations. The cross-section can be determined from Equation (1.13) in the same manner as Equation (1.8) was derived from Equation (1.7). If we impose the hard-sphere approximation, where we treat the two species as solid spheres of radii R_1 and R_2 , we can then estimate the rate for neutral-neutral interactions to be (at LTE):

$$k = \langle \sigma \upsilon \rangle = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \pi (R_1 + R_2)^2. \tag{1.14}$$

Since $\sigma = \pi (R_1 + R_2)^2 \approx 10^{-15} \text{ cm}^2$, the average value for these rates is at $\sim 10^{-11} - 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, and is temperature-dependent. If the reaction has no barrier, the temperature dependence is typically $\propto T^{1/2}$ (note the opposite sign for neutral-neutral reactions than for ion-neutral reactions), and if there is a barrier, as is often the case, the rate is greatly reduced by a factor of $e^{-E_a/kT}$, where E_a is the activation energy.

Recombination reactions are of the two types:

$$A^{+} + e^{-} \to A + h\nu; \tag{1.15}$$

$$A^+ + e^- \to C + D, \qquad (1.16)$$

referred to as radiative recombination and dissociative recombination, respectively. The reaction must induce change in the products, either by the electron releasing energy in the form of light, or by dissociating the reactant. The basic Coulomb attraction dominates the interaction rate. Radiative recombination can typically be estimated to good accuracy quantum-mechanically, and rates are typically on the order of $10^{-12} - 10^{-11}$ cm³ s⁻¹.

The bulk rate for dissociative recombination involves considering whether the input energy of the electron is sufficient to break bonds. This rate is typically very high, and of the form $k \sim 10^{-7} (T/300 \text{ K})^{-1/2} \text{ cm}^3 \text{ s}^{-1}$. The great challenge is in determining which electron bonds will be broken. Calculating branching ratios often involves detailed *ab initio* methods, and even then, uncertainties are often very high. Cyclotron experiments utilizing storage rings have been of great

use in constraining these branching ratios. In some cases, branching ratios are guessed based on the energetics of the different possible products; this guessing method is used very often, and when compared with detailed quantum mechanical calculations and experiments (where available) is often quite inaccurate.

We will briefly touch on radiative association rates, which are of the form:

$$A + B \to AB + h\nu. \tag{1.17}$$

These reactions are necessary when the interaction between the two species favors elastic collisions, and some energy would have to be released for the reactants to become bound to a product. Typically, in terrestrial conditions, a third body interacts with A and B and absorbs the excess energy, allowing the A and B to combine to form AB. In the ISM, this is not the case, because the density is too low for three-body collisions. Radiative rates often involve forbidden transitions, and are therefore typically very low. The classic example is the formation of molecular hydrogen:

$$\mathbf{H} + \mathbf{H} \to \mathbf{H}_2 + h\nu, \tag{1.18}$$

which has a rate of $< 10^{-20}$ cm³ s⁻¹ (Gould & Salpeter 1963), and would not produce observed amounts of molecular hydrogen over the age of the universe.

Fortunately, there is another very efficient mechanism for hydrogen formation. Molecular hydrogen can form on the surface of grains, with the grain absorbing the excess energy in the reaction, thermalizing the energy in its many available modes (Gould & Salpeter 1963). It turns out that many molecular species form on the surface of grains, and surface chemistry is now an important part of astrochemical modelling. Surface reactions, though three-body interactions technically, are often split up into the event of adsorption onto a grain, reaction on the grain, and desorption off of the grain. These mechanisms are discussed in greater detail in Chapter 4.

All two-body rate coefficients can be parametrized for second-order processes in terms of three values, α , β and γ , where α is the temperature-independent rate, β is the exponent for power-law temperature dependence, and $\gamma = E_a$, and accounts for endothermicity or for reaction barriers. Rate

coefficients for second-order processes are therefore expressed as:

$$k = \alpha \left(\frac{T}{300\mathrm{K}}\right)^{\beta} e^{-\gamma/kT}.$$
(1.19)

First-order processes, discussed in Section 1.3, have a different parametrization.

The predictions astrochemical models make are in terms of abundances, and abundances must be inferred spectrocopically. A careful understanding of spectroscopy is therefore necessary in order to compare theory to observation.

1.2 Observing Chemistry in the Interstellar Medium

Chemical abundances in the interstellar medium are estimated from characteristic transitions of these species. The relative strength of these transitions, and the shape of the lines tells us a great deal about the environment in which the chemical exists, as well as the amount present. There are various relevant aspects to transition profiles: the rest frequency of the transition, the velocity shift, the velocity profile, and the strength of the transition. A discussion of transition energies follows closely the work of Bernath (2005), his Chapters 6 and 7. The review of transition strengths and Einstein coefficients uses both Friedrich (2006), his Section 2.4 and Bernath (2005), Chapter 1.

The rest-frequency of a transition is determined by quantum mechanical properties of the species. The transitions are separated into three kinds: electronic, vibrational and rotational. Rovibrational transitions are illustrated in Figure 1.2. The frequencies for these transitions are related to the energies, and these electronic energy states are determined from the eigenfunction of the electronic Hamiltonian through the Born-Oppenheimer approximation.

Molecular species have characteristic vibrational states that are determined quantum-mechanically as eigenvalue solutions to the Schrodinger Wave Equation with a harmonic potential. We consider only the diatomic molecule in the J = 0 rotational state, with a potential of $\frac{1}{2}kx^2$, where k is the spring constant and $x = r - r_e$ is the displacement from the equilibrium distance. Applying standard solutions from a Taylor expansion of the harmonic-oscillator potential about the equilibrium position, we find the energies of the vibrational states for a non-rotating diatomic molecule. The energy is represented in terms of the reduced mass (for a diatomic molecule with atomic masses m_1 and *m*₂):

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2},\tag{1.20}$$

the spring constant, and the vibrational quantum number v. The vibrational energies are:

$$E_{\nu} = hv_0 \left(\nu + \frac{1}{2} \right),$$
 (1.21)

where $h = 6.626 \times 10^{-27}$ erg s is Planck's constant, and:

$$\nu_0 = \frac{1}{2\pi} \left(\frac{k}{\mu} \right). \tag{1.22}$$

The vibrational states for larger linear molecules and non-linear molecules are far more complex, because of the variety of vibrational modes. For example, water (H_2O) has three characteristic vibrational modes: the O-H bend, the symmetric O-H stretch and the asymmetric O-H stretch, which form the basis set for the vibrational energies of water.

For linear molecules, the rotational energy depends on the rotational quantum number J, the moment of inertia scalar for the linear molecule, and factors describing higher order terms in the Hamiltonian characterizing the motion. A rotational level J has energy:

$$E_{J,\nu} = B_{\nu}J(J+1) - D_{\nu}[J(J+1)]^2 + \dots$$
(1.23)

For v = 0, the first term is the Eigenvalue solution to the simple Hamiltonian (\hat{H}) :

$$\hat{H} = \frac{1}{2I}\hat{J}^2;$$
 (1.24)

$$\hat{I}^2 |\psi\rangle = J(J+1)|\psi\rangle. \tag{1.25}$$

This has a characteristic energy of $B_e J(J + 1)$ where $B_e = \hbar/2I$ and $\hbar = \hbar/2\pi$. For $\upsilon > 0$, the vibrational excitation changes the average separation between the atoms, and affects the energy such that (for a diatomic molecule):

$$B_{\nu} = B_{e} - \alpha_{e}(\nu + 1/2) + \dots, \qquad (1.26)$$

where α_e is also characteristic of the system, and is typically ~ $10^{-2}B_e$. The next term in Equation (1.23) represents the centrifugal distortion. The linear molecule is not strictly a rigid rotor, and the

angular momentum will affect the internuclear spacing. D_{ν} captures this distortion, where for $\nu = 0$, $D_{\nu} = D_e$ and:

$$D_e = \frac{B_e^2}{\pi^2 v_0^2},$$
(1.27)

where B_e is from Equation (1.26) and v_0 is from Equation (1.22). When v > 0, the centrifugal distortion is also affected, and:

$$D_{\nu} = D_e + \beta_e(\nu + 1/2) + \dots \tag{1.28}$$

The value of D_{ν} is characteristic to the molecule, and is typically much smaller, on the order of $10^{-6}B_e$. Because transitions can be calculated and measured to impressive accuracy, these small factors can become very important when calculating transition energies.

Molecular geometry is very important for determining transition energies and strengths. Rotational transitions for linear molecules can be described by treating the molecule as a rod, with one or two axes of symmetry, therefore reducing the quantum numbers necessary to describe the transition to one. Some non-linear molecules also have a single axis of symmetry, such as symmetric rotor molecules, for example ammonia (NH₃), where the three hydrogen atoms form a "tripod" below the nitrogen atom. The rotational states for symmetric rotors can be described by both the total rigid framework angular momentum, *J*, and the projection of this momentum into the axis of symmetry *K* (where K = -J, ..., -1, 0, 1, ..., J). The proportionality for these two quantum numbers depends on the two eigenvalues of the moment of inertia tensors, *I_A* and *I_B*. In the case of the prolate symmetric top, *I_B* is the eigenvalue for the degenerate eigenstate; for the oblate symmetric top, *I_A* and the energy of the *J*, *K* state is:

$$E_{J,K} = BJ(J+1) + (A-B)K^2, \quad \text{for a prolate top, and}$$
(1.29)

$$E_{J,K} = AJ(J+1) + (B-A)K^2, \quad \text{for an oblate top.}$$
(1.30)

Asymmetric rotor molecules have no axis of symmetry, and are described by a single quantum number, $L^2 = L_x^2 + L_y^2 + L_z^2$, where each of the values L_x, L_y, L_z change with the motion. There is no exact solution for asymmetric rotors. In addition to having more complicated rotational and vibrational modes when compared to diatomic molecules, polyatomic molecules may also have other modes, such as torsional modes, which will not be discussed here.

Examples of velocity profiles for absorption transitions for OH^+ , H_2O and HF in Orion KL are given in Figure 1.3.

Transition strengths can be quantified in terms of Einstein Coefficients. We will describe a simple two-state system, S, with a state ℓ and a state u, with energies $E_u > E_{\ell}$. The first Einstein coefficient we consider is the coefficient for the reaction:

$$S(u) \to S(\ell) + h\nu, \tag{1.31}$$

with a rate coefficient of $A_{u\ell}$. In order to calculate this coefficient, we first consider the case where the electromagnetic field before the transition is empty, and after the transition the field contains one photon of energy $\Delta E = E_u - E_\ell$ and polarization vector $\hat{\pi}$. The resulting field can be quantified in terms of the vector potential, **A**, and a scalar electrostatic potential, Φ . If we adopt the radiation gauge, we set $\Phi = 0$ for the Hamiltonian, and if we ignore higher-order terms (A^2 , etc.), the Hamiltonian can be approximated in terms of the electronic Hamiltonian, $\hat{H}_e = \sum_i \hat{p}_i/2\mu + \hat{V}$, the electromagnetic Hamiltonian, $\hat{H}_{\rm EM}$, and the first-order interaction between the atom and electromagnetic field, \hat{W} , treated as a perturbation:

$$\hat{H}_0 = \hat{H}_e + \hat{H}_{\rm EM};$$
 (1.32)

$$\hat{H} = \hat{H}_0 + \hat{W}.$$
 (1.33)

The interaction term, \hat{W} , will depend on both the vector potential and the electronic momentum. We treat **A** as a plane-wave with phase $e^{i\mathbf{k}\cdot\mathbf{r}}$, where **r** in this case is the position vector from the stationary nucleus, and **k** is the wave-vector, pointing in the direction of propagation of the plane-wave with magnitude $k = \omega/c$ (where $\omega = 2\pi\nu$). We now make the **dipole approximation**, which amounts to approximating the plane-wave as homogeneous over the scale-length of the atom or molecule, which is to take $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$. This approximation allows us to separate the electromagnetic and atomic wave-functions. The interaction term for the transition from $u \rightarrow \ell$, with the summation over all N electrons in the system is:

$$\langle \ell | \hat{W} | u \rangle = \mathcal{N} \frac{e}{\mu c} \left(\frac{2\pi\hbar c^2}{\omega} \right)^{1/2} \sum_{i=0}^{N} \langle \ell | \hat{\pi}^* \hat{p}_i | u \rangle, \tag{1.34}$$

where N is the normalization constant for the vector-potential. If we treat the momentum operator as independent of the electromagnetic field, which the dipole approximation above accomplishes, and if we neglect all momentum-dependent corrections, we can apply the fundamental commutation relation, $\hat{p}\hat{r} - \hat{r}\hat{p} = [\hat{p}, \hat{r}] = -i\hbar$, and we find that:

$$\hat{p} = \frac{i\mu}{\hbar} [\hat{H}_e, \hat{r}]. \tag{1.35}$$

We note that $\langle \ell | \hat{H}_e = E_\ell$ and $\hat{H}_e | u \rangle = E_u$, so therefore, applying Equation (1.35) to Equation (1.34):

$$\langle \ell | \hat{W} | u \rangle = \mathcal{N} \frac{i\Delta E}{\hbar c} \left(\frac{2\pi \hbar c^2}{\omega} \right)^{1/2} \hat{\pi}^* \langle \ell | \hat{d} | u \rangle, \qquad (1.36)$$

and:

$$\hat{d} \equiv -e \sum_{i=0}^{N} \hat{r}_i. \tag{1.37}$$

At this point, we apply Fermi's Golden Rule, which relates the probability of transition from state $u \rightarrow \ell (P_{u\ell})$ to the square of the interaction term from Equation (1.36). This gives us the probability of transition to produce a photon of polarization $\hat{\pi}$ into a solid angle $d\Omega$:

$$P_{u\ell} d\Omega = \frac{e^2 \omega^3}{2\pi \hbar c^3} |\hat{\pi}^* \langle \ell | \hat{d} | u \rangle|^2 d\Omega.$$
(1.38)

By integrating over all directions and assuming that any particular photon emitted over a given time *dt* will have random polarization such that $|\hat{\pi}^* \langle \ell | \hat{d} | u \rangle|^2 = \frac{1}{2} \sin^2 \theta |\langle \ell | \hat{d} | u \rangle|^2$, we determine the probability per unit time for transition, which we define as:

$$A_{u\ell} \equiv \frac{4}{3} \frac{e^2 \omega^3}{\hbar c^3} |\langle \ell | \hat{d} | u \rangle|^2.$$
(1.39)

There are two other Einstein coefficients. The absorption reaction:

$$S(\ell) + h\nu \to S(u), \tag{1.40}$$

has a rate-coefficient of $B_{\ell u}u(v)$, where u(v) is the electromagnetic energy density at frequency v (erg cm⁻³), and $B_{\ell u}$ (cm³ s⁻¹ erg⁻¹) is the Einstein B coefficient for absorption. The coefficient for spontaneous emission,

$$S(u) + h\nu \to S(\ell) + 2h\nu, \tag{1.41}$$

is $B_{u\ell}u(v)$. We can relate the Einstein B coefficients to the Einstein A coefficient by the rate equations for the two-state transition, in terms of the number densities of species S in states u and ℓ of n_u (cm⁻³) and n_ℓ (cm⁻³), respectively:

$$\frac{dn_{\ell}}{dt} = [A_{u\ell} + B_{u\ell} u(v)] n_u - B_{\ell u} u(v) n_{\ell};$$
(1.42)

$$\frac{dn_u}{dt} = B_{\ell u} \, u(\nu) \, n_\ell - \left[A_{u\ell} + B_{u\ell} \, u(\nu)\right] \, n_u. \tag{1.43}$$

If the species is in local thermodynamic equilibrium (LTE), the radiation field becomes the blackbody radiation field, and so the radiation energy density becomes:

$$[u(\nu)]_{\rm LTE} = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}.$$
 (1.44)

Equilibrium also requires that the transitions have reached a steady state, and that the two states have reached equilibrium with each other. This means that, if g_u and g_ℓ are the degeneracies of the u and ℓ states, we can apply Boltzmann's thermodynamic relationship between population of states, where k is Boltzmann's Constant and T is the temperature, and therefore:

$$\frac{dn_{\ell}}{dt} = \frac{dn_u}{dt} = 0; \tag{1.45}$$

$$\frac{n_u}{n_\ell} = \frac{g_u}{g_\ell} e^{-\Delta E/kT}.$$
(1.46)

Applying Equations (1.45),(1.46) and (1.44) to Equation (1.43), we determine that for the limits $T \rightarrow 0$:

$$B_{\ell u} = \frac{c^3}{8\pi h \nu^3} A_{u\ell},\tag{1.47}$$

and if $T \to \infty$:

$$B_{u\ell} = \frac{g_u}{g_\ell} B_{\ell u} = \frac{g_u}{g_\ell} \frac{c^3}{8\pi h v^3} A_{u\ell}.$$
 (1.48)

Since Equation (1.43) is valid for all temperatures, the relations in Equations (1.47) and (1.48) hold for all temperatures.

When transitions are observed from an interstellar source, all the material experiencing the transition is integrated together, into a column-density,

$$N_{\ell u} = \int n_{\ell u} \, dl, \tag{1.49}$$

where dl is the pathlength, and $n_{\ell u}$ is the amount of material undergoing the transition. If there is a small amount of material undergoing a transition, the number of photons will be directly related to the column density of the transitioning species, and if the species is in LTE, the column of the transitioning species is statistically related to the total column of the species.

If, however, there is a large column of the species, since the photons spontaneously emitted also are of the frequency to excite the same material, the species becomes excited by its own emissions; this is called self-excitation. When this happens, the transition is referred to as being saturated, and the velocity profile often becomes flattened, because the emission transition from $n_2 \rightarrow n_1$ is being stifled by the photons from this transition being absorbed, $n_1 \rightarrow n_2$. The optical depth, τ , can be introduced, where if $\tau < 1$, the environment is optically thin, but if $\tau > 1$, the environment is optically thick. The parameter τ is related to radiative transfer, a process that will be discussed in greater detail in Chapter 2. In all optically thin environments, the transitions remain unsaturated.

When the environment is optically thick, the transition can become saturated. The flat portion in the curve begins to appear at $\tau \gtrsim 10$, and the flat portion of the curve of growth can be related to the transition strength and the velocity broadening. When τ is greater than a particular quantity τ_{damp} (see Draine 2011, his Eqn. 9.25), the transition becomes completely saturated.

In cases where the transition is saturated, the procedures to determine abundances are often too involved and include too high an uncertainty to be usefully implemented. In such cases, if certain isotope ratios are known, the abundance of the isotopologue, which is typically not saturated, can be determined, and the ratio can be applied to estimate the abundance of the saturated species. Also, in some cases, higher energy transitions can be used.

In many cases, the best way to explore the properties of chemical species in interstellar conditions is to experimentally reproduce aspects of the interstellar environment, and measure the relevant parameters. It is unrealistic to reproduce all interstellar conditions, because then measurements may need to be on astronomical time-scales. Various conditions, sometimes density and temperature, are very different in experiments, compared to interstellar conditions. This allows for a time-scale that could be survived by the experimentalist. These compromises also mean that results may be unreliable, to a degree, and is often one of the main reasons why different techniques may result in different experimental values for the same rate.



Figure 1.2: An illustration of rotational and vibrational states, under the harmonic oscillator approximation. An electronic transition would involve moving the electron to a new harmonic potential at higher energy, itself populated with rotational and vibrational states.

Experimental techniques can be applied to measure formation and destruction rates for interstellar species. The experimentally determined rates are often inaccurate to within \sim 50%, far less accurate than Einstein coefficient measurements, which can be accurately determined to 1%. Because interstellar species exist in two phases, in the gas and on the surface of grains, experiments also tend to concentrate on one of these two phases, and there are solid-state experiments and gas phase experiments. Gas-phase experimental techniques are reviewed by Smith et al. (1978) and Smith (2011), and some surface experimental techniques are given a detailed overview in Katz et al. (1999), for Thermal-Programmed Desorption techniques, and Öberg et al. (2009) for the photodesorption technique.

1.3 Introducing Physical Conditions into the Rate Model

As mentioned in the beginning of Section 1.1.2, rates coefficients with units of s^{-1} account for the coupling between physics and chemistry in the interstellar medium. We will discuss these rates now, in general terms, as they are included in the chemical network. Because the topic of this thesis deals with these rates and their connection with physical forces and effects, the next chapter will provide



Figure 1.3: A sample profile for OH^+ , water and HF absorption, with line fitting used to estimate the relative abundance for OH^+ (green line). From Gupta et al. (2010).

a detailed review of these rates and their chemical impact.

There are four first order processes we will consider: cosmic ray ionization, X-ray ionization, photoionization, and photodissociation.

Cosmic ray ionization rates correspond to the reactions:

$$A + CRP \to A^+ + CRP + e^-, \tag{1.50}$$

and have rate coefficients of the form $k = \alpha \zeta$, where ζ is the cosmic ray ionization rate for molecular hydrogen, and α is the proportionality between ζ and the ionization rate for species A. X-ray ionization has an identical form, but with $k = \alpha \zeta_X$, with the subscript "X" to denote X-rays. In detailed X-ray-driven chemical models, such as those of Meijerink et al. (2012), this rate will be very different from the cosmic ray ionization rate for most species, and will also apply to reactions of the form:

$$A^{+} + X - Ray \rightarrow A^{2+} + CRP + e^{-},$$
 (1.51)

or double-ionization reactions.

Photoionization reactions are of the form:

$$A + h\nu \to A^+ + e^-, \tag{1.52}$$

and photodissociation reactions are of the form:

$$A + h\nu \to B + C. \tag{1.53}$$

These have rate coefficients:

$$k_{\nu} = \alpha \chi e^{-\beta \tau}, \tag{1.54}$$

where χ is the UV field intensity in Draine units (Draine 1978, discussed in detail in Chapter 2), τ is the optical depth into the cloud, β is the extinction factor, and α is the photoionization or photodissociation rate when $\chi = 1$ and $\tau = 0$.

The connection of physical effects to the parameters ζ , ζ_X and χ is the topic of Chapter 2, in which we discuss in some detail the connection between these parameters and interstellar physics and the typical impact these factors have on interstellar chemistry. The application of these tech-

niques to two interstellar environments, the Horsehead Nebula and Orion KL, are discussed in Chapters 3 and 4 respectively. Our results are summarized in Chapter 5.

Chapter 2

CONNECTING CHEMISTRY AND PHYSICS IN THE INTERSTELLAR MEDIUM

There are two great prizes to be won through successfully joining physical conditions to chemical abundances. By joining physical conditions to chemical abundances, the chemist can reduce the number of variables in her chemical kinetics calculations, and consider primarily whether the calculated or experimental rates are accurate; she can also predict the chemical evolution in our universe, and may be able to trace how the precursors to the origin of life first formed. The other prize is better constraints on physical conditions in the interstellar medium obtained through careful comparison between astrochemical models and observations.

Precise knowledge of the physical conditions will allow us to truly understand star formation by knowing better the environments in which stars form, and how this environment changes over time. The conditions themselves relate to galaxy formation, the energetic consequences of supernovae and elemental ratios. Chemical models can even be applied to early universe conditions, and can help determine the interstellar and intergalactic environment in the reionization era. The chemical reward, equally interesting, helps answer questions pointed in the other direction, to the physical and chemical conditions on our early planet, and where our chemistry started. Did life on earth begin in some pond somewhere on our surface? Or were our chemical ancestors evolving on the mantles of comets?

This overview of the connections between chemistry and physics in the interstellar medium will look at the effects of low-energy cosmic rays in Section 2.1. Ultraviolet photons are discussed in Section 2.2 and X-rays in Section 2.3. We combine all these elements into robust astrochemical codes, and an introduction to how these physical effects are all incorporated is given in Section 2.4. These detailed models will be applied to two environments, introduced in Sections 2.5 and 2.6 and reviewed fully in Chapters 3 and 4.

2.1 Overview of ζ and Chemistry

The cosmic ray ionization rate, ζ is a per-second rate incorporated into the chemical kinetics as discussed in Chapter 1. There are a variety of cosmic ray ionization rates depending on the species being ionized, the ionizing particle, and other factors, such as the energy of the electron ejected from the newly ionized atom or molecule.

The first ionization rate we discuss is the bare ionization rate of a hydrogen atom, and is particle dependent. The ionization rate is different for protons, electrons, alpha particles and other types of cosmic rays. This ionization rate, ζ_i , is dependent on the cross-section between species *i* and H, σ_{i-H} and the flux of cosmic rays of species *i*, which depends on both energy and direction. We integrate these two variables over all directions and over the energy, from the ionization energy for atomic hydrogen, *I*, to infinity. For a cosmic ray type *i*, the ionization rate is therefore:

$$\zeta_i = \int_I^\infty dE \ \sigma_{i-\mathrm{H}}(E) \int_0^\pi \int_0^{2\pi} d\theta \, d\phi \ j_i(E,\theta,\phi).$$
(2.1)

The primary ionization rate (ζ_p) is the total ionization rate of a hydrogen atom by cosmic rays. It is a sum over *i* of Equation (2.1), or:

$$\zeta_p = \sum_i \int_I^\infty dE \ \sigma_{i-\mathrm{H}}(E) \int_0^\pi \int_0^{2\pi} d\theta \ d\phi \ j_i(E,\theta,\phi).$$
(2.2)

The ionization rate of atomic hydrogen, ζ_H , also incorporates ionization by secondary electrons. One method for calculating the secondary ionization would be to determine their energies as a function of the initial cosmic ray energy; $W(E) \approx \alpha E$ for E < 1 GeV (see Cravens & Dalgarno 1978; Dalgarno et al. 1999), then the flux of the secondary electrons $j_2(W)$, and finally to integrate, as with Equation (2.1), to find the ionization rate for secondary electrons:

$$\zeta_2 = \int_I^\infty dW \,\sigma_{e-H}(W) \int_0^\pi \int_0^{2\pi} d\theta \,d\phi \,j_2(W,\theta,\phi).$$
(2.3)
With this approach, we find the total ionization to be:

$$\zeta_H = \zeta_2 + \zeta_p \tag{2.4}$$

If we assume that the angular dependence is identical between the total cosmic ray flux $j(E, \theta, \phi)$ and $j_2(W, \theta, \phi)$, and since we know W(E), we can say that:

$$\frac{d\zeta_2}{dE} = \frac{dW}{dE} j(W)\sigma_{e-H}(W)$$
(2.5)

Furthermore, the flux $j_2(W)$ is in a power-law form, which solving for the electron-abundance via kinetics equations will establish. The power for the flux is $-\beta$, and we can integrate, to find:

$$\zeta_2 = \alpha^{\beta+1} \zeta_p \tag{2.6}$$

$$\zeta_{H} = (1 + \alpha^{\beta+1}) \sum_{i} \int_{I}^{\infty} dE \ \sigma_{i-\mathrm{H}}(E) \int_{0}^{\pi} \int_{0}^{2\pi} d\theta \ d\phi \ j_{i}(E, \theta, \phi).$$
(2.7)

Since $\alpha^{\beta+1} = 0.67$, often authors will state that $\zeta_H = 1.67\zeta_p$. For all the other cosmic ray ionizations, ζ_{He}, ζ_{CO} , etc., the cross-sections are compared between the species and *H*, and the value is adjusted by the factor separating them. In the case of molecular hydrogen, $\zeta_{H2} \sim 2\zeta_H$.

When cosmic rays ionize interstellar matter, they produce free electrons, accounted for most accurately by the Equation (2.3). If the environment is molecular (most of the hydrogen is in molecular form), then most of the secondary electrons will be produced by ionizing hydrogen molecules, with the rate ζ_{H2} . When these free electrons are produced, they may collide with another hydrogen molecule, and because of their substantially lower energy, will often excite this molecule instead of ionizing it. The molecules, once excited, will spontaneously emit photons with rates discussed at the end of Chapter 1. These UV photons, called secondary photons, then photodissociate and photoionize the medium. These processes are reviewed in Gredel et al. (1989). The way the secondary photon processes are incorporated into the rate method is by a separate set of secondary photoionization and photodissociation rates. These rates are standard in the OSU astrochemical model, the UMIST model and in the gas-grain networks (Garrod et al. 2008). They are also accounted for in the results discussed below.

The value of ζ is determined by the cross-section, which can be calculated or measured exper-

The total flux spectrum, $j =$	Reference
$0.22(p_2/p_1)^{-2.7}(p/p_2)^{-2} (E < 0.2 \text{ GeV})^a$ $0.22(p/p_1)^{-2.7} (E > 0.2 \text{ GeV})$	(Indriolo et al. 2009)
$5.12 \times 10^7 (580E + 400)^{-2.6}$	(Ip & Axford 1985)
$1/2(0.85 + E)^{-2.6}(1 + 0.01/E)$	(Spitzer & Tomasko 1968)
$0.2E^{-1.5}$	(Nath & Biermann 1994)
$1000E (E < 0.01 \text{ GeV}) 0.1/E (E < 0.1 \text{ GeV}) 10^{-4}/E^2 (E > 0.1 \text{ GeV})$	(Hayakawa et al. 1961)
21E (E < 0.07 GeV) 1.5 (E < 0.2 GeV) 0.3/E (E > 0.2 GeV)	(Herbst & Cuppen 2006)

Table 2.1: Various Cosmic Ray Spectra as a function of Energy

Notes. ^(*a*) $p_1 = p(1 \text{GeV})$ and $p_2 = p(0.2 \text{GeV})$

imentally, and the cosmic ray flux. A variety of cosmic ray fluxes have been proposed, based on theoretical calculations of cosmic ray production, measurements of the solar system cosmic ray flux and attempts to determine the effects of the solar wind and magnetosphere on cosmic rays, as well as determinations based on scintillation and astrochemical tracers. We list the variety of cosmic ray fluxes and the papers that proposed them in Table 2.1. We plot these fluxes as functions of energy (< 1 GeV) in Figure 2.1. All the fluxes listed are in units of nucleon cm⁻² sr⁻¹ s⁻¹ GeV⁻¹, and energies are in units of GeV/nucleon. Momenta, p, are in units of GeV/c. Note that all of these spectra are angle-independent.

The varieties of cosmic ray flux-spectra converge at energies greater than GeV. This is because there are detections of cosmic rays with the Voyager satellite. The divergence below 1 GeV is due to speculation that the solar wind and magnetic field may be deflecting the low-energy cosmic rays, and this is why they are depleted in observation (Jokipii 1976). The first detection of extrasolar cosmic rays fit best with the spectrum of Spitzer & Tomasko (1968). As Voyager began detecting cosmic rays farther from the influence of the solar wind, the observed abundance of cosmic rays has increased. Current measurements from Voyager, from Webber (1998), support a cosmic ray ionization rate closer to that of Ip & Axford (1985). The Voyager satellite is still well within the influence of the solar wind and magnetic field, and the detectors will not survive past their influence. Voyager will not detect the "ambient" cosmic ray flux in the interstellar medium.

We can expect that high-energy cosmic rays (in this context, any cosmic ray with greater than 1 GeV energy) will have the same spectrum, for the most part, throughout the galaxy, except near supernovae, supernova remnants, and very dense clouds, with $N > 10^{24}$ cm⁻², where even high energy cosmic rays are depleted because of pion-production processes. For more standard interstellar conditions and columns, the high-energy spectrum is expected to be pretty-much the same everywhere in our galaxy, though the low-energy flux spectrum may be very different from source to source.

This is due to two processes: the formation and destruction of low-energy cosmic rays. It is not known how low-energy cosmic rays form. The prevalent view is that low-energy cosmic rays are formed in supernova remnants via shocks (see Axford 1981, for a review), but more recent studies suggest that cosmic rays may be produced in great abundances in the atmospheres of massive stars, such as OB stars (Turner 1991, for example). The destruction of cosmic rays is due primarily to energy loss in magnetic field interactions and ionizing and excitation collisions. We have calculated the effects of this energy loss on the flux of cosmic rays, and therefore on the ionization rate. Our cosmic ray transport calculations are detailed in Appendix A, and the results of these and similar calculations are implemented into the chemical modelling for the Horsehead and Orion KL investigations, summarized below in Sections 2.5 and 2.6. The detailed discussions of these models form the primary content of this thesis.

It will be helpful, in order to develop an intuitive understanding of cosmic ray ionization and its impact on interstellar chemistry, to consider a simple gas-phase one-point astrochemical model, and to apply this model repeatedly, varying the cosmic ray ionization ζ^2 . In later sections, we will also vary the UV flux. In these models, we hold the temperature and density constant. We ran these series of models to steady state for two conditions: a dense cloud ($n = 10^6$ cm⁻³, T = 30 K) and

 $^{2}\zeta$ without a subscript in this thesis refers to ζ_{H2}

a diffuse cloud ($n = 100 \text{ cm}^{-3}$, T = 100 K). The results are briefly discussed below. The general impact on chemistry for the ionization rate is that the abundance of cosmic-ray produced species is increased with the increasing rate, up to a particular value of ζ , and then decreases. The value of ζ for which this happens depends largely on the complexity of the species and the processes of destruction.

The chemical species H_3^+ has long been considered one of the best tracers for cosmic ray ionization (Oka 1981; McCall et al. 1999; Indriolo et al. 2007). The species HCO and HCO⁺ are also good tracers of cosmic ray ionization, although only under certain conditions.

For the dense results for H_3^+ , HCO⁺ and HCO, the steady-state relationship is nearly linear and increases with ζ until $\zeta = 10^{-15} \text{ s}^{-1}$, at which time the slope decreases somewhat, because of the electron fraction. Once $\zeta = 10^{-14} \text{ s}^{-1}$, the ionization fraction rapidly increases by an order of magnitude, and the increased electron fraction greatly enhances the electron recombination rate, thereby depleting H_3^+ significantly. Similar affects occur for HCO⁺ and HCO. Interestingly, for $\zeta > 2.5 \times 10^{-14} \text{ s}^{-1}$ in the dense case, H_3^+ increases again, though more slowly, probably because its formation is so closely connected to the cosmic ray ionization rate, and the electron fraction does not change as rapidly for $\zeta > 10^{-14} \text{ s}^{-1}$.

Since HCO⁺ and HCO are not so closely connected to the cosmic ray ionization rate, they tend to either level off or continue to decrease after 2.5×10^{-14} s⁻¹. Indeed, because of the strong electron affinity for HCO⁺ and its dependence on the CO abundance (also depleted in conditions of ultrahigh ionization), the HCO⁺ levels off after 5×10^{-16} s⁻¹. Bayet et al. (2010) has produced similar results for HCO⁺, and they agree with this assessment.

For the diffuse results, HCO is not abundant enough to be of note, and so is not included. For $\zeta > 10^{-15}$ s⁻¹ both H₃⁺ and HCO⁺ begin to decrease, and are severely depleted for $\zeta > 10^{-14}$ s⁻¹. This is because in the diffuse case, the temperature is higher. This, combined with the low density, keeps electrons from recombining as rapidly, and allows the electron fraction to rise to a much higher steady-state fraction. Since the electron fraction is much more closely tied to H₃⁺ and HCO⁺ destruction, a much higher electron fraction eventually overwhelms the formation pathways. The low density and exceptionally high ionization breaks complex chemistry apart, and the majority of the positive charge is in free thermalized protons, or H⁺.

The hydrocarbons are only very abundant at higher densities, and so the diffuse results are uninteresting, and are not included. The hydrocarbon results for high density are plotted in Figure 2.3. The formation and destruction of hydrocarbons is very complex, and we do not go into detail about the chemical channels here, although they are discussed in great detail in Chapter 3. The formation of many of these species is connected to CH⁺ and HCO⁺, both of which are closely tied to the cosmic ray ionization rate. All of these species increase quickly from $\zeta = 10^{-17} - 10^{-16} \text{ s}^{-1}$, and C₂H shows more stability to the rapidly increasing electron fraction at $\zeta > 10^{-14} \text{ s}^{-1}$, increasing even more rapidly until 2.5 × 10⁻¹⁴ s⁻¹, before decreasing. All these hydrocarbons decrease rapidly at $\zeta \ge 10^{-14} \text{ s}^{-1}$. The nitrogen-bearing molecule, cyanoacetylene (HC₃N) is included in this plot to show that nitrogen-bearing species even more strongly affected by the electron fraction, decreasing even more rapidly than the hydrocarbons over a ζ of 10^{-14} s^{-1} .

The species OH^+ , H_2O^+ and H_3O^+ have become very important in astrochemistry since the recent detection of both OH^+ and H_2O^+ in high abundance, and the surprising non-detection of H_3O^+ . The chemical pathways of these species are surprisingly involved, closely connected to ζ , and are discussed in detail in Chapter 4. Our results for these species are plotted for the dense phase in Figure 2.4, and for the diffuse phase in Figures 2.6 and 2.7. In this case, the OH^+ and H_2O^+ find the rapid increase in electron fraction for $\zeta > 10^{-14} \text{ s}^{-1}$ to be very favorable, with H_2O^+ being perturbed slightly by the rapid electron fraction increase, but OH^+ continuing to increase without much of a change. H_3O^+ decreases very quickly over $\zeta > 10^{-14} \text{ s}^{-1}$. Our results suggest that OH^+ and H_3^+ , may be the best tracer of cosmic ray ionization above $\zeta = 10^{-14} \text{ s}^{-1}$.

It is important to note that, for the diffuse phase in particular, these species are very timedependent. For the steady state, at $\zeta < 5 \times 10^{-15} \text{ s}^{-1}$, $\text{OH}^+ < \text{H}_2\text{O}^+ < \text{H}_3\text{O}^+$, which is expected, since OH^+ , H_2O^+ are destroyed by molecular hydrogen, and H_3O^+ is not. At $\zeta > 5 \times 10^{-15} \text{ s}^{-1}$, the ratios are reversed, and become what is observed in the diffuse medium, $\text{OH}^+ > \text{H}_2\text{O}^+ > \text{H}_3\text{O}^+$. It turns out, however, that such an extreme cosmic ray ionization is not necessary for the diffuse phase, because at earlier times, $\sim 10^5$ years, $\text{OH}^+ > \text{H}_2\text{O}^+ > \text{H}_3\text{O}^+$ for $\zeta > 10^{-17} \text{ s}^{-1}$, and approach the observed ratios at $\zeta = 2.5 \times 10^{-16}$, in agreement with Neufeld et al. (2010).



Figure 2.1: Various cosmic ray spectra in the literature. See Table 2.1 for the functions used and references.



Figure 2.2: Dense Case: H_3^+ , HCO⁺, HCO vs. ζ at $t = 10^8$ years.



Figure 2.3: Dense Case: Hydrocarbons vs. ζ at $t = 10^8$ years.



Figure 2.4: Dense Case: OH^+ , H_2O^+ , H_3O^+ vs. ζ at $t = 10^8$ years.



Figure 2.5: Diffuse Case: H_3^+ , HCO⁺, HCO vs. ζ at $t = 10^8$ years.



Figure 2.6: Diffuse Case: OH^+ , H_2O^+ , H_3O^+ vs. ζ at $t = 10^5$ years.



Figure 2.7: Diffuse Case: OH^+ , H_2O^+ , H_3O^+ at $t = 10^8$ years.

2.2 Overview of χ and Chemistry

The chemical impact of ultraviolet radiation is typically parametrized, and the parameter used is χ . To define χ , we first need to discuss how to describe the strength of a radiation field at a particular location (**x**), and time *t*, oriented toward a given direction with unit-vector $\hat{\mathbf{n}}$. This can be accomplished in terms of specific intensity, which is the electromagnetic power per unit area (erg s⁻¹ strad⁻¹ cm⁻²) of the radiation at a frequency between *v* and *v* + *dv*, in the solid angle $d\Omega$:

$$I(\nu, \hat{\mathbf{n}}, \mathbf{x}, t) \, d\nu \, d\Omega. \tag{2.8}$$

At local thermodynamic equilibrium (LTE), the intensity is equal to the black-body intensity or:

$$I(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1},$$
(2.9)

where *k* is Boltzmann's Constant and *h* is Planck's Constant. A more useful quantity, for astrochemical purposes, is the specific energy density, *u* (erg cm⁻³ s):

$$u(v, \mathbf{x}, t) = \frac{1}{c} \int I(v, \hat{\mathbf{n}}, \mathbf{x}, t) \, d\Omega, \qquad (2.10)$$

and the value vu(v) (erg cm⁻³) is the energy density at the frequency v. The value of vu(v) near a star is related to the spectral type of the star and the distance between the star and the medium. The distance reduces the radiation field by a geometrical dilution factor, $W = 1.27 \times 10^{-16} [(R_*/R_{\odot})/(r/\text{pc})]^2$, and therefore:

$$\nu u(\nu) = \frac{8\pi h \nu^4}{c^3} \frac{W}{e^{h\nu/kT} - 1}.$$
(2.11)

We define, in the same manner as Draine (1978):

$$\chi \equiv \frac{[\nu u(\nu)]_{1000\text{\AA}}}{4 \times 10^{-14} \,\mathrm{erg} \,\mathrm{cm}^{-3}}.$$
(2.12)

For an example, an O star with surface temperature 30000 K at 3.5 pc has a value of $\chi \approx 105$. The reason 1000 Angstroms is chosen as the wavelength is because it is near the middle of the 1100-912Å range where H₂ primarily absorbs UV in a neutral region (Draine 2011). The value of χ when very distant from stellar sources is due to the standard interstellar radiation field (ISRF). At ISRF, $\chi = 1.71$ in Draine units.

All rate equations for photoionization assume blackbody radiation terms and the standard ISRF. The standard form for a dissociation or ionization reaction is:

$$k_{\nu} = \alpha \chi e^{-\tau}, \qquad (2.13)$$

where α (s⁻¹) is typically on the order of 10^{-11} s⁻¹ for photodissociation reactions, and $10^{-12} - 10^{-13}$ s⁻¹ for photodissociation of ions or photoionization. There are strong exceptions to these ranges.

The chemical impact of the UV field is very different from that of the cosmic ray ionization. Cosmic rays tend to ionize species, where UV photons tend to dissociate them. As such, for all results shown here, Figures 2.8 - 2.11, increasing the radiation field tends to destroy the species. This is overly simplistic, since increasing both ionization and dissociation can actually boost species, for example, since H_3O^+ is rapidly destroyed in a strong radiation field due to the electron fraction, H_2O will be dissociated by photons and, if the cosmic ray ionization rate is sufficiently high, the result will be very high OH abundances. There are virtually infinite permutations of different parameters, each with different and potentially interesting results, but the simple results here afford us an intuition when changing parameters. This intuition is very important for more robust models, where computational calculations are on the order of days instead of seconds.

2.3 Overview of X-Rays and Chemistry

X-rays are not accounted for in a robust way in this thesis, and so this discussion will be rather short. X-rays ionize the interstellar medium much as cosmic rays do, and are often treated like cosmic rays in astrochemical models, except for a few important differences. X-rays have a different penetration than cosmic rays, X-rays will more likely ionize atoms and molecules with many electrons, and X-rays often favor inner-shell ionization. The X-ray ionization is represented as a per-second rate constant, ζ_X .

The depth-dependence of X-rays affects the way X-ray spectrum is accounted for; the spectrum for ionizing X-rays is likely different for each object, and insignificant for objects at too great a distance from X-ray sources. This is because cosmic ray ionization decreases with depth as a power law (see Maloney et al. 1996, their Eqn. A1), and the X-ray ionization decreases exponentially with



Figure 2.8: Dense Case: H_3^+ , HCO⁺, HCO vs. χ



Figure 2.9: Dense Case: Hydrocarbons vs. χ



Figure 2.10: Dense Case: OH^+ , H_2O^+ , H_3O^+ vs. χ



Figure 2.11: Diffuse Case: H_3^+ , HCO⁺, HCO vs. χ

depth. Though this is true for UV sources as well, UV sources are far more ubiquitous, and feed the ISRF, whereas X-ray sources are not so common, and so X-ray influences can be neglected in many environments. X-ray ionization is very important in violent environments, such as accretion disks around black holes, and clouds near OB-associations. The advent of Chandra especially has opened our eyes to the rich landscape of X-ray observation (McNamara et al. 2000). Of particular interest to this thesis is the observation of the Orion Nebula Cluster and BN/KL Region in X-rays by Chandra (Garmire et al. 2000).

Because X-rays favor species with many electrons, and because they typically have a much higher flux than cosmic rays, when they are dominant, their influence results in multiply ionized species and in keV lines associated with inner-shell excitations, such as the 6.7 keV line for Iron. Detections of doubly-ionized species and the keV lines associated with inner-shell effects can help differentiate X-ray influence from cosmic-ray influence. Even with this differentiation, it is often very difficult to chemically distinguish X-ray impact from cosmic ray impact, except sufficiently deep within an object, where X-rays would be excluded.

2.4 Radiative Transfer and PDR, XDR, CRDR Models

Astrochemical models are distinguished by the number of dimensions they incorporate. The zero dimensional models are the most basic astrochemical models, and are often the gas-phase or gas-grain models constructed around the major chemical networks (Garrod et al. 2008). The one-dimensional models are often called photon-dominated region models, if they concentrate on UV photon effects, and how these effects are attenuated with depth. Models that carefully incorporate cosmic rays are called CRDR models, for cosmic-ray dominated region models, and are applied to regions where the primary ionizing influence is cosmic rays (Bayet et al. 2010). X-ray dominated region (XRDR) models concentrate on the attenuated effect of X-rays, and typically receive this label only if they treat X-ray penetration and X-ray specific effects (inner-shell excitations, double ionization) accurately (Meijerink et al. 2012). Two-dimensional models are typically applied to accretion disks (Harada et al. 2011) and to protoplanetary disks (Bergin et al. 2003). Aikawa et al. (2008) pioneered a three-dimensional hydrodynamic astrochemical model, but as this is the first such model, and is still in very early stages, the unique applications for three dimensional modelling for chemistry are currently exceptionally limited.

For our work, we consider only one-dimensional models. These models treat an object as a series of slabs, typically radiated only at one end. The radiative transfer is solved by considering the radiation field at the slab closest to the radiating edge, solving for the radiation in that slab, and applying the result to the next slab. This process is continued until the model reaches a given depth, typically of optical extinction ~ 10. For a radiation field of intensity I(v) entering a slab, the field exiting the slab will be equal to I(v) + dI(v) where dI(v) is parametrized by an attenuation coefficient $\kappa(v)$, which typically accounts for absorption, although via a mathematical trick of flipping the sign can account for stimulated emission, and j(v), which accounts for spontaneous emission along the path perpendicular to the slab. We define a quantity to account for the ratio of emission to adsorption:

$$S(v) \equiv \frac{j(v)}{\kappa(v)} \tag{2.14}$$

And we also relate the pathlength, s (cm), to a dimensionless frequency-dependent depth τ by setting:

$$d\tau(v) \equiv \kappa(v) \, ds \tag{2.15}$$

Therefore, over the change in depth from one side of the slab (τ) to the other ($\tau + d\tau$), the intensity changes by:

$$dI(v) = -I(v) d\tau + S(v) d\tau.$$
(2.16)

The factor S(v) can be solved by knowing the properties of the medium, and applying the Einstein A coefficient. We consider zero depth to be $\tau = 0$, and integrate to solve for the depth-dependent intensity (ignoring scattering; see Draine (2011), their Eqn. 7.19 and following discussion):

$$I(\nu,\tau) = I(\nu,0) e^{-\tau(\nu)} + \int_0^{\tau(\nu)} e^{-(\tau(\nu)-\tau)} S(\nu,\tau) d\tau, \qquad (2.17)$$

where the parameters $\tau(v)$ and S(v) are often related to S_V and $A_V \approx 1.086$, which are the optical scale and optical extinction respectively. Figure 2.12 has an illustration of the radiative transfer.

The depth incorporates the dust extinction and the scale incorporates self-shielding and potentially masers. The calculation of and incorporation of dust extinction is presented in Section 2.4.1



Figure 2.12: Radiative transfer through one slab of length ds and frequency-dependent depth $d\tau(\nu)$.

and the self-shielding of molecular hydrogen and carbon monoxide is discussed in Section 2.4.2. The process of combining these two factors, and including astrochemistry in a computationally efficient manner is presented in detail in Section 2.4.3.

2.4.1 Grain Extinction

Extinction by grains is often the dominant factor in radiative transfer calculations. Extinction from atoms and small molecules can be determined to high accuracy using the Rayleigh approximation for scattering; that is, assuming that the wavelengths are large compared to particle size. The results from this assumption are simple and elegant, arising from dimensional analysis, so that for an initial intensity, I_0 , the intensity of the scattered light, I_s , could be determined, and the ratio of these would be proportional to the wavelength, λ as $1/\lambda^4$. This is often expressed as an efficiency factor for the extinction, Q_{ext} . However, the observed relationship between Q_{ext} and λ for interstellar clouds follows instead a proportionality of:

$$Q_{\rm ext} \propto \frac{1}{\lambda},$$
 (2.18)

and no simple approximation yet produces this particular relationship. Mie theory, an exact solution to scattering off of perfect homogeneous spheres, was developed by Gustav Mie in 1908, and matches this particular ratio well when the size of the particle *a* is approximately the size of the wavelength (Bohren & Huffman 1983). The coefficient of extinction , C_{ext} , is related to the efficiency by the classical cross-section $Q_{\text{ext}} = C_{\text{ext}}/\sigma$. The extinction coefficient is an infinite summation of Mie coefficients a_n and b_n , functions of the wavelength and the index of refraction, *m*, of the form:

$$C_{\text{ext}} = \frac{\lambda^2}{2\pi} \sum_{n=1}^{\infty} (2n+1) \operatorname{Re}\{a_n(m,\lambda) + b_n(m,\lambda)\}.$$
(2.19)

This particular solution is valid no matter the size of the spheres. For a plot of Q_{ext} as a function of x, the circumference of the particle is divided by λ . Mie solved the problem by a separation of variables in Maxwell's Equations with the boundary conditions at the spheres surface. Since then, other techniques have been developed, such as the T-matrix method (a more flexible formalization for the exact solution), and the discrete dipole method, a computationally intense method that does, at high enough order, reproduce the $1/\lambda$ relationship, for a grain-size distribution of $n \propto r^{-3.5}$; see Draine & Lee (1984), esp. their Eqn. 5.1).

2.4.2 CO and H₂ Self-Shielding

When UV photons impinge on the edge of a cloud, they will ionize and dissociate chemical species at that edge. Since the two most abundant species in a molecular cloud are H_2 and CO, these molecules will be the most common species ionized and dissociated. The photochemistry of these species involve line processes or processes over narrow frequency ranges, when self-shielding is efficient.

The primary channel for photodissociating hydrogen is the photoexcitation of Hydrogen from the X Σ_g^+ State to the first and second electronic excited states, B ${}^{1}\Sigma_u^+$ and C ${}^{1}\Pi_u^+$, and is discussed in Lefebvre-Brion (2004), their Chapter 7, esp. Tables 7.2 - 7.4. Since the excitation is via an allowed absorption line, the transition electric dipole will be non-zero for some decay channels. The majority (~ 85%) of the time, the decay channel will be to a vibrationally excited ground state. A fair fraction of the time, however, the state will spontaneously decay into the vibrational continuum, and the molecular hydrogen will dissociate. This process, an important process for photodissociation of hydrogen, is a line-process, and therefore significantly affected by self-shielding.

At each slab from the edge, the photons nearest these line transition energies will be more severely depleted. This will affect both the ionization and dissociation of H_2 and, to a lesser extent CO, as well as the ionization and dissociation of any other species that has important narrow transition pathways close to the line-transition frequencies as H_2 and the narrow transition frequencies of CO. This principle is called self-shielding; the H_2 and CO, by depleting photons at line transition frequencies, protect H_2 , CO and other species from destruction by UV radiation. Indeed, the most robust self-shielding calculations will account for all the possible excitations of H_2 and CO, because these excitation energies may be coincident with ionization or dissociation energies for other species.

The most comprehensive way to account for self-shielding is to track every transition at every slab, and adjust vu(v) at that point due to photons absorbed and emitted by H₂ and CO, and ultimately other species, at or sufficiently close to that frequency. The Meudon PDR code accounts for radiative transfer in pretty-much this way, considering all the relevant transitions for H₂ and CO, and many for helium, water and other species. For all time-dependent models to this date, as well as our own, a relatively simple analytical expression for H₂ and CO self-shielding is incorporated.

In our discussion of depth and extinction due to dust particles above, $\tau(\nu)$ refers to the depth due to dust extinction at a particular frequency ν . We apply a similar sort of parameter to selfshielding, and introduce $\theta(H_2)$ and $\theta(CO)$, which are extinction parameters for the sum of these frequency ranges, and represent the fraction of ionizing and dissociating radiation still present at a given column of $N(H_2)$ and N(CO), respectively. These depths account for the extinction of the UV field along the dissociation and ionization frequencies (defined as in Lee et al. 1996b).

Since the extinction for different lines will depend on transition strengths, and therefore on quantum mechanical factors, the dependence of the extinction is complex, and cannot be fit very well analytically. Instead, tables of these self-shielding parameters are produced, relating the column of H_2 and CO to the values of θ . The self-shielding equation for H_2 is very straight-forward, but the CO

self-shielding is more involved, because of a strong overlap with various H_2 excitation lines and CO photodissociation lines, relating H_2 column to the CO self-shielding. Also, broad dust absorption lines shield CO, and this relates CO self-shielding to the optical extinction due to dust. The rates of CO and H_2 photodissociation are therefore calculated in the time-dependent case as:

$$k_{\nu}(\mathrm{H}_2) = \chi \, \alpha_{H2} \, \theta(\mathrm{H}_2);$$
 (2.20)

$$k_{\nu}(\text{CO}) = \chi \,\alpha_{CO} \,\theta(\text{CO}) \,\theta(\text{H}_2) \,e^{-\tau}, \qquad (2.21)$$

where we take values for θ from Lee et al. (1996b). See eg. their Tables 10 and 11.

2.4.3 Modelling: The PDR, XDR and CRDR

For the gas-grain PDR model developed in Chapter 4, we incorporate self-shielding and grainextinction in our radiative transfer calculations, in the manner they have been presented in Sections 2.4.1 and 2.4.2. Because, for any given slab, the column of H₂ and CO must be derived for all the slabs closer to the radiation source, parallelization of the code is somewhat more involved. Our method for parallelization is to solve the chemistry at the edge (slab number sn = 1) at time-step tn = 0, and then simultaneously solve for the edge at tn = 1 and at the next slab, sn = 1 at tn = 0. The parallelization therefore becomes more extensive until the half-way point, after which the parallelization is scaled down until we calculate for the final slabs at the final times. Figure 2.13 gives a graphical representation of the parallelization implemented in the gas-grain PDR in Chapter 4. This parallelization allows the code to run substantially faster than if each slab at each time were run separately. For an $m \times n$ grid, the non-parallelized code will run each step at a time, δt , so $t_{total} = nm \delta t$. The parallelized code will run each diagonal series of steps simultaneously, which means that $t_{total} = (n+m-1) \delta t$, which for large values of n, m is a substantial difference in run-time.

2.5 Chemistry in a Calm Environment: The Horsehead Nebula

The Horsehead nebula is an ideal candidate for studying the impact of physical parameters on chemical evolution. It is a relatively calm environment, with a typical radiation field for having an O-type star nearby. Its geometry is also edge on, so we can see a cross-section of the chemistry, through-



Figure 2.13: The Parallel Processing Computational Scheme: All red sections are run simultaneously. For each red section, the time-step ts increases to ts + 1, with the chemical abundance and parameters sent to the next time-step up (orange arrows to the pink boxes); a new pink box is started at ts = 0 at a depth step ds + 1. The blue arrows represent column-density information passed from the edge, through the grey boxes and red box and into the pink box, to calculate radiative transfer (as per Fig. 2.12).

out the object. We see the object in the same way we see the slabs in Figure 2.12. The density and temperature also vary with depth, but the Horsehead Nebula is not clumpy. It instead segues between high and low density rather smoothly. This gives us a way to explore heating effects, cosmic ray transport, and UV field effects in a single object with a standard range of parameters. Our investigation and its results are reviewed in detail in Chapter 3.

2.6 Chemistry in an Extreme Environment: The Orion KL Region

The Orion KL region, in contrast to the Horsehead Nebula, is close to over twenty OB stars and thousand of other stars, and is being bombarded with radiation, X-rays and cosmic rays. It is one of the most extreme environments in our galaxy, about which we are aware. It is, like the Horeshead Nebula, relatively close, only \sim 400 parsecs away. Because of the extreme nature of the Orion KL region, it is very clumpy, and has many velocity components and spatially extended regions, which look like tendrils. The components interact with each other over relatively short (\sim 1000 year) time-scales (Wakelam et al. 2004).

This object also has an unfortunate geometry, and its primary source for radiation is probably behind it. Though different regions, such as the low-velocity outflow in the plateau and the compact ridge, can be separated by Doppler velocity, within these regions and within the substantial overlap of their velocity profiles, much of our information about the depth-dependence of the source will be lost. Teasing out column-dependence will be difficult. Nevertheless, the violent nature of the Orion KL region, and its chemical richness and many chemical mysteries, make it too tantalizing a candidate not to explore. A detailed presentation of our model results and solutions to some of the chemical mysteries in the Orion KL region are given in Chapter 4.

Chapter 3 Typical Environment: The Horsehead Nebula

3.1 Introduction

Ion-neutral reactions are the most important driving processes for gas-phase chemistry. Therefore it is important to understand the mechanisms by which chemical species in the interstellar medium become ionized, in order to have a more accurate picture of the chemistry in various interstellar sources. Near the edge of dense clouds and throughout diffuse clouds, UV photons can provide a powerful ionizing force upon the medium, especially if there is a sufficiently strong source of radiation nearby. These photons do not penetrate very far into dense clouds, decreasing exponentially with the column density. Other ionizing agents, like X-rays, will penetrate farther into dense clouds, but deep within the object, high-energy (≥ 100 MeV) cosmic rays are the dominant ionizing force.

The recent detection of unexpectedly large abundances of H_3^+ , however, in an assortment of diffuse clouds has raised the old question as to whether the high ionization rate needed is caused by a high flux of cosmic rays of < 1 GeV (McCall et al. 2003; Indriolo et al. 2007). Such low energy cosmic rays would not be expected to penetrate deeply into dense clouds, so that a column-dependent ionization rate due to cosmic rays might exist in denser sources. This question is best explored by examining the influence of cosmic ray ionization at different depths into a single object, and the Horsehead Nebula is an ideal candidate for such an investigation.

The Horsehead Nebula, also called Barnard 33, is a dark nebula of size about 5' in the bright nebula IC434. It is illuminated by σ Ori from a distance of about 30' (Anthony-Twarog 1982).

The radiation field incident on the cloud is most commonly taken to be $\chi = 60$ in Draine units (Draine 1978; Habart et al. 2005), and the geometry of the cloud is described as nearly "edge-on", meaning that the line between σ Ori and the Horsehead Nebula is nearly perpendicular to the line of sight. This makes the Horsehead Nebula ideal for observing column-dependent variables in a single source. It has an ambient magnetic field of $< 6 \,\mu$ G (Zaritsky et al. 1986) and a steep density gradient ranging from 10^2 to 10^5 cm⁻³, and contains a pre-stellar core as well as at least one other dense region near the "throat" that will be able to be studied in greater detail by the Atacama Large Millimeter Array (ALMA) (Ward-Thompson et al. 2006).

High abundances of small carbon-bearing molecules were observed by Teyssier et al. (2004) and by Pety et al. (2005), with higher abundances of certain molecules (CCH, $c-C_3H_2$, C_4H) observed near the edge than at the center. This led Pety et al. to posit that polycyclic aromatic hydrocarbons (PAH's) near the edge of the cloud are being destroyed by incident radiation, and that the products of their destruction are these small hydrocarbons. A number of other molecules have been detected, including the ions HCO⁺ and HOC⁺ (Goicoechea et al. 2009b), the carbon-bearing neutrals HCO (Gerin et al. 2009), $1-C_3H$, and $c-C_3H$ (Teyssier et al. 2004), and the sulfur-bearing species CS and HCS⁺ (Goicoechea et al. 2006b), although, except for HCO⁺, little information of their column dependence is available.

Chemical modeling of the Horsehead Nebula was discussed by Winnewisser & Herbst (1993). Teyssier et al. (2004) provided the first detailed chemical PDR model of the Horsehead Nebula, using the Meudon PDR code (Le Bourlot et al. 1993; Le Petit et al. 2002). A year later, Pety et al. (2005) modeled the Horsehead Nebula with the same code, comparing the results with observations at three different lines of sight, and incorporating PAH's into the model. Habart et al. (2005) determined a column-dependent temperature via thermal balance. None of these models is able to account for the high abundances of small hydrocarbons at the edge, or the HC₃N abundance.

Deuterium fractionation of HCO⁺ ([DCO⁺]/[HCO⁺] ~ 0.02) has been observed in the Cloud region at $A_V \approx 10$, and used to constrain its temperature to about 20 K (Pety et al. 2007). Neutral atomic oxygen has also been detected (Goicoechea et al. 2009a), with hopes for Herschel's heightened resolution to provide abundances of atomic oxygen for different regions in the cloud.

The effect of a higher sulfur abundance was considered by Goicoechea et al. (2006b), using

the Meudon code (Le Petit et al. 2006). Pety et al. (2007) also used this code to better understand deuterium fractionation at the Horsehead edge. The abundance of the negative ion C_6H^- was calculated by Millar et al. (2007), although negative ions have not yet been observed in this region. Morata & Herbst (2008) developed a time-dependent PDR code, and first applied it to the Horsehead Nebula, with mixed success. This is the code we make use of in this chapter, in tandem with the Meudon PDR code, which we use to determine some of the physical conditions.

Compiègne et al. (2007) and Goicoechea et al. (2009b) have performed some recent modeling of the Horsehead region; Compiègne et al. (2007) explored the dust emission. Goicoechea et al. (2009b) self-consistently modeled the observed spatial distribution and line intensities with detailed depth-dependent predictions coupled with a nonlocal radiative transfer calculation for H¹³CO⁺, DCO⁺ and HOC⁺. They compared their model results with the Gerin et al. (2009) observations of HCO⁺ in order to constrain the electron fraction. Goicoechea et al. determined a very steep relative electron abundance of $n_e/n_H \sim 10^{-4} - 10^{-8}$ (where $n_H = n(H) + 2n(H_2)$) at $A_V \approx 0.6 - 2.0$ from the cloud edge, based on a faint emission line attributed to HCO⁺ near the edge.

In this chapter, we report our investigation on the effect of a column-dependent cosmic ray ionization rate $\zeta(N_H)$ on model results for molecular abundances and their spatial variation in the Horsehead Nebula. This is offered as a partial explanation of the high abundances of small hydrocarbons at the edge of the Horsehead nebula. In Section 3.2, we discuss the determination of three different $\zeta(N_H)$ functions, including a discussion of the role played by the magnetic field. In Section 3.3, we provide a detailed description of the PDR model used, and compare our calculated abundances with observational values using two different sets of elemental abundances. We also provide predicted abundances for observable species. In Section 4.6, we discuss the implications of these results, and a better determination of $\zeta(N_H)$ from single sources after the advent of ALMA.

3.2 The Determination of $\zeta(N_H)$

The cosmic ray ionization of the interstellar medium is caused primarily by relativistic protons, alpha particles, and electrons. This ionization rate, labeled ζ , is typically represented as a per-

$\zeta_{H2} (\times 10^{-17} \text{ s}^{-1})$	Source
100	Solomon & Werner (1971)
1	Herbst & Klemperer (1973)
3 - 2000	Hartquist et al. (1978)
10 - 100	McCall et al. (2003)
25	Le Petit et al. (2004)
100	Goto et al. (2008)
6 – 24	Neufeld et al. (2010)
5000	Gupta et al. (2010)

Table 3.1: Some values of ζ_{H2} used in previous models

second rate at which cosmic rays ionize atomic hydrogen. Given the process

$$H + CR \rightarrow H^+ + e^- + CR$$
,

where CR represents ionizing cosmic rays, ζ is defined by the kinetic equation

$$\frac{d[\mathrm{H}^+]}{dt} = \zeta[\mathrm{H}],$$

where the brackets signify concentration. The ionization rate of other species, such as H₂ and He, is usually determined in chemical networks by multiplying ζ by a constant. Even near the edge of dense clouds, the majority of hydrogen is molecular in nature, so it is important to note that, to a good approximation, $\zeta_{H2} \approx 2\zeta$ (Glassgold & Langer 1974).

In the last decade, results from diffuse sources, from McCall et al. (2003), Le Petit et al. (2004) and Indriolo et al. (2007), including recent observations with Herschel (Gerin et al. 2010), have most often indicated that in these environments ζ is more than an order of magnitude higher than the generally accepted value of 10^{-17} s⁻¹. Earlier values for ζ ranging from $10^{-17} - 10^{-15}$ s⁻¹ had been proposed (Spitzer & Tomasko 1968; Hartquist et al. 1979; Dalgarno 2006). Table 3.1 contains a limited historical overview of some of the values of ζ utilized in previous models. These actually refer to molecular rather than atomic hydrogen.

The observations indicating a high ζ , along with this wide range of values, led us to initiate a calculation of column-dependent functions of ζ . At the same time, Padovani et al. (2009) undertook similar calculations. They used the ionization and energy loss cross sections for collisions between

cosmic rays and atomic and molecular hydrogen (Cravens & Dalgarno 1978) as well as Helium to follow the flux-spectra of cosmic rays through a cloud and, from the flux spectra as a function of position, obtained the column-dependent cosmic-ray ionization rate for a number of initial fluxspectra. Here we report similar calculations but with a Monte Carlo approach in which we also include magnetic field effects.

3.2.1 Initial Spectrum

We begin by considering the form of the initial cosmic ray flux-spectrum j(E) (cm⁻² s⁻¹ sr⁻¹ GeV⁻¹ per nucleon), as a function of energy. The spectrum has only been directly observed within our solar system, where the solar wind would have depleted the low energy cosmic rays (Parker 1958).

Different cosmic ray spectra have been proposed based on assumptions about the origin of the cosmic rays. Supernova shocks are currently the favored explanation for the origin of cosmic rays (Biermann et al. 2010; Axford 1981). The spectrum due to the supernova blast alone imposes a low-energy cutoff at about 100 MeV because of energy loss due to debris and strong magnetic field effects (Hayakawa et al. 1961; Ip & Axford 1985). It is suspected that shocks in the debris may re-accelerate some of the thermalized cosmic rays (Ip & Axford 1985; Indriolo et al. 2009).

Shock models favor a steep power law for low-energy cosmic rays, with a new cutoff at 1 MeV, below which most cosmic rays would again lose a significant fraction of their energy into the debris, and would either be reabsorbed into the remnant, or would travel too slowly to propagate throughout the galaxy. Alternate theories for cosmic ray acceleration exist, but these also predict similar spectra for low-energy cosmic rays (Butt 2009).

Comparison between measurements of the cosmic ray flux and theoretical cosmic ray spectra have been very useful. Basic statistics, "leaky-box" models, convection methods, and Monte Carlo methods have been applied to better constrain cosmic ray spectra, often by examining the elemental composition of the cosmic rays themselves. Strong et al. (2007) contains an excellent review of these methods. Webber (1998) incorporated the newest results from Voyager into their Monte Carlo model, in order to determine the low energy spectrum better.

Nevertheless, Voyager is still in a region where solar winds have a substantial effect. In fact, the farther the Voyager satellite travels, the steeper the low energy spectrum becomes (Webber 1998).

Indeed, as recently as Putze et al. (2011), statistical, Monte Carlo, and "leaky box" models have been unable to constrain the low energy cosmic ray spectrum, due to a lack of direct measurement of low energy cosmic ray protons outside the solar influence.

Indriolo et al. (2009) list many of the proposed cosmic ray spectra. We consider three representative spectra (Hayakawa et al. 1961; Spitzer & Tomasko 1968; Nath & Biermann 1994), which are shown in Figure 3.1. These three spectra span the range of low energy cosmic rays. The spectrum from Spitzer & Tomasko (1968) is based on solar system measurements of the low energy cosmic ray flux, and contains the minimum low-energy cosmic ray spectrum. Nath & Biermann (1994) assume that the power-law for the cosmic ray spectrum at 1 GeV continues down until a hard cut-off at 1 MeV. Theirs is the highest published estimate of the low energy cosmic ray flux. We chose to use these three spectra in order to provide the full range of impact that different low energy cosmic ray flux spectra have on the ionization rate. The spectrum of Nath & Biermann (1994) increases the most steeply towards lower energies, that of Spitzer & Tomasko (1968) actually decreases towards lower energies, and that of Hayakawa et al. (1961) lies in the middle.

3.2.2 Cross Sections

We calculate the loss of energy by considering 10^4 cosmic ray protons with energies, E (in eV unless otherwise noted), distributed according to the three spectra selected above. The particles stream into a cloud of a number density n (cm⁻³). At each distance increment, the particles are each assigned a random number, which is compared with the probability of an ionizing or other inelastic collision over an incremental distance, determined by cross-sections, σ (cm²). For ionizing collisions by protons we use the form of σ_i from Spitzer & Tomasko (1968). The cross section (cm²) for ionization of a hydrogen atom as a function of E and the rest-energy of the proton (E_P) is given by

$$\tau_{i,\mathrm{H}} = 7.63 \times 10^{-20} \left(1 - \left(\frac{E_P}{E + E_P} \right) \right)^{-1} + 1.23 \times 10^{-20} \log \left(\left(\frac{E + E_P}{E_P} \right)^2 - 1 \right) - 5.29 \times 10^{-21}.$$
(3.1)

The first term is dominant for "low" energies (500 keV < E < 50 MeV), so for E < 50 MeV, $\sigma_{i,H} \propto 1/E$, down to $E \approx 500$ keV, when Equation (3.1) ceases to be accurate. This cross-section is also used below for determining the cosmic ray ionization rate of atomic hydrogen. For molecular hydrogen, we simply multiply the cross section by a factor of 2.

Inelastic collisions are considered for atomic and molecular hydrogen only, and we use the cross-sections from Cravens et al. (1975), accounting for rotational, vibrational and electronic excitation as well as dissociation reactions. For the ionization of helium, the differential cross-section from Dalgarno et al. (1999) is integrated to yield a total cross section:

$$\sigma_{i,\text{He}} = 1.5\epsilon_0 A(E), \tag{3.2}$$

where $A(E) (\propto 1/E$ for $E \leq 100$ MeV; $\propto \log(E)$ for $E \geq 1$ GeV) and ϵ_0 are parameters fit to the measurements of Shah et al. (1987).

3.2.3 Energy Loss

The energy loss calculation assumes a column great enough that the cosmic rays will collide with gaseous atoms and molecules many times. Since our model is one-dimensional, we do not consider the effects of elastic collisions on the exclusion of low energy cosmic rays from molecular clouds.

Because there are many collisions, we are justified in utilizing the average energy lost by cosmic ray in an ionizing collision, \overline{W} . This is equal to the ionization energy plus the average energy of the ejected electron. For molecular hydrogen, this is determined from the differential cross-section by Cravens & Dalgarno (1978); Dalgarno et al. (1999) to be

$$\overline{W}$$
 (eV) = 7.92 $E^{0.082}$ + 4.76, (3.3)

where E (eV) is the energy of the cosmic ray before the ionizing event. The energy losses from other types of inelastic collisions with molecular hydrogen, as well as ionizing and other inelastic collisions with H and He are taken from the detailed forms in Cravens et al. (1975).

This energy loss is subtracted from the initial energy of the cosmic ray, and becomes the new energy. At each increment, a new flux-spectrum, $j(E, N_H)$, is calculated, and new random numbers are assigned to the cosmic rays. Because of the energy-dependence of the σ functions, lower energy

cosmic rays have more ionizing collisions. In the case of the spectrum of Nath & Biermann (1994), cosmic rays with E < 50 MeV contribute 99% to the value of ζ (see Section 3.2.5). To complicate matters, however, there is energy loss from magnetic effects in addition to the loss from collisions. Magnetic energy loss is assigned based on interactions with Alfvén waves, as discussed below, using a static magnetic field of 3 μ Gauss.

3.2.4 Magnetic Field Effects

Magnetic fields play an important role in the transport of cosmic rays. The Lorentz force is the largest magnetic force acting on cosmic rays, and affects energy loss by increasing the path length cosmic rays travel, as they spiral along the magnetic field lines. This resulting increase in path length is not, however, the primary source of energy loss. Rather, the dominant magnetic field effect on cosmic rays is due to irregularities in the magnetic field.

Because of the neutralization of low-energy cosmic rays, there will be far fewer cosmic rays at the center of the cloud than at the edge. Since cosmic rays are overwhelmingly positively charged, these losses introduce a charge imbalance in the cloud. Electrons are attracted to the edge, and their motion generates magnetic field irregularities moving from the center to the edge of the cloud with velocity $v_A = B(4\pi\rho)^{-1/2}$. These irregularities, called Alfvén waves, are the dominant source of energy loss, as discussed in Skilling & Strong (1976). Hartquist et al. (1978, 1979) first applied the work of Skilling & Strong (1976) to calculate cosmic ray ionization rates, and proposed different values of ζ , depending on the object.

Following Skilling & Strong (1976), we determine the charge imbalance using the Monte Carlo simulation with B = 0, and consider it in terms of a characteristic column density, $\lambda(E)$ (cm⁻²), determined by the simulation, at which the number of cosmic rays will be depleted by a factor of e. This means that N_H must be $\geq \lambda(E)$ for cosmic rays of energy E to be significantly affected by magnetic field irregularities. This function will appear later in the analysis.

Alfvén waves are driven by the charge imbalance, and are damped by the friction between ions and the surrounding gas, as discussed by McIvor (1975) in terms of the collision rate Γ (s⁻¹) between ions and neutrals (Dalgarno & Dickinson 1968). The larger Γ is, the less effect the waves have. The static magnetic field enhances the damping by absorbing smaller irregularities. However, the larger static magnetic field also increases v_A , and thus the frequency of collisions between the cosmic rays and the Alfvén waves.

This mechanism for cosmic ray energy loss by Alfvén wave effects is important for $N_H < 10^{24}$ cm⁻² when $B \leq 6$ mG and $n_H \leq 10^9$ cm⁻³. At a given column density, cosmic ray energy is substantially affected by Alfvén waves for energies less than the energy E_0 . The static magnetic field outside denser regions is assumed to be much smaller than the field inside these regions. Because the difference between the magnetic field inside and outside the cloud significantly dampens the Alfvén waves for mid to high energy cosmic rays, E_0 cannot be greater than 50 MeV (Cesarsky & Volk 1978). E_0 is dependent on various physical parameters of the source in question. For typical cold and dense interstellar conditions, n(HI) = 1 cm⁻³, $n_H = 10^4$ cm⁻³, T = 20 K, and $B = 3 \,\mu\text{G}$. Under these conditions, the use of $j_0(E)$ from Nath & Biermann (1994) leads to $E_0 = 1$ MeV at $N_H = 10^{19}$ cm⁻², while for $N_H > 10^{21}$ cm⁻², $E_0 = 50$ MeV.

Integrating over energies up to this cutoff value, we can obtain the magnetohydrodynamic solution for $j_{IC}(E, N_H)$, the "In-Cloud" cosmic ray flux-spectrum at a given N_H , to be (Skilling & Strong 1976)

$$j_{\text{IC}}(E < E_0, N_H) = \frac{\lambda(E)}{E} \left[\frac{E_0 j(E_0, N_H)}{\lambda(E_0)} + \frac{2\upsilon_A}{N_H} \int_{E'=E}^{E_0} \frac{\alpha j(E', N_H)}{\upsilon(E')} dE' + \frac{U_M \Gamma}{\pi^2 m \upsilon_A \Omega_0 N_H} \ln \left(\frac{\gamma_0^2 - 1}{\gamma^2 - 1} \right) \right];$$
(3.4)

$$j_{\rm IC}(E > E_0, N_H) = j(E, N_H)$$
 (3.5)

In this expression, $j(E, N_H)$ is the spectrum determined using the Monte Carlo simulation in the absence of magnetic field effects, the magnetic energy density $U_M = B^2/2\mu_0$ (erg/cm⁻³), Ω_0 is the gyromagnetic frequency (s⁻¹), the Compton-Getting factor α (Gleeson & Axford 1968) is

$$\alpha = -\frac{10}{9} \frac{E}{j_0(E)} \frac{\partial j_0}{\partial E},$$

where j_0 is the initial cosmic ray flux-spectrum, $\gamma = (1 - v^2/c^2)^{-1/2}$ and $\gamma_0 = (1 - v_0^2/c^2)^{-1/2}$ where v_0 is the velocity of a cosmic ray of energy E_0 .

Given a steep initial $j_0(E)$, the approximate effect of the Alfvén waves and Lorentz Force is to shift the cosmic ray spectrum, and thus the ionization rate (see next section), from $\zeta(N_H)$ to $\zeta(5N_H)$, so that the ionization rate decreases more strongly with column.

For cosmic ray flux-spectra that are not very steep (m < 2 for $j \propto E^{-m}$), the shift is less extreme. Of course, for the full description of the relationship of ζ to the column density, Equation (3.5) must be calculated for $E < E_0$.

3.2.5 The Column-Dependent Ionization Rate

The value of $\zeta(N_H)$ is calculated by integrating the product of the flux-spectrum from eq. (3.5), $j_{\text{IC}}(E, N_H)$, and $\sigma_{i,\text{H}}(E)$ from eq. (3.1), as a function of "depth" N_H into a cloud, with various correction factors:

$$\zeta(N_H) = 1.8 \times \frac{5}{3} \times \int_0^\infty 4\pi \sigma_{i,\rm H}(E) j_{\rm IC}(E, N_H) dE.$$
(3.6)

The factor of 5/3 (Spitzer & Tomasko 1968; Dalgarno et al. 1999) takes into account the additional ionization caused by secondary electrons, while the factor of 1.8 accounts for ionization due to α particles (He⁺²). These particles are the second most important source of ionizing cosmic rays ($\zeta_{\alpha} \approx 0.8\zeta_p$). By comparison, relativistic electrons, the third most important ionizing source, have little effect: $\zeta_e \sim \zeta_p/100$.

Three different functions for $\zeta(N_H)$ have been calculated, based on the cosmic ray flux-spectra in Figure 3.1, which are chosen to be widely divergent below $E \approx 500$ MeV to account for the uncertainty in the low-energy region (Hayakawa et al. 1961; Spitzer & Tomasko 1968; Nath & Biermann 1994). Analytical expressions for $\zeta(N_H)$, used in the models below, are:

$$\zeta_{H,\text{Hayakawa}} = \frac{5 \times 10^4}{N_H} + 10^{-17} \text{ s}^{-1}, \qquad (3.7)$$

$$\zeta_{H,\text{Nath}} = 0.002(N_H)^{-0.6} + 10^{-17} \text{ s}^{-1}, \qquad (3.8)$$

and are valid for 10^{24} cm⁻² $\gtrsim N_H \gtrsim 5 \times 10^{19}$ cm⁻². These analytical expressions do not seem to change significantly for 100 cm⁻³ $< n < 10^6$ cm⁻³ and 5 K < T < 1000 K, beyond which the effects of the density and temperature on magnetic field effects becomes significant.

The results are depicted in Figure 3.2, in terms of the visual extinction between the cloud and
the UV source (A_V) . We determine $A_V \approx 4.3 \times 10^{-22} N_H$, using *Q* efficiencies from Laor & Draine (1993) with a grain distribution (in terms of the "radius" of the grain, *a*) of $n \propto a^{-3.5}$ with $r_{\min} = 5$ nm and $r_{\max} = 1 \,\mu$ m. With these assumptions, the analytical expressions for $\zeta(A_V)$ are:

$$\zeta_{H,\text{Hayakawa}} = \frac{2.2 \times 10^{-17}}{A_{\text{V}}} + 10^{-17} \text{ s}^{-1}, \qquad (3.9)$$

$$\zeta_{H,\text{Nath}} = 3.05 \times 10^{-16} (A_{\text{V}})^{-0.6} + 10^{-17} \text{ s}^{-1}.$$
(3.10)

These expressions are later referred to as "mid-range" and "high-range" values, respectively.

The wide range of the ionization rate demonstrates the importance of low-energy cosmic rays, especially at low N_H or A_V . Other calculations of $\zeta(N_H)$ have been performed, either for high column densities (> 10^{24} cm⁻²) where low energy cosmic rays do not penetrate (Umebayashi & Nakano 1981; Finocchi & Gail 1997), without consideration of the magnetic field (Padovani et al. 2009), or in regions where there are no ionization losses (Padoan & Scalo 2005). Recently, Padovani & Galli (2011) have incorporated the effect of magnetic mirroring, whereas we have treated the effects of Alfvén waves on cosmic ray streaming. The results in this chapter suggest that Alfvén waves may have a more substantial effect on ζ , with factor of ~10 impact on ζ at certain N_H for Alfvén waves versus a factor of ~2-4 impact on ζ from magnetic mirroring. Ultimately, a robust magnetohydrodynamics simulation of cosmic ray transport would be necessary to determine what magnetic field effects have the most significant impact on cosmic ray penetration.

In our study below, we determine the effect of four different functions for ζ on the chemistry in the Horsehead Nebula. We consider the $\zeta(N_H)$ functions based on flux spectra from Nath & Biermann (1994) and Hayakawa et al. (1961), as well as constant values for ζ of 10^{-15} s⁻¹, and 10^{-17} s⁻¹, the latter of which is effectively the $\zeta(N_H)$ derived from the spectrum of Spitzer & Tomasko (1968).

3.3 Modeling the Horsehead Nebula

We have used the PDR model of Morata & Herbst (2008) with the OSU 03/2008 gas-phase network.³ This network is a purely gas-phase one that treats the PDR as a semi-infinite series of slabs with the radiation source impinging on one edge. It does not account for freeze-out or any surface

³http://www.physics.ohio-state.edu/~eric/research.html



Figure 3.1: Three different cosmic ray flux spectra, taken from Hayakawa et al. (1961) (dashed line), Spitzer & Tomasko (1968) (dotted line), and Nath & Biermann (1994) (solid line).



Figure 3.2: The results of the one-dimensional Monte Carlo model for ζ described in Section 3.2 in terms of A_V . The solid red, dashed green, and dotted blue lines derive from the flux-spectra of Nath & Biermann (1994), Hayakawa et al. (1961), and Spitzer & Tomasko (1968), respectively. These lines fit the averaged result of dozens of iterations of the Monte Carlo model. The results from a single Monte Carlo run using the flux-spectrum of Hayakawa et al. (1961) are included (pink dotted) in order to show error.

chemistry, aside from a simple approximation for H_2 formation on grains and selected ion recombination processes. Radiative transfer and self-shielding of H_2 and CO (Draine & Bertoldi 1996; Lee et al. 1996b) are calculated in progression, starting with the slab at the edge. The chemistry is solved with a time-dependent gas-phase kinetics model for each slab. This model, like our model for cosmic rays, is one-dimensional (1D). Because cosmic rays are thought to stream in from all sides, the effects of the geometry are mostly lost in this model. However, even with cosmic rays streaming in from all angles, low energy cosmic rays will dominate at the edge, and will be absent from the center. The average value of ζ at a slab near the edge will be close to the value determined from the 1D Monte Carlo model. Because the majority of slabs near the center will not have low-energy cosmic rays, the average ζ near the center also be close to the 1D value. Thus the average value of ζ at different slabs of the cloud will be close to the 1D values we use for ζ found in Figure 3.2.

Following Pety et al. (2005), we compare, when possible, observations with model results for three regions at different optical extinctions (A_V) from the edge of the Horsehead PDR. These are the IR-edge ($A_V = 1.56 \pm 0.73$), IR-Peak ($A_V = 4.55 \pm 1.7$), and the Cloud ($A_V = 11.7 \pm 4.1$). The error bars in A_V are based both on the beam size of the observations and uncertainty in the density profile of the cloud, as discussed in the next section. We determine the error in fractional abundance by taking the ratio between the observed column density of the species and the error in that column density, both from Pety et al. (2005).

3.3.1 Physical Conditions and Initial Chemical Abundances

The density profiles used are taken from Habart et al. (2005). The temperature profile is calculated from thermal balance (Le Petit et al. 2006). Cosmic rays heat the interstellar medium through the thermalization of secondary electrons and photons, (Field et al. 1969; Glassgold & Langer 1973). Thermal heating by cosmic rays begins to dominate at $A_V > 3$, but the thermal impact of different cosmic ray ionization rates is not very significant until $\zeta > 10^{-16} \text{ s}^{-1}$. Since even the highest $\zeta(N_H)$ drops to $\approx 10^{-16} \text{ s}^{-1}$ at the Cloud region, the temperature difference here between the high $\zeta(N_H)$ and $\zeta = 10^{-17} \text{ s}^{-1}$ is only about 4 K. The density and temperature profiles are shown in Fig. 3.3.

The gas density increases with spatial distance into the nebula as a power law with an exponent

 β (Habart et al. 2005), which in terms of column density can be written as:

$$n_{H}(N_{H}) = \begin{cases} n_{H,0} \left[\frac{(\beta+1)N_{H}}{x_{0}n_{H,0}} \right]^{\beta/(\beta+1)} & N_{H} \le N_{H,0} \\ n_{H,0} & N_{H} > N_{H,0}, \end{cases}$$
(3.11)

where $\beta \ge 1$ is a dimensionless constant used to parameterize the steepness of the number density, $n_{H,0} = 2 \times 10^5 \text{ cm}^{-3}$, $x_0 = 0.02 \text{ pc}$ is a length scale, and $N_{H,0} = (1 + \beta)^{-1} 1.23 \times 10^{22} \text{ cm}^{-2}$ is the column density at a depth of x_0 . For our analysis, we show the results for $\beta = 1$, and discuss results for both $\beta = 1$ and $\beta = 4$. The steeper density gradient impacts the UV photon flux and the resulting thermal balance. There are different total densities for the IR-edge and IRpeak regions. The difference in UV penetration, temperature and density at different values of A_V noticeably impacts the chemistry. The cosmic ray ionization, however, is not significantly altered by the density gradient, because for the ranges of density of 100 to 10^5 cm^{-3} , ζ is column-dependent, but not density dependent.

Other densities and density profiles have been proposed. Pety et al. (2005) used several uniform number densities and profiles, while Goicoechea et al. (2009b) proposed a slowly changing piecewise function for the density, with three sections instead of two, reaching 2×10^5 cm⁻³ at $A_V \approx 5$ instead of $A_V \approx 1.0$, as used here. Until the number density is better determined, significant uncertainties in the extinction at a given angular depth will persist.

The UV radiation field impinging on the Horsehead surface has been a topic of much discussion and uncertainty (Anthony-Twarog 1982; Zhou et al. 1993; Abergel et al. 2003). Values of $\chi = 30$ to $\chi = 100$ in Draine units (Draine 1978) have been proposed. We use $\chi = 60$, because this is the most commonly used value for the Horsehead PDR. The external UV field is important to the chemistry only for the IR-edge. For the IR-peak and the Cloud regions, cosmic rays are the primary ionizing and photochemical agent.

The initial chemical abundances used for the Horsehead PDR (Lee et al. 1996a; Morata & Herbst 2008) are listed in Table 3.2 and represent abundances for a dark cloud prior to the onset of a nearby star. These abundances comprise observed values for small (less-than-six-atom) species in TMC-1, as well as calculated early-time values from Smith et al. (2004) for atoms and small molecules that have not been observed, based on so-called "low-metal" elemental abundances.



Figure 3.3: The temperature (dashed line) and density (solid line) profiles as functions of visual extinction with $\zeta_{H,\text{Nath}}$. The density profile is in the form of Habart et al. (2005), our equation (3.11), with $\beta = 1$. The temperature is from thermal balance (Le Petit et al. 2006). At $A_V = 10$, $\zeta \approx 10^{-16} \text{ s}^{-1}$, which raises the temperature by $\approx 4 \text{ K}$ at the center compared to a ζ of 10^{-17} s^{-1} .

In addition to these initial abundances, we also investigated cases with much higher elemental abundances of sulfur, based primarily on the analysis of CS and HCS⁺ by Goicoechea et al. (2006b), who place the total elemental sulfur abundance with respect to $n_{\rm H}$ at 3.5×10^{-6} . On the other hand, Teyssier et al. (2004) used a value of [S] ~ 10^{-7} , similar to the low-metal value used in this part of the chapter. To determine the effect of raising the sulfur abundance, we utilized elemental abundances for sulfur, relative to hydrogen, of 10^{-6} and 10^{-5} , starting primarily from the neutral atomic form.

The abundances are calculated from time t = 0 to steady state ($t = 5 \times 10^6$ yr). Since the age of the Horsehead Nebula is not well-determined, values from $10^4 - 10^6$ yr have been considered (Morata & Herbst 2008). We focus only on the time of 10^5 yr, because in general the calculated results are closest to observational values at this time. We also use this time because it is a reasonable age for a molecular cloud, given its size and velocity gradient (see Pound et al. 2003). Time-dependence was investigated by Morata & Herbst (2008) albeit with a different density profile from

what is used here. They found that at times between 10^5 yr and steady-state, the abundances of carbon chain species in the Cloud region become sharply lower, as is found in standard cold dark clouds. They also investigated times as early as 10^4 yr, at which time the abundance profiles are flatter. Our calculations for carbon chain species have reached steady state by 10^4 years for $A_V < 5$. For $A_V > 5$, our calculations confirm their findings.

In Figures 3.4 to 3.6, we show the calculated abundances of various molecules as continuous functions of visual extinction with observed values in boxes to delineate the uncertainties in both abundance and A_V . The calculated abundances are plotted with two fixed values of ζ : 10^{-17} s⁻¹ and 10^{-15} s⁻¹, as well as with two column-dependent ionization rates depicted in Figure 3.2: the mid-range $\zeta(N_H)$ (dashed green line), and the high-range $\zeta(N_H)$ (solid red line). The fixed value of $\zeta = 10^{-17}$ s⁻¹ is equivalent to the lowest-range $\zeta(N_H)$ in Figure 3.2, which utilizes only high-energy protons. Neither of the two fixed values for ζ is likely to be physically reasonable; the low value can pertain to the inner Cloud region but is less likely to pertain to a region near the edge, where at least some low-energy cosmic rays exist, while the high value is more likely to pertain only to the edge of the PDR. Unless specified, the low elemental abundance of sulfur is utilized.

3.3.2 Results: C_2H , $c - C_3H_2$ and C_4H

Hydrocarbons are not direct tracers of ζ ; nevertheless, an enhanced ζ at the surface of the Horsehead nebula may help to explain the high abundances of these small hydrocarbons at the edge. C₂H, $c - C_3H_2$ and C₄H are formed by a complex network of reactions, linked at least partially to the cosmic ray ionization rate via several sequence of reactions based on C and C⁺. The sequence involving neutral atomic C starts with the reactions:

$$H_2 + CRP \rightarrow H_2^+ + e^- + CRP \tag{3.12}$$

$$H_2^+ + H_2 \to H_3^+ + H$$
 (3.13)

$$C + H_3^+ \to CH^+ + H_2,$$
 (3.14)

and CH⁺ initiates a series of chemical reactions that eventually results in C_2H , $c - C_3H_2$ and C_4H via recombination with electrons. The C⁺ ion is produced in three ways depending on physical

	a (* *) 1	~ ·	a (- -) 1
Species	$f(X)^1$	Species	$f(X)^1$
H_2	0.5	C_2H	1.0×10^{-8}
Н	7.5×10^{-5}	CO_2	1.3×10^{-8}
He	0.14	H_2O	3.5×10^{-8}
С	2.8×10^{-8}	HCN	1.0×10^{-8}
0	1.0×10^{-4}	HNC	1.0×10^{-8}
Ν	1.3×10^{-5}	NH ₃	$1.0 imes 10^{-8}$
S	7.2×10^{-8} ²	SO_2	$5.0 imes 10^{-10}$
Si	$7.8 imes 10^{-9}$	C_3H	5.0×10^{-9}
Cl	4.0×10^{-9}	C_4H	4.5×10^{-8}
Fe	3.9×10^{-10}	$c - C_3H_2$	5.0×10^{-9}
Mg	1.9×10^{-9}	HC ₃ N	1.0×10^{-8}
Na	4.7×10^{-10}	C^+	4.7×10^{-9}
Р	3.0×10^{-9}	H^+	4.2×10^{-10}
CH	$1.0 imes 10^{-8}$	He ⁺	3.5×10^{-10}
CN	2.5×10^{-9}	Fe ⁺	2.6×10^{-9}
CO	7.3×10^{-5}	Mg^+	5.1×10^{-9}
CS	2.0×10^{-9}	Na ⁺	1.5×10^{-9}
N_2	4.2×10^{-6}	S^+	1.2×10^{-9}
NO	1.5×10^{-8}	Si ⁺	2.5×10^{-10}
O_2	8.1×10^{-8}	H_3^+	1.4×10^{-9}
OH	1.0×10^{-7}	HCO+	4.0×10^{-9}
S_2	1.8×10^{-9}	HCS^+	2.0×10^{-10}
SO	1.0×10^{-9}	N_2H^+	2.0×10^{-10}

Table 3.2: Initial fractional abundances with respect to n_H

conditions: at low extinction ($A_V < 2.5$), it is formed principally by photoionization, and can reach a fractional abundance as high as 10^{-4} , whereas at high extinction ($A_V > 4.5$) it is formed less efficiently by the reaction between He⁺ and CO. In the middle region ($2 < A_V < 5$), secondary photons from cosmic rays form a large amount of the C⁺. Once produced, it can radiatively associate with H₂ to form the CH⁺₂ ion, which initiates a series of reactions similar to those initiated by CH⁺ (Herbst & Millar 2008). Because of these alternate pathways, small hydrocarbons may not be as sensitive to ζ very close to the edge or deep within the Horsehead PDR. Regardless, our robust chemical network allows us to explore in detail the effect of a column-dependent ζ on the Horsehead Nebula.

The model abundances for C₂H, c – C₃H₂, and C₄H vs A_V can be found in Figure 3.4, where observed abundances with estimated uncertainties are plotted as boxes for the three regions studied: the IR-edge, the IR-peak, and the Cloud. For C₂H, our use of temperature and density profiles seems to account for the observed abundance at the IR-edge, regardless of the value of ζ , probably because C₂H formation is so dependent on photon effects at the edge. The results diverge for the IR-peak and Cloud, where the high-range $\zeta(N_H)$ and $\zeta = 10^{-15}$ s⁻¹ seem to do better than the other two choices of ζ . In the IR-peak, the abundances obtained with the high-range $\zeta(N_H)$ and $\zeta = 10^{-15}$ s⁻¹ come within a factor of ≈ 5 of the observed value, and are closer still for the Cloud region.

For c – C₃H₂, and for C₄H, none of the four plots comes particularly close to the observed values at the center of the IR-edge, although the curves obtained with the high-range $\zeta(N_H)$ and $\zeta = 10^{-15}$ s⁻¹ graze the lower portion of the observation box for C₄H. This discrepancy suggests that, though a high surface ζ is important, there are likely other factors that must be taken into account, such as PAH fragmentation (Pety et al. 2005). For the IR-peak region, the high-range $\zeta(N_H)$ and $\zeta = 10^{-15}$ s⁻¹ models lead to results that graze portions of the observational boxes for both species , with the others models exhibiting much too low an abundance. Finally, for the Cloud region, the high-range $\zeta(N_H)$ and $\zeta = 10^{-15}$ s⁻¹ models do quite well for C₄H, and c-C₃H₂. while the lower ionization models show reasonable agreement only for the latter.

It would appear that, on balance, the results obtained with the high constant ζ and the highrange column-dependent ζ are closer to observation in most instances for these three hydrocarbons. To further distinguish between these two sets of results, we focus on the abundance ratios between IR-peak and Cloud regions for the three carbon-chain species. The ratios are taken at the visual extinctions where the models agree best with the observations, and are listed in Table 3.3. The reason for taking these ratios is that we can better compare results between a fixed and a column-dependent ionization rate in this manner. These ratios are examined only as a way to distinguish between a constant and a column-dependent ζ , and their use beyond this function is severely limited. For example, the C₂H emission attributed to the Cloud region may be from the FUV illuminated surface (for an analogous example involving HCO, see Gerin et al. 2009). It is likely that the observed ratios will change and will be far better constrained when the Horsehead Nebula is explored at higher angular resolution.

For C₂H and c – C₃H₂, the ratios are much closer to observation for the column-dependent $\zeta(N_H)$ than for $\zeta = 10^{-15}$ s⁻¹. In both of these cases, the ratios from the $\zeta(N_H)$ model are within a factor of 2 of the observed ratios. For $\zeta = 10^{-15}$ s⁻¹, model ratios disagree by a factor of 5-7. In the case of C₄H, the ratio from the constant ζ agrees slightly better with observations than for $\zeta(N_H)$, although the ratios of both models are close to observation. Also, examining the C₄H abundances from Figure 3.4, it is evident that, within the Cloud region, the results from $\zeta(N_H)$ are much closer to observation than the results from $\zeta = 10^{-15}$ s⁻¹. In summary, as well as being unphysical, the results from a model with a constant $\zeta = 10^{-15}$ s⁻¹ do not agree as closely as the results from a model with a column-dependent $\zeta(N_H)$.

For $\beta = 4$ at $t = 10^5$ yr, the results are not significantly changed for the IR-edge, and the model underestimates the small hydrocarbon abundances for the IR-peak region by about an order of magnitude. The reasons for this seem to be as involved as the hydrocarbon chemistry. The most significant factor is that the production of these hydrocarbons at a higher density requires a higher ζ , and for $\beta = 4$, the density is much higher at the IR peak than for $\beta = 1$. Also, with the steeper density gradient, photons are more effective at ionizing and dissociating at the IR-Edge, but fall off more abruptly at higher A_V . The difference in C⁺ formation by photons between $\beta = 1$ and $\beta = 4$ density profiles is a factor of three, and only present at $A_V < 2.5$.

It should finally be mentioned that thermal balance from photons depends somewhat on the density, and so the temperature profiles with $\beta = 1$ and $\beta = 4$ are different. At $A_V = 0.001$, the gas-phase temperature for $\beta = 1$ is about 300 K, where for $\beta = 4$, $T \approx 600$ K. The gas-phase

	IR-peak/Cloud ¹							
Species	Obs.	$\zeta(N_H)$	10^{-15} s^{-1}					
C ₂ H	14	8.6	2.7					
$c-C_3H_2$	25	13	3.3					
C_4H	5	8	4					

Table 3.3: Abundance Ratios for Carbon-chain Species Between IR-peak and Cloud Regions

temperatures for the two density profiles converge at $A_V = 1$, and this undoubtedly has some impact on the chemistry. It should be emphasized that $\zeta(N_H)$ is similar for the steep and gradual density gradients.

3.3.3 Results: HC₃N, HCO⁺, HCO and the electron fraction

Only one line of the carbon-chain species HC₃N has been detected, and this with a very large beamsize (Teyssier et al. 2004). We follow Teyssier's tabulated value for A_V , and treat the emission as originating in the IR-peak, though there is some uncertainty about the origin of this emission. The four models all under-produce the observed abundance of HC₃N by a little less than an order of magnitude or more, as can be seen in Figure 3.4, with the models with the high-range $\zeta(N_H)$ and the fixed $\zeta = 10^{-15} \text{ s}^{-1}$ coming closest.

Cyanoacetylene (HC_3N) is not as dependent as the other species on cosmic ray ionization for much of the range of visual extinction. Two reactions primarily lead to its formation:

$$CN + C_2H_2 \rightarrow HC_3N + H,$$

 $C_3H_2N^+ + e^- \rightarrow HC_3N + H.$

At the edge, the first reaction is directly related to ζ through C₂H₂, but the second reaction involves C₃H₂N⁺, the formation of which is not strongly dependent on ζ . In the Cloud region, the situation is reversed: C₂H₂ is less dependent on ζ , and C₃H₂N⁺ is then closely linked with cosmic ray ionization. Because of the two channels for HC₃N we expect less dependence on A_V except in the middle range: $1 < A_V < 5$. The results, shown in Figure 3.4, roughly bear this out. Interestingly, both the observed and calculated abundances for HC₃N are much lower than the initial value, which is taken from the TMC-1 abundance. The discrepancy with the Cloud value, over three orders of





Figure 3.4: Fractional abundances of C₂H, $c - C_3H_2$, C₄H, and HC₃N as functions of A_V. The boxes represent observations with error bars, and the lines are the model results for $\zeta = 10^{-17}$ s⁻¹ (blue dashed), $\zeta = 10^{-15}$ s⁻¹ (pink dotted), and, from Figure 3.2, the mid-range $\zeta(N_H)$ (green dashed) and high-range $\zeta(N_H)$ (red solid).

magnitude, is especially large and very different from the analogous cases for the hydrocarbons in Figure 3.4.

Figure 3.5 contains the observations and model results for HCO⁺ and HCO. Since HCO⁺ is optically thick, the carbon-13 isotopologue was used for observations. H¹³CO⁺ was observed in emission at $\approx 40^{\prime\prime}$ from the PDR edge (Gerin et al. 2009), corresponding to an $A_V \approx 10$, which is essentially the Cloud region. Following the analyses of Gerin et al. (2009) and Goicoechea et al. (2009b), we determined the abundance of HCO⁺ from H¹³CO⁺ by assuming ¹²C/¹³C = 60. A faint emission feature attributed to H¹³CO⁺ was also seen at $\approx 10^{\prime\prime}$ from the PDR edge, corresponding to an $A_V \approx 2$ with our density profile, and so lies essentially at the IR-edge.

In the immediate neighborhood of $A_V = 2$, however, none of the models produces enough HCO⁺, but the increase in abundance with increasing extinction is steep and by $A_V = 3$, all but possibly the $\zeta = 10^{-17}$ s⁻¹ model produce a comparable result to what is observed at the IR-edge. Goicoechea et al. (2009b) did much better fitting the HCO⁺ abundances at the edge by including PAH's. They also modeled profiles for H¹³CO⁺ and DCO⁺.

For the Cloud value, all models are in reasonable agreement with observation for HCO^+ , coming within factors of 2-5 of the observed abundance. The formation of HCO^+ by cosmic rays is very direct at high extinction; in regions where UV photons cannot penetrate, it is almost solely the product of the destruction channel for protonated molecular hydrogen with carbon monoxide. At the IR-edge, however, the UV driven formation by the reactions $H_2 + CO^+$ and $H_2O + C^+$ dominates. In all regions, HCO^+ is destroyed mainly by recombination.

For neutral HCO, all model results are too low by an order of magnitude or more at both the IRedge and Cloud regions, even with the relatively fast reaction between CH_2 and O (from Gerin et al. 2009). Our results disagree with the model results from Gerin et al. (2009) and Goicoechea et al. (2009b) partly because the Meudon reaction network includes a formation mechanism absent in the OSU network, the photodissociation reaction

$$H_2CO + h\nu \to HCO + H, \qquad (3.15)$$

where hv represents an external UV photon. This reaction is also discussed in Gerin et al. (2009). Including this reaction enhances the HCO abundance by a factor of 5 in the PDR, bringing the HCO abundance within an order of magnitude of the observed value.

The ionization fraction, $f(e^{-})$, is a measure of elemental abundances, ionization rate, density, and chemistry, as well as a constraint on the coupling of the magnetic field to the matter in the cloud. The ionization fraction from our models, as shown in Figure 3.5, ranges from ~ 10^{-4} in the PDR to ~ 10^{-8} in the Cloud region. This range of fractions agrees generally with the profile in Goicoechea et al. (2009b, their Figure 4). Their inferred profile for the ionization fraction would favor the mid-range $\zeta(N_H)$ from the cosmic ray flux-spectrum of Hayakawa et al. (1961).

For the steeper density profile with $\beta = 4$ and the high $\zeta(N_H)$, our results are somewhat different. The HCO⁺ abundances are not significantly changed, and the modeled HCO abundances increase by a factor of two in the IR-Edge and IR-Peak regions (at 10⁵ yr). Significantly, our calculated abundance of HC₃N comes into good agreement with the Cloud region observation; it is a factor of 3 higher than the observed abundance at $t = 10^5$ yr.

3.3.4 Tabulated Abundances

Calculated fractional abundances (with respect to $n_{\rm H}$) obtained with the standard elemental abundances are listed for more than twenty species in Table 3.4, including both observed and undetected molecules. The calculated results are for a time of 10⁵ yr and pertain to the center points of the IRedge, IR-peak, and Cloud regions (Pety et al. 2005), for which observational results are also shown, when available. Some of the tabulated abundances, HOC⁺ especially, seem to be possible tracers for the cosmic ray ionization, because their fractional abundance becomes more dependent on the extinction when ζ depends on column density, than when ζ is a constant value.

In this table, we consider only the model with the high-range $\zeta(N_H)$, because it is evident that, at least for carbon-chain species, use of this column-dependent ζ leads generally to better agreement with observations than models with lower ionization, and it is more physical than the constant highionization model. Also, we do not include the case of the steeper density profile in this table. Predictions are discussed below in Section 3.3.6.

Species ⁰	IR	-edge	IR-	peak	C	loud
•	Obs.	Mod.	Obs.	Mod.	Obs.	Mod.
O (10 ⁻⁵)		11		7.3		5.9
N (10 ⁻⁶)		16		1.1		1.3
$CN (10^{-8})$		2.3		1.0		0.2
NO (10 ⁻⁹)		0.07		77		103
O ₂ (10 ⁻⁷)		< 0.01		7.2		62
OH (10 ⁻⁷)		0.01		1.8		1.3
CO (10 ⁻⁵)		6.0		9.6		9.9
$H_2O(10^{-9})$		0.4		170		193
$C_2H(10^{-8})$	3.3	1.6	3.0	0.3	0.2	0.07
$c - C_3 H (10^{-10})$		1.9	5.4	0.6		1.4
$l-C_3H(10^{-10})$		1.0	2.9	8.0		0.9
$c - C_3 H_2 (10^{-10})$	13	2.3	11	10	0.4	2.3
$C_4H(10^{-9})$	9.5	1.3	3.6	2.0	0.8	0.1
$CH_4 (10^{-9})$		0.03		33		50
$C_6H(10^{-11})$		1.4		4.1		0.2
HCO (10 ⁻¹⁰)		0.03	17^{1}	0.1		0.2
NH ₃ (10 ⁻⁸)		< 0.01		1.2		2.5
HCN (10^{-10})		0.8		40		26
HNC (10^{-10})		0.9		67		17
$HC_3N(10^{-11})$		< 0.01	5.7^{2}	0.7		0.3
$HC_5N(10^{-12})$		< 0.01		4		0.13
CH^{+} (10 ⁻¹²)		5		0.02		< 0.01
CO^{+} (10 ⁻¹³)	$\leq 5^3$	20		3.2		1.3
$HCO^{+} (10^{-9})$	0.9^{4}	0.02		10	3.9^{4}	11
$HOC^{+} (10^{-12})$	4 ⁵	6		73		27
$OH^+ (10^{-13})$		4		15		5
H_2O^+ (10 ⁻¹³)		8		33		12
H_3O^+ (10 ⁻¹⁰)		0.1		45		37
CH_3^+ (10 ⁻¹¹)		23		10		0.2
$C_2H_4^+$ (10 ⁻¹³)		1.5		19		12
$CS(10^{-8})$	1.6^{6}	0.04	4.0^{6}	0.04		0.01
$HCS^{+}(10^{-11})$		0.07	4.0^{7}	0.08		0.1

Table 3.4: Observations and model results for fractional abundances at $10^5 \ \rm yr.$



Figure 3.5: Relative abundances of HCO⁺, HCO and the ionization fraction as functions of A_V . The boxes represent observations with error bars, and the lines are the model results for $\zeta = 10^{-17}$ s⁻¹ (green dashed), $\zeta = 10^{-15}$ s⁻¹ (pink dotted), and, from Figure 3.2, the mid-range $\zeta(N_H)$ (blue dotted) and high-range $\zeta(N_H)$ (red solid).

3.3.5 The Sulfur-Rich Case

We considered sulfur-bearing species, both with the standard initial abundances, and also for a sulfur-rich environment. We found that the higher the elemental sulfur (up to a relative abundance of 10^{-5}), the closer the model matches observations for sulfur-bearing molecules. Our results and those of Goicoechea et al. (2006b) for the chemistry and radiative transfer agree very well.

The results for the observed sulfur-bearing species CS and HCS⁺ vs A_V at 10⁵ yr can be found in Figure 3.6 as a function of the sulfur elemental abundance. There are two sets of curves, depending upon the rate coefficient for the charge-exchange reaction

$$S + H^+ \rightarrow S^+ + H,$$

which can affect the abundances of CS and HCS⁺ at low sulfur abundances. This reaction has a listed rate coefficient of 1.3×10^{-9} cm³ s⁻¹ (Prasad & Huntress 1980) but a more likely value of 1×10^{-14} cm³ s⁻¹ has been calculated.⁴

The agreement attained by increasing the elemental abundance, [S], to 10^{-5} comes at a cost: at 10^{5} yr, all the carbon-bearing species in this scenario are reduced by up to a factor of 10 except at

⁴This rate has been tabulated in The Controlled Fusion Atomic Data Center (http://www-cfadc.phy.ornl.gov/astro/ps/data/cx/hydrogen/rates/cti.dat).



Figure 3.6: Relative abundances of HCS⁺ and CS as a function of A_V . The boxes are the observations with error bars, and the lines are the model results with $[S] = 10^{-5}$ (red), $[S] = 10^{-6}$ (green) and $[S] = 7.2 \times 10^{-8}$ (blue), all using the high column-dependent ζ from Figure 3.2. The solid lines use a rate for S + H⁺ \rightarrow S⁺ + H of 1.3×10^{-9} cm³ s⁻¹ (Prasad & Huntress 1980) and the dashed lines use a rate of 1×10^{-14} cm³ s⁻¹

the IR-edge. This effect is most severe in the Cloud region. This depletion occurs in part because the high sulfur abundance destroys hydrocarbons by reactions with S^+ and also with S at higher extinctions and because of the increased fractional ionization. The depletion of carbon-bearing species worsens agreement for all observed species except HCO⁺, which is brought to within a factor of 2 of observation in the Cloud region.

This problem may suggest that a more realistic gas-phase sulfur elemental abundance for the Horsehead Nebula should lie somewhere around 10^{-6} , in agreement with Goicoechea et al. (2006b). The abundances of observed and predicted molecules with $[S] = 10^{-6}$ are in Table 3.5 for the same species as listed in Table 3.4. Even with this intermediate sulfur abundance, the calculated abundances of carbon chain species in particular are lowered considerably compared with the corresponding values in Table 3.4, leading to worse agreement with observation.

3.3.6 Some Predictions

A high column-dependent ζ brings with it implications for chemistry in the Horsehead PDR. This column-dependent ζ varies from $\approx 2 \times 10^{-16} \text{ s}^{-1}$ at the IR-edge to $\approx 7 \times 10^{-17} \text{ s}^{-1}$ in the Cloud region and so leads to profiles distinctive from models with fixed ionization rates, as can be seen for carbon-chain species in Figures 3.4 to 3.6.

Also, other molecules are predicted to be in amounts in principle observable, and these are listed among the species in Tables 3.4 and 3.5. Because our $\zeta(N_H)$ produces reasonable abundances of C₄H and HC₃N in selected regions with a low elemental abundance of sulfur, we would also expect to observe, albeit with some difficulty, the more complex carbon-chains C₆H and HC₅N, based on our predictions for these regions. In addition, the molecule HCN should definitely be present in observable quantities, especially in inner regions, and its isomer, HNC, should also be observed with a ratio HCN/HNC ≈ 1 . We predict ammonia in observable quantities at $A_V > 4$, for the low-sulfur case.

Given the observations of high amounts of the reactive molecular ions OH^+ and H_2O^+ in many molecular objects (Gerin et al. 2010; Gupta et al. 2010), it would be useful to consider predicted abundances of these species. Our model predictions for OH^+ , H_2O^+ and H_3O^+ in the Horsehead Nebula are contained in Tables 3.4 and 3.5. These predictions show low abundances for the first two ions that are rather independent of which of the three regions we consider. The basic problem is the low abundance of atomic hydrogen except at the border of the PDR (Neufeld et al. 2010). Even at the IR-Edge, H_3O^+ is more than an order of magnitude higher than either OH^+ or H_2O^+ , though none of these species should be sufficiently abundant to be detected. In the Cloud Region, where the electron density is at the low level of a cold dark cloud, H_3O^+ is depleted rather slowly by reactions with electrons, and should achieve a high enough column to be detectable.

3.4 Discussion

We have modeled the Horsehead Nebula as a PDR with time-dependent gas-phase chemistry using a column-dependent cosmic ray ionization rate $\zeta(N_H)$, as well as the temperature and density profiles of Habart et al. (2005). At a cloud age of 10⁵ yr, the incorporation of a high $\zeta(N_H)$ improves

Species ¹	IR-	edge	IR-peak		Cloud	
	Obs.	Mod.	Obs.	Mod.	Obs.	Mod.
O (10 ⁻⁵)		12		9.9		4.9
N (10 ⁻⁶)		16		1.3		0.3
$CN (10^{-8})$		1.1		0.08		0.02
NO (10 ⁻⁹)		0.1		69		123
$O_2(10^{-7})$		< 0.01		18		260
OH (10 ⁻⁷)		0.01		1.0		1.0
CO (10 ⁻⁵)		5.5		7.3		7.3
$H_2O(10^{-9})$		0.4		420		390
$C_2H(10^{-8})$	3.3	1.1	3.0	0.3	0.2	< 0.01
$c - C_3 H (10^{-10})$		1.8	5.7	0.2		0.01
$l - C_3 H (10^{-10})$		1.0	2.9	0.1		< 0.01
$c - C_3 H_2 (10^{-10})$	13	2	11	0.4	0.4	0.03
$C_4H(10^{-9})$	9.5	0.7	3.6	0.1	0.8	< 0.01
$CH_4 (10^{-9})$		0.05		30		22
$C_6 H (10^{-11})$		1.2		< 0.01		< 0.01
HCO (10^{-10})		0.9	17^{1}	0.5		0.06
$NH_3 (10^{-8})$		< 0.01		< 0.01		< 0.01
HCN (10^{-10})		0.6		18		10
HNC (10^{-10})		0.9	_	39		27
$HC_3N(10^{-11})$		< 0.01	5.7^{2}	0.03		0.01
$HC_5N(10^{-12})$		< 0.01		< 0.01		0.01
$CH^+ (10^{-12})$		2.9		< 0.01		< 0.01
$CO^{+}(10^{-13})$	$\leq 5^3$	1.5		0.7		0.5
$HCO^{+}(10^{-9})$	0.9^{4}	0.02		0.7	3.9^{4}	6.2
$HOC^{+}(10^{-12})$	4 ⁵	4		20		10
$OH^+ (10^{-13})$		3.1		9.3		3.6
H_2O^+ (10 ⁻¹³)		5.3		15		7.4
$H_3O^+ (10^{-10})$		0.1		50		40
CH_3^+ (10 ⁻¹¹)		20		3.2		0.3
$C_2H_4^+$ (10 ⁻¹³)	-	2.1	-	3.2		0.8
$CS(10^{-8})$	1.6^{6}	0.5	4.0^{6}	0.9		0.2
$HCS^{+}(10^{-11})$		1.1	4 .0 ⁷	1.8		1.7

Table 3.5: Observations and model results for fractional abundances with $[S] = 10^{-6}$ at 10^5 yr.

agreement between model and observation for the small carbon-bearing molecules HCO^+ , HC_3N , C_2H , $c - C_3H_2$, and C_4H compared with a more standard constant ionization rate. With a higher abundance of elemental sulfur than our standard value, the results for small sulfur-bearing species are improved, but at the expense of our calculated values for carbon-chain species. There are also predictions of abundances and profiles for other species, some not yet observed in the Horsehead Nebula, which should be in principle observable, including HCN, HNC, NH₃, C₆H, HC₅N, and H₃O⁺. Some of these predictions are strongly affected, however, by an increase in the assumed sulfur elemental abundance.

Our results for $c-C_3H_2$ and C_4H (but not for C_2H) also indicate that the fracturing of PAH's may play an important role in the production of these molecules towards the edge of the PDR, but our model does not incorporate the effects of PAH's. Strong aromatic emission, observed by Compiègne et al. (2007), poses some problems, however, for the hypothesis that PAH fracturing is the source of small hydrocarbons. These authors claim a high concentration of neutral PAH's in the HII region, which suggests that PAH's may endure the radiation at the IR-edge, instead of breaking apart into the observed hydrocarbons.

The detailed form of the calculated abundance profiles in Figures 3.4 through 3.6 cannot be observed because observations up to the present lack sufficient resolution, and because the density profile is not well-determined. With the advent of the Atacama Large Millimeter Array (ALMA), the estimated increase in angular resolution, to $\sim 0.1''$ (Wootten 2003), should allow us to observe the form of these abundance profiles, so as to better determine the initial flux-spectrum for cosmic rays for the Horsehead Nebula.

It appears, from Indriolo et al. (2010), that there is some environmental influence on the low energy flux of cosmic rays. It would be of great interest to not only examine the Horsehead Nebula at greater angular resolution, but to also observe and model other PDR's such as the Orion Bar, IC-63, L1688-W, and portions of Sgr B2 to determine how the low energy cosmic ray flux varies in our Galaxy. Sgr B2 is of special interest given the high values of ζ inferred from H⁺₃ observations in this region (Oka et al. 2005). Given the strong dependence of ζ on the path cosmic rays travel, it is very likely that the low-energy cosmic ray flux will be object-dependent.

Chapter 4 Violent Environment: The Orion KL Region

4.1 Introduction

The Orion Nebula is a violent and immensely complex cloud. It is populated by thousands of stars, resulting in extreme ultraviolet radiation fields and high fluxes of X-rays. The rapidly expanding atmospheres of the more massive stars in Orion also generate shocks and flows. This makes for a system with an exceptionally complex velocity and density structure. Because of its distance and location in the sky, the Orion Nebula is an ideal environment in which to study star formation under violent conditions. A particularly well-studied star forming region, referred to as the Kleinmann-Low or KL region, named after its co-discoverers Kleinmann & Low (1967, independently discovered by Becklin & Neugebauer 1967), has been an object of sustained great interest.

Although Orion KL is a small region within the greater nebula, it is still quite heterogeneous. It is small enough that many observations have angular resolution near the size of the entire region. The Orion KL region is typically split up into parts, distinguished by their velocity components and angular extension. The hot core is a dense portion of Orion KL that is moving away from us at the bulk velocity of the nebula, ~ 5 km/s. There is another portion of Orion KL, referred to as the compact ridge, because of its relatively narrow velocity profile centered at ~ 9 km/s. It is surrounded by a region called the plateau, which has the same average velocity, but its velocity profile is broader. The plateau is divided into two flows, a low-velocity flow at 4-24 km/s and a high velocity flow at 10-150 km/s. There is also an outflow with a broad velocity, from 10–50 km/s toward us (identified

by Genzel & Stutzki 1989). Some of these velocity components were identified in the original chapters, but were first categorized in these terms by Downes et al. (1981). This view of Orion KL is oversimplified; the region is exceptionally clumpy, with various different sources extended spatially as well as many other velocity components (Wang et al. 2010; Friedel & Widicus Weaver 2011). Objects referred to as Peak 1, Peak 2 and IRc2 are the primary sources of high temperature and internal radiation within the KL region (for an overview of these sources, see Boonman et al. 2003). A cross-section of this region from an edge-on perspective may be of great conceptual help. An illustration of the Orion KL region is presented in Figure 4.1. This artistic rendition is still over-simplified, but should provide a helpful intuition about the geometry of the region

Orion KL has a rich and diverse chemistry, and therefore has been of great interest to astrochemists as a source of study. It is considered, second to Sgr B2, as the most molecularly diverse region that has been observed, and was considered along with Sgr B2 as a possible source of Glycine (Kuan et al. 2003). It is also the only known source to contain detectable abundances of molecular oxygen (see Goldsmith et al. 2011). Because of the intense interest in Orion KL, hundreds of chapters have been written on its chemistry, and dozens of surveys over an impressively wide range of frequencies have been performed on the region. Because of the great number of chapters, it will be impossible to reference all of them. Many important contributions will no doubt be missing from this overview. Only the portion of research most relevant to the recent observation of the hydroxyl and water ions (Gupta et al. 2010) will be included here.

Kutner et al. (1977) performed the first chemical study of Orion KL, mapping KL and the surrounding region in CO. Since then, there have been many maps of Orion KL in different molecules, as well as spectral surveys and several searches for specific molecules in the region.

Observations of the velocity profile for NH_3 by Ho & Barrett (1978) allowed them to separate Orion KL into two regions; a more detailed NH_3 map of nearby filaments was performed by Wiseman & Ho (1998). Plambeck & Wright (1988) were able to map toward Orion KL in several species, and as well as observing a methanol maser, were able to use the maps to determine important information about the kinetics of the region. Maps have since been made in HC_3N (Chung et al. 1991), H₂CO, DCN, HDO, SO₂, SiO, SO, HCO⁺ (Wright et al. 1996), as well as CN, C₂H, SO (Ungerechts et al. 1997). Boonman et al. (2003) mapped Orion KL and surrounding



Figure 4.1: An illustration of Orion KL, highlighting the different components resolved in the velocity profile and with our angular resolution. The species OH^+ and H_2O^+ are observed in the blue-shifted outflow and in the low-velocity component of the Plateau. Thanks to Jose Madrid for creating this illustration.

regions in CO_2 , among other species, and provided a very useful chemical distinction between the spatially separate parts of the hot core in Orion KL, namely the infrared radiation sources IRc2 and IRc4, and regions Peak 1 and Peak 2, which they discuss in some detail. Wang et al. (2009, 2010) provide a high-resolution map of Orion KL and the nearby region in a variety of complex molecules.

The first spectral scan of Orion KL was performed over the 72.2 - 91.1 GHz range by Johansson et al. (1984). There have since been numerous searches for specific molecules in Orion KL, as well as broad molecular line surveys over relatively wide frequency ranges. These searches and surveys have allowed us to chemically distinguish between the different velocity components in Orion KL. The information some of these transitions provide tell us not only about the chemistry but also help constrain physical parameters, especially density and temperature. Turner (1991) performed a scan of Orion KL, observing numerous complex molecules, and compared the chemistry to Sgr B2. The chemical similarity between the two objects suggests a similar cosmic ray ionization rate (Turner 1991). There are also many sources of X-rays near the KL region (Garmire et al. 2000), contributing to an enhanced X-ray ionization rate as well.

Two more scans over wide frequency ranges, including 26 different species, helped provide chemical tracers to distinguish the compact ridge, extended ridge and core (Ziurys & McGonagle 1993; Sutton et al. 1995). An interferometric survey of Orion KL over a 4 GHz bandwidth, reported in Blake et al. (1996), has helped determine that a source very close to IRc2, called Source "I", a young stellar object, is responsible for the majority of the internal radiation in Orion KL (see Okumura et al. 2011, for the relationship between Source I and IRc2). A careful analysis of 929 transitions in Orion KL by Comito et al. (2005) determined the temperature of the core to be on the order of 250 K, though Wang et al. (2010) claim a temperature peak of 620 K in the hot core. Olofsson et al. (2007) scanned Orion KL looking for anions, specifically SH⁻, and Tercero et al. (2011) surveyed Silicon-bearing species over a range from 80 to 280 GHz. The most comprehensive survey of Orion KL, to date, is the HEXOS survey, discussed by Crockett et al. (2010). Current observations suggest that the majority of radiation in Orion KL is coming from outside OB stars and a nearby explosive stellar event (Zapata et al. 2010).

Searches for individual molecules have also revealed much about the structure of Orion KL, and provide a benchmark for astrochemical modeling. Some of these searches are of particular interest

to the modeling work in this chapter. The molecules SO₂, SO, SiO and H₂S tend to be abundant in outflow regions (Watt et al. 1986; Ziurys 1988, 1990, 1991). Because of the shock-driven nature of the outflows, SO and SiO especially may experience population inversion, and masers have been observed in the outflows (Wright & Plambeck 1983; Cho et al. 2005). The hot core is distinguished by CH₃CN, OCS and NO, as well as vinyl cyanide and ethyl cyanide and other large organics (Ziurys & McGonagle 1993). CH₃CCH and (CH₃)₂O are primarily in the extended ridge (Ziurys & McGonagle 1993), which is traced also by H₂CS, HCS⁺ (see Persson et al. 2007, for an excellent overview of tracers for different regions in Orion KL). Cyanoacetylene is often named as a tracer for the core and compact ridge both, but observations by Tatematsu et al. (2010) show that it is wide-spread throughout the region. HNCO is a good tracer of both core and compact/extended ridge (Zinchenko et al. 2000). Orion KL itself can be distinguished from its surrounding environment. It tends to have a substantially higher HCN/HNC ratio than the nearby region (Goldsmith et al. 1986; Schilke et al. 1992), and CS is also a useful tracer of Orion KL as a whole.

Orion KL can also be distinguished by the large quantities of water present there, compared with other regions. Moore et al. (1986) and Knacke et al. (1988) observed water in the hot core at an abundance relative to hydrogen nuclei of $10^{-5} - 10^{-4}$. Since then, Melnick et al. (2010) have observed water in the outflow, hot core, ridge and in the extended warm gas between these regions. Melnick et al. (2010) report total water abundances of the order of 10^{-5} for all regions except the ridge, where $f(H_2O) \approx 7 \times 10^{-5}$. Hydronium, H_3O^+ , was observed first by Hollis et al. (1986), although the identification is still tentative (Gupta et al. 2010).

There have also been numerous theoretical examinations of Orion KL. The first theoretical work on Orion KL was by Glassgold & Langer (1973), who used the early CO map to calculate the impact of OB stars on the region; their work is exceptionally relevant to our own calculations. Ohishi et al. (1987) were first to chemically distinguish the different velocity components of Orion KL, and Brown et al. (1988) applied the first robust astrochemical model to the hot core region. Particularly relevant to this chapter, Neufeld & Dalgarno (1989) predicted the presence of the hydroxyl ion (OH⁺) at observable abundances. Later astrochemical modeling applied UV photolysis to grains in order to produce observable levels of CO₂ and H₂S, implying highly efficient recent grain evaporation (Minh et al. 1993).

Rodgers & Millar (1996) included deuterium to further explore the ice mantles, and found that fractionation should be the same on the grain surface as in the gas phase. This may not be true in higher temperature regions, where dust temperature is 30 - 40 K, because rate methods can be highly inaccurate especially at these temperatures. Both the work of Rodgers & Millar (1996) and Kuan et al. (1999) suggest highly active surface chemistry on grains, and rapid desorption, even in the hot core. The high abundance of deuterated methanol in the hot core suggests that this region, and likely the outflows and extended ridge, are far from steady state (Mauersberger et al. 1988).

The work of Mauersberger et al. (1988) and Millar et al. (1991) both suggest a chemical timescale of $10^4 - 10^5$ years after the onset of OB irradiation. Wakelam et al. (2004) consider the chemistry of S-bearing molecules as a good clock for hot cores, and estimate the chemical age of Orion KL at 3000 years from mantle evaporation. Since Wang et al. (2010) have determined a temperature of more than 600 K near the hot core, high temperature chemistry is likely important in this region, and may impact time-scale. Favre et al. (2011) developed density and temperature profiles for Orion KL based on the single molecule, HCOOCH₃.

Millar et al. (1991) included an inflow of water in their chemical calculations of Orion KL, and found this improved the accuracy for certain species. Their chemistry has a remarkable similarity to water chemistry on comets (see Hjalmarson & Odin Team 2002; Hjalmarson et al. 2003, to compare). Lerate et al. (2010) applied a radiative transfer model to Orion KL, though in a timeindependent case, and compared the results to far-IR lines observed, to estimate the water abundance.

Recently, observations have been made of OH⁺ and H₂O⁺ by Herschel in diffuse clouds (see Gerin et al. 2010, for reference), and in the Orion KL region (Gupta et al. 2010). The high abundances and OH⁺/H₂O⁺ ratio in diffuse clouds are explained by an H/H₂ ratio of ~ 1, and only require an ionization rate of $\zeta \sim 10^{-16}$ s⁻¹. In dense clouds, where typically H/H₂ \ll 1, virtually unphysical values for parameters, such as $\zeta \sim 10^{-13}$ s⁻¹ seem necessary to account for the observed OH⁺/H₂O⁺ ratio in Orion KL of ~ 1, and the nondetection of H₃O⁺.

These extensive chemical studies have given us a picture of the structure of Orion KL that is much more messy than the simple picture of three regions. Since the OH^+ and H_2O^+ are observed in both the blue-shifted outflow and in a 9 km/s component, we do not consider these molecules to

be abundant in the hot core, though in Section 4.5 we will compare our results with observations both of the low-velocity outflow and the core. For all our calculations, we integrate from the edge of the outflow to $A_V = 10$. For thermal balance, in all cases, we adopt the findings of Zapata et al. (2010), and treat all the radiation as external; internal radiation is neglected in all cases.

In this chapter, we discuss the structure and results of two models, an H_2O inflow model and a grain desorption PDR model, where radiation field, cosmic ray ionization and very simplified Xray ionization, and the resulting thermal balance are time-dependent, and scaled to the formation time-scales and populations of Orion Nebula stars. We show how both these models can explain the surprisingly high abundances of OH^+ and H_2O^+ , as well as the non-detection of H_3O^+ , without resorting to non-physical values for parameters. Throughout the entire chapter, we split the Orion KL object into **two regions**, the **Outflow**, which we treat as having chemistry similar to both the blueshifted outflow and the low-velocity component of the plateau, and the **Core** which directly corresponds to the hot core in Orion KL. We model only for the Outflow, but we list the observed abundances of molecular species in the core as a way to chemically differentiate the two regions.

In Section 4.2, we discuss the stellar populations in Orion, and how these populations and lifetimes are incorporated to determine a time-dependent radiation field and ionization rate. Section 4.3 is an overview of OH^+ and H_2O^+ chemistry in the interstellar medium. We apply this chemistry within a gas-phase model with a water inflow, and present the model results in Section 4.4. The gas-grain PDR and its results are presented in Section 4.5. In both of these sections, OH^+ and H_2O^+ chemistry is emphasized, as well as specific predictions that will help distinguish between these two models. An overview of the results, method, as well as future direction of work on Orion KL is discussed in Section 4.6.

4.2 Physical Conditions in the Orion Nebula and KL Region

The Orion KL region includes many of phases of the ISM within its outflows to its hot core (even if it is not a stellar hot core; see Zapata et al. 2010). Our model greatly simplifies this picture, treating the entire outflow as being of uniform density, with $n = 10^4$ cm⁻³ and temperature solved via thermal balance. The sophistication of the model is in the robust chemical network, for both gasphase and grain codes, as well as the time-dependence for the gas-grain model. For the gas-phase code, we utilize the Meudon PDR code with the chimie06 network (Le Petit et al. 2006), and for the gas-grain model, we use the Ohio State University gas-grain network and code (Garrod et al. 2008). The code is modified to incorporate depth-dependence and time-dependence of various parameters; simple radiative transfer has also been added to the gas-grain model. Reactions and rates discussed in Section 4.3 are included in both networks as given in Table 4.3.

The radiation field in the time-independent water inflow model (Section 4.4) is set to $\chi = 10^4$ in Draine units (Draine 1978), and the cosmic ray ionization rate to a column-independent $\zeta = 5 \times 10^{-15}$ s⁻¹. For the time-dependent gas-grain model, χ , ζ_{CR} and ζ_X , and resultantly the temperature, are time-dependent. The time-dependence is scaled to the star-formation times and populations. The time-dependence of χ is discussed in Section 4.2.1, and ζ is discussed in Section 4.2.2. The density and thermal balance are described in Section 4.2.3.

4.2.1 Star Formation and the UV Field

Hillenbrand (1997), hereafter H97, performed a comprehensive survey of the stars in the Orion Nebula Cluster, and determined the spectral types for the majority of main sequence stars (H97, their Fig. 24). The Orion Nebula cluster is comprised of about twenty OB stars, about 40 AFG stars, and more than a thousand stars of spectral type K and M. The luminosity of these stars is also catalogued in H97. Palla & Stahler (1999) connects the spectral type the time from protostar to Zero Age Main Sequence (t_{ZAMS}), which we use to determine the time-dependence of the UV radiation intensity.

We estimate the Far UltraViolet (FUV) radiation intensity in terms of χ in Draine units (Draine 1978). The Orion Nebula has a radiation intensity $10^4 - 10^5$ times higher than the standard $\chi = 1$ (Walmsley et al. 2000; Young Owl et al. 2000). We choose the final value of $\chi = 10^4$ for the Orion KL region. We then estimate the fraction of FUV radiation intensity each star of a particular spectral type *s* contributes, F_s , by treating each star as a black body and performing the integral over the Planck distribution (with integration limits determined by Tielens & Hollenbach (1985), and $\beta =$

Spectral Type	t_{ZAMS} (y)	Number of Stars
OB	5×10^{4}	20
AFG	3×10^{6}	40
Κ	7.5×10^{7}	200
Μ	2×10^{8}	> 500

Table 4.1: Estimated Star Formation Time-Scale for the Orion Nebula Cluster

 k_BT):

$$F_{s} = C \int_{6\,\mathrm{eV}}^{13.6\,\mathrm{eV}} \frac{E^{2}dE}{e^{\beta E} - 1}.$$
(4.1)

The constant in the front, *C*, is set such that, summing spectral types *s* (N_s is the total number of stars of spectral type *s*):

$$\sum_{s} N_s F_s = 1. \tag{4.2}$$

Performing these operations, we determine that each OB star contributes approximately 4.65% of the total radiation. From Palla & Stahler (1999, their Table 1) and the relationship between mass and spectral type from H97 (their Table 4) we find the approximate relationship between spectral type and t_{ZAMS} , listed in Table 4.1.

We accept the argument from H97, that the OB association is young, on the order of $10^5 - 10^6$ years old. The lack of black holes or supernova remnants provides support for this age-range. A simple model for stellar populations, Flexible Stellar Population Synthesis (FSPS), from Conroy et al. (2009) using the the calibration of Conroy & Gunn (2010), agrees within a factor of a few to Gaussian distributions of star formation in time, one distribution for OB formation and another for AFG formation, with a standard deviation of $\sim t_{ZAMS}/3$. K and M stars are treated as being present for all times considered by the model.

The K and M stars contribute less than a factor of 10^{-4} to the FUV radiation. AFG stars contribute 7% of the FUV radiation, and OB stars altogether contribute 93% to the radiation. Because of the large variation in time-scales, over three orders of magnitude, the evolution of Orion KL is divided into three phases. Phase 1 begins after the K and M stars are formed, and covers the time of formation for the AFG stars. Phase 2 spans the violent OB star forming age, and Phase 3 is the time from the birth of the OB stars to one million years later. The time-dependence for χ is determined by applying a Gaussian distribution, Φ to star formation with t_{ZAMS} for the different spectral types of stars, with t_0 being the length of the phase and $\chi(t_0)$ the value of χ at the end of the phase. At the beginning of Phase 1, $\chi_0 = 1$. At the end of Phase 1 and beginning of Phase 2, $\chi_0 = 700$. At the end of Phase 2, $\chi_0 = 10^4$. The value of χ is held constant throughout Phase 3. The integrated distribution determines the UV field to be:

$$\chi(t) = \Phi\left(\frac{t - t_{\text{ZAMS}}}{\sigma}\right) [\chi(t_0) - \chi(0)] + \chi(0)$$
$$\Phi(x) = \frac{1}{2} \left[1 + \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx\right],$$

where σ is the standard distribution, which is taken to be $t_{ZAMS}/3$, to match with a simple population analysis (Conroy et al. 2009).

The radiation intensity is given in terms of χ as a function of time in Figure 4.2.

4.2.2 Cosmic Ray and X-Ray Ionization Rate

The cosmic ray and X-ray flux at the surface of the Orion KL region increases from 10^{-4} the final value of the cosmic ray flux at the beginning of Phase 1 to 7% of the final value at the beginning of Phase 2, and to the final value at the beginning of Phase 3. For the cosmic ray flux at the surface, j(E) (nucleons cm⁻² s⁻¹ GeV⁻¹ per steradian), we begin Phase 1 with the flux-spectrum from Spitzer & Tomasko (1968), and end Phase 1 with the flux-spectrum from Hayakawa et al. (1961). We begin Phase 2 with Hayakawa et al. (1961)'s spectrum, and end this phase with the flux-spectrum of Nath & Biermann (1994) multiplied by a factor of 8. We use the ionization rates $\zeta(A_V)$ (s⁻¹) from (Rimmer et al. 2012, Eqn. 9,10), accurate to within a factor of 2 between 0.05 < $A_V < 100$:

$$\zeta_{\text{CR,Phase 1}} = 10^{-17} \text{ s}^{-1},$$

$$\zeta_{\text{CR,Phase 2}} = \frac{2.2 \times 10^{-17}}{A_{\text{V}}} + 10^{-17} \text{ s}^{-1},$$

$$\zeta_{\text{CR,Phase 3}} = 2.5 \times 10^{-15} (A_{\text{V}})^{-0.6} + 10^{-17} \text{ s}^{-1}.$$

Below $A_V = 0.05$, $\zeta_{CR}(A_V) = \zeta_{CR}(0.05)$.

The X-ray flux, F (cm⁻² s⁻¹ keV⁻¹) and penetration we use is from (Maloney et al. 1996, their

Eqn. A1-A4), with their F_0 scale factor for the flux, and is a function of time. We can apply the exponential dependence of the flux on optical depth (Maloney et al. 1996, their Eqn. A3) to produce equations similar to the relationship between ζ and A_V above. We use this analytical form when describing X-ray penetration, accurate to within a factor of 2 for $A_V < 6$:

$$\zeta_X = \zeta_{X,0} \times \exp(-4A_{\rm v}^{0.4}). \tag{4.3}$$

For $A_V > 6$, ζ_X diverges from the above equation rapidly, but the divergence is rather insignificant because past this depth $\zeta_X < 10^{-19} \text{ s}^{-1}$ even at the highest X-ray flux, and no longer has a significant impact on the chemistry. The value $\zeta_{X,0}$ takes the value of zero for Phase 1, $3 \times 10^{-16} \text{ s}^{-1}$ for Phase 2, and $5 \times 10^{-14} \text{ s}^{-1}$ for Phase 3, which at $A_V = 1.0$ corresponds to the value cited in Gupta et al. (2010).

The total ionization, produced by cosmic rays and X-rays, is given the expression:

$$\zeta = \zeta_X + \zeta_{\rm CR}.\tag{4.4}$$

We do not distinguish between X-rays and cosmic rays except in terms of their penetration. Timedependence is incorporated in the model by an interpolation between the ζ values of the different phases, scaled such that *t* is the time into a particular phase, and t_0 is the length of the phase. $\zeta(t_0)$ is the ζ value at the end of a particular phase, and $\zeta(0)$ the value at the beginning of the phase. $\zeta(t)$ becomes:

$$\zeta(t) = \left[\zeta(t_0) - \zeta(0)\right] \left(\frac{t}{t_0}\right)^{1/2} + \zeta(0).$$
(4.5)

The 1/2 power is applied to reduce the computational stress on the model, which treats time logarithmically. Since there are more points for which the model is solved at earlier times, we have the ionization rate change more rapidly at earlier times. It becomes less rapid at later times. This 1/2 power has a substantial impact on computational time, reducing the runtime by a factor of five. The value of ζ at $A_V = 1.0$ is shown in Figure 4.2 as the dotted line.

The specific time-dependence of ζ is rather ad-hoc. The values at the beginning and end of the phases is justified by speculation that shocks in OB atmospheres may drive up cosmic ray fluxes (see Bykov & Fleishman 1992, for the argument), and that the observed X-ray sources are associated

Table 4.2: Physical	Parameters and	Gas and Dust	Temperatures	at $A_{\rm V} = 1$
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Phase	t_0^a	$\chi(0)$	$\chi(t_0)$	$\zeta(0)^b$	$\zeta(t_0)^b$	$T_{g}(0)^{c}$	$T_g(t_0)^c$	$T_d(0)^c$	$T_d(t_0)^c$
Phase 1	$1.0(7)^d$	1.0(0)	7.0(2)	1.0(-17)	1.0(-16)	10	110	10	34
Phase 2	5.0(4)	7.0(2)	1.0(4)	1.0(-16)	5.0(-15)	110	400	34	95
Phase 3	1.0(6)	1.0(4)	1.0(4)	5.0(-15)	5.0(-15)	400	400	95	95

Notes. ^(*a*) In units of years; ^(*b*) In units of s⁻¹; ^(*c*) In units of Kelvins. ^(*d*) Notation is $A(B) \equiv A \times 10^{B}$.

with the OB stars, and therefore also probably increase at a similar rate as χ increases.

4.2.3 The Temperature Profile

The temperature profile is determined from thermal balance using the Meudon PDR code with parameters from Figure 4.2 and discussed in Sections 4.2.1,4.2.2. The Meudon model was utilized three times, one with parameters from beginning of Phase 1, another with parameters from the beginning of Phase 2, and a third with parameters from the beginning of Phase 3. Gas and dust temperatures were derived from this thermal balance. The gas temperature at $A_V = 1$ is shown in Figure 4.2, and the parameters applied to the Meudon PDR code along with the resulting gas and dust temperatures are listed in Table 4.2. The temperatures were interpolated using a method identical to the method for cosmic rays, following Equation (4.5).

4.3 OH⁺, H₂O⁺ Chemistry in Dense Regions

There are a variety of important reactions in the hydroxyl and water ion network. Different reactions are important under different physical conditions. We will first discuss the formation and destruction of OH^+ , followed by H_2O^+ and H_3O^+ . This discussion of reactions will mention channels that are dominant for both the inflow model and the gas-grain PDR model. Reactions and rates discussed here are summarized in Table 4.3.

In dense regions with significant UV radiation, there are three important formation pathways for



Figure 4.2: UV radiation intensity, χ (in Draine units), cosmic ray ionization rate ζ (s⁻¹) and gas temperature T_{gas} (K) at a depth of $A_V = 1.0$ over all phases. It should be noted that the scale of the x-axis is not the same for all phases, and that the variation of parameters in Phase 2 is exceptionally rapid.

OH⁺. The first is the series of reactions beginning with the ionization reaction:

$$\mathbf{H} + \mathbf{IA} \to \mathbf{H}^+ + e^-; \tag{4.6}$$

$$\mathbf{H}^{+} + \mathbf{O} \leftrightarrow \mathbf{O}^{+} + \mathbf{H}; \tag{4.7}$$

$$O^+ + H_2 \rightarrow OH^+ + H; \tag{4.8}$$

where IA represents an ionizing agent, in our case a cosmic ray or X-ray. In this chapter, we treat the ionization by X-rays identically as the ionization by cosmic rays, though we treat X-ray and cosmic ray penetration differently.

The charge exchange, as indicated in Reaction (4.7) occurs in both directions. However, the charge exchange from H⁺ to O⁺ depends very-much on the population of oxygen atoms in the ground (J = 2) state, and because of this is slightly endothermic, with an activation energy of 226 K (see Spirko et al. 2003). The reverse direction (O⁺ to H⁺) is exothermic (Stancil et al. 1999). We utilize the rates from Spirko et al. (2003), and expect channel to be dominant near the edge of the region ($A_V \sim 1$), due to the high fraction of atomic hydrogen at these depths. Several rates have been calculated for this charge exchange, from semi-classical techniques (Field & Steigman 1971; Herbst & Klemperer 1973) to full quantum mechanical treatments (Chambaud et al. 1980;

Stancil et al. 1999; Spirko et al. 2003).

The ionization of atomic hydrogen, Reaction (4.6), is treated in the standard way, using the ionization cross-section and ionization from secondary electrons from Spitzer & Tomasko (1968); Glassgold & Langer (1973); Dalgarno et al. (1999). The final Reaction (4.8) has been well-studied, and we use the standard rates taken from Herbst & Klemperer (1973), Viggiano et al. (1980), and Smith et al. (1978). Because the radiation field is exceptionally high, there is a larger region of dense hot gas that is being bombarded with cosmic rays and X-rays. As such, the formation of OH⁺ by the reaction H⁺ + OH is also important, though it is never the dominant channel for OH⁺ production.

Deep into the cloud, at an optical extinction of >3, most of the hydrogen is in a molecular form, and OH⁺ is produced almost entirely by the series of reactions:

$$H_2 + IA \to H_2^+ + e^-;$$
 (4.9)

$$H_2^+ + H_2 \rightarrow H_3^+ + H;$$
 (4.10)

$$H_3^+ + O \to OH^+ + H_2.$$
 (4.11)

The rate for Reaction (4.11) is well-established, first calculated by Felisenfeld (1976) and explored most recently by Milligan & McEwan (2000). Reactions (4.9,4.10) have also been explored in great detail.

In the middle region, $1 < A_V < 3$, a significant fraction of OH⁺ is produced by the photodissociation reactions:

$$H_2O^+ + h\nu \to OH^+ + H; \qquad (4.12)$$

$$\mathrm{H}_{3}\mathrm{O}^{+} + h\nu \to \mathrm{H}_{2}\mathrm{O}^{+} + \mathrm{H}; \tag{4.13}$$

$$H_3O^+ + h\nu \to OH^+ + H + H. \tag{4.14}$$

The above reactions are not common in astrochemical models. Equation (4.12) is included in the UMIST and Meudon networks, with the edge-of-cloud rate of 10^{-12} s⁻¹ at standard ISRF, taken from a chapter in preparation by Van Dishoeck and others. We assign a rate to the H₃O⁺ photodissociation identical to the rate Van Dishoeck assigned for H₂O⁺ dissociation, with a branching ratio between

Reactions (4.13) and (4.14) of 50%. These rates are very uncertain, and we strongly encourage a detailed study into these reactions in order to better constrain future astrochemical models for dense regions with high impinging UV fields.

The majority of H_2O^+ and H_3O^+ is produced by reaction with molecular hydrogen (Jones et al. 1981):

$$OH^+ + H_2 \rightarrow H_2O^+ + H;$$
 (4.15)

$$H_2O^+ + H_2 \to H_3O^+ + H.$$
 (4.16)

At the edge of the Orion KL region, the H₂ fraction is relatively low, and the photon flux and electron fraction are extremely high. As such, for $A_V < 3$, photodissociation and electron recombination play an important, sometimes the dominant, role in OH⁺ and H₂O⁺ destruction. In all regions, electron recombination is the main destroyer of H₃O⁺, resulting in various products (Herd et al. 1990; Jensen et al. 2000).

4.4 Water Inflow Model

The first model that we consider is a model with a water inflow. Models like this have been applied to Orion KL outflows before (Millar et al. 1991), justified by the high velocities, the wide range of velocities, and the very high abundances of water observed in the general region (Moore et al. 1986, for example), and recently in these outflows themselves (Lerate et al. 2010). Since the inflow model involves steady-state calculations, all parameters are time-independent.

For the inflow model, we take a set density of $n = 10^4 \text{ cm}^{-3}$, a temperature gradient determined by the Meudon model, and an ionization rate of $\zeta = 5 \times 10^{-15} \text{ s}^{-1}$ at all extinctions. This ionization rate is used because it is the lowest ionization rate that will achieve the observed OH⁺/H₂O⁺ ratio, and therefore functions as a lower-limit to the cosmic ray ionization for this model. We model for an inflow of water by adding a source term, *S*, to the rate equations, like this:

$$\frac{dn(H_2O)}{dt} = S + k_1 n(H_3O^+)n(e^-) + \dots$$
(4.17)

The source term clearly has units of $cm^{-3} s^{-1}$, and can be approximated in terms of the flux (the

Reaction	Eqn	α	β	γ (K)	Network
Preliminary Reactions					
${\rm H} + {\rm IA} \rightarrow {\rm H}^+ + e^-$	(4.6)	0.46^{1}	_	_	OSU^2
$H_2 + IA \rightarrow H_2^+ + e^-$	(4.9)	0.93 ¹	_	_	OSU
$H^+ + O \rightarrow O^{+} + H$	(4.7)	0.7^{3}	0.0	232	OSU
$\rm H + \rm O^+ \rightarrow \rm H^+ + \rm O$	(4.7)	0.7^{3}	0.0	0.0	OSU
$H_2^+ + H_2 \rightarrow H_3^+ + H$	(4.10)	2.1^{3}	0.0	0.0	OSU
OH^+ Chemistry					
$\mathrm{O^{+}} + \mathrm{H_{2}} \rightarrow \mathrm{OH^{+}} + \mathrm{H}$	(4.8)	1.6^{3}	0.0	0.0	OSU
$H_3^+ + O \rightarrow OH^+ + H_2$	(4.11)	0.8^{3}	0.0	0.0	OSU
$H^{+} + OH \rightarrow OH^{+} + H$		16 ³	0.5	0.0	OSU
$H_2O^+ + h\nu \rightarrow OH^+ + H$	(4.12)	1.0^{4}	2.0	_	UDFA ⁵
$H_3O^+ + h\nu \rightarrow OH^+ + 2H$	(4.14)	0.5^{4}	2.0	_	6
$OH^+ + e^- \rightarrow O + H$		6.3 ³	0.48	0.0	OSU
$OH^+ + h\nu \rightarrow O + H^+$		7.2^{4}	1.8	_	OSU
H_2O^+ Chemistry					
$OH^+ + H_2 \rightarrow H_2O^+ + H$	(4.15)	1.1^{3}	0.0	0.0	OSU
$H_3O^+ + h\nu \rightarrow H_2O^+ + H$	(4.13)	0.5^{4}	2.0	_	6
$H_2O + H^+ \rightarrow H_2O^+ + H$		7.3^{3}	0.5	0.0	OSU
$H_2O^+ + e^- \rightarrow \text{products}$		430^{3}	0.5	0.0	OSU
H_3O^+ Chemistry					
$H_2O^+ + H_2 \rightarrow H_3O^+ + H_3O^+$	(4.16)	0.61 ³	0.0	0.0	OSU
$H_3O^+ + e^- \rightarrow \text{products}$		436 ³	0.5	0.0	OSU

Table 4.3: Formation and Destruction Reactions and Rates for OH^+ , H_2O^+ and H_3O^+

Notes. ⁽¹⁾ k_{CR} (s⁻¹) = $\alpha \zeta$ ⁽²⁾ OSU designates the OSU 09/2008 gas-phase network. ⁽³⁾ k (cm³ s⁻¹) = $\alpha \times 10^{-9} (T/300 \text{ K})^{-\beta} e^{-\gamma/T}$ ⁽⁴⁾ k_v (s⁻¹) = $\alpha \times 10^{-12} \chi e^{-\beta A_v}$ ⁽⁵⁾ UDFA designates the UMIST Database for Astrochemistry 2006, a gas-phase network.

⁽⁶⁾ van Dishoeck, private communication.

number density of the inflow, n_I , times the inflow velocity, v_I) divided by a scale length (L):

$$S = \frac{n_I \upsilon_I}{L},\tag{4.18}$$

Given the velocity of the lines in the outflow, we use $v_I = 10^6$ cm/s. Since we are only interested in the water, we take the n_I to be the number density of water in the inflow, or $n_I = 1$ cm⁻³. The scale length is on the order of the size of the region, or 10^{18} cm.

Applying these parameters to Equation (4.18), we obtain a source term of $S = 10^{-12}$ cm⁻³ s⁻¹, which is the same source term used by Millar et al. (1991) to model water injection into the Orion compact ridge. This source term allows for a steady-state condition, and adds to the steady-state abundance of H₂O by a factor of:

$$\frac{S}{\sum \nu_d + \sum_X k_d^X n(X)},\tag{4.19}$$

where v_d is the destruction rate for zero-order processes (photodissociation, cosmic ray ionization, etc.) and k_d^X is the destruction rate for two body reactive collisions, with *X* being the species reacting with the water.

Adding this source term to the Meudon PDR model, the amount of water in the region increases significantly, and drives up the photodissociation of water as well as H_2O^+ . These reactions drive up H_2O^+ and OH^+ abundances, and the increased abundance of water does increase H_3O^+ abundances somewhat, though not to the degree H_2O^+ and OH^+ are increased. The inflow model incorporates all reactions listed in Table 4.3 except Reactions (4.13) and (4.14). A comparison of reactions, and the percentage of OH^+ , H_2O^+ and H_3O^+ they form and destroy, at different extinctions is made in Table 4.4.

Near the edge, between $1 < A_V < 3$, H_2O^+ can also be produced by H_2O reacting with H^+ . This reaction is only important for the inflow model, and does not appear to be very significant for the gas-grain model, possibly because the flow of water is limited to grain desorption in that model, and the desorption does not involve the high injection rate of water.

The relative abundances predicted by the inflow model are tabulated below in Table 4.6. The results of the chemical model, and a comparison with observations when possible, is made for H/H_2 in Section 4.4.1, H^+ and e^- in Section 4.4.2 and the basic carbon chemistry in Section 4.4.3. The
$A_{\rm V}$	OH ⁺	Percentage	H_2O^+	Percentage	H_3O^+	Percentage
< 1						
	Form.		Form.		Form.	
	$H_2 + O^+$	99 – 72%	$H_2 + OH^+$	99%	$H_2O^+ + H_2$	100%
	$H_2O^+ + hv$	0 - 28%				
	Dest.		Dest.		Dest.	
	$OH^+ + e^-$	25 - 28%	$H_2O^+ + e^-$	5 - 20%	$H_{3}O^{+} + e^{-}$	77 – 91%
	$OH^+ + hv$	72 - 8%	$H_2O^+ + h\nu$	95 - 72%	$H_3O^+ + h\nu$	16 - 4%
	$OH^+ + H_2$	0 - 62%				
1 – 3						
	Form.		Form.		Form.	
	$H_{2} + O^{+}$	72 - 65%	$H_2 + OH^+$	99 - 82%	$H_2O^+ + H_2$	100%
	$H_2O^+ + h\nu$	28 - 1%	$H_2O + H^+$	0 - 18%		
	$OH + H^+$	0 - 32%				
	Dest.		Dest.		Dest.	
	$OH^+ + e^-$	28 - 3%	$H_2O^+ + e^-$	20%	$H_{3}O^{+} + e^{-}$	91 - 95%
	$OH^+ + H_2$	62 - 96%	$H_2O^+ + hv$	72 - 0%	$H_3O^+ + hv$	4 - 0%
			$H_2O^+ + H_2$	5 - 75%		
> 3						
	Form.		Form.		Form.	
	$H_2 + O^+$	65 - 59%	$H_2 + OH^+$	82 - 99%	$H_2O^+ + H_2$	100%
	$OH + H^+$	32 - 16%	$H_2O + H^+$	18 - 0%		
	$O + H_{3}^{+}$	2 - 21%				
	Dest.		Dest.		Dest.	
	$OH^+ + H_2$	96 – 99%	$H_2O^+ + H_2$	75%	$H_{3}O^{+} + e^{-}$	95%
	_		$H_2O^+ + e^-$	20 - 16%	-	

Table 4.4: Reactions of formation and destruction for the H₂O inflow model.

results for OH and water are discussed in Section 4.4.4 and for OH^+ , H_2O^+ and H_3O^+ in Section 4.4.5. Finally, predictions are given in Section 4.4.6.

4.4.1 Inflow results: H/H₂

The hydrogen chemistry in any astrophysical environment is complex, requiring both gas-phase and grain surface chemistry. This chemistry is connected to many physical processes, such as the UV field, gas and grain temperatures, density and cosmic ray ionization. The ratio between H and H_2 also has a vital impact on the hydroxyl cation chemistry, as Neufeld et al. (2010) discusses and as we reviewed in Section 4.3.

If $H/H_2 \gg 1$ then formation of OH^+ by H_2 is seriously impacted. If, on the other hand, $H/H_2 \ll 1$, the high abundance of H_2 will quickly destroy much of the OH^+ and H_2O^+ , producing large amounts of H_3O^+ . The impact of this ratio is somewhat mitigated by the water inflow; when water is flowing into the system, other channels for OH^+ and H_2O^+ production, by photodissociation and photoionization of the water, open up. Even with this mitigating factor, high cosmic ray and X-ray ionization and a high flux of UV photons ($\chi = 10^4$ and $\zeta > 5 \times 10^{-15} \text{ s}^{-1}$), as well as a relatively low density ($n \leq 10^4$) is necessary to keep $H/H_2 \sim 1$.

The average ratio for H/H₂ in this model is 0.58, though for $A_V < 3$, H/H₂ > 10, while at $A_V > 5$, H/H₂ < 0.3. Though the ratio is much lower than one deeper into the region, the violent physical environment keeps the ratio atypically high throughout. Typical ratios of H/H₂ at $A_V > 1$ are H/H₂ < 0.01. The high ratios in the KL region distinguishes this environment from the more typical PDR chemistry (see Tielens & Hollenbach 1985, for a discussion of typical PDR chemistry), and will have a strong impact on the rest of the chemical abundances, especially on the OH⁺ and H₂O⁺ ratios.

4.4.2 Inflow results: H^+ and e^-

Unsurprisingly, the inflow model with the high ionization rate we are employing has an exceptionally high ionization fraction, at 10^{-3} at the surface of the object, and decreasing only to 10^{-4} at $A_{\rm V} > 1$, but staying at this level until $A_{\rm V} \approx 10$. The electron fraction does not fall to 10^{-8} , as is typical for PDR ionization profiles. Because of the high ionization and dissociation in Orion KL, and because of the comparatively high H/H₂ ratio throughout the outflow, there is a much higher abundance of H⁺ than is typical. The relationship between H⁺ and the ionization is complex, because H⁺ is destroyed not by reacting with H₂ but by electron recombination and charge exchange. The fractional abundance of H⁺ ranges from 10^{-3} at the edge to 5×10^{-5} at depths greater than A_V of 5. As was discussed in Section 4.3, the H⁺ abundance has a strong relationship with the OH⁺ and H₂O⁺ chemistry, both because of the charge exchange with oxygen atoms, and also because it destroys H₂O and OH, forming OH⁺ in the process.

4.4.3 Inflow results: C⁺, C and CO

PDR chemistry is characterized in large part by the abundances of C⁺, C and CO, with the standard progression from C⁺ dominating at $A_V < 1$ to C at $1 < A_V < 3$ and ending at $A_V > 3$ with the majority of the carbon in CO. At $A_V > 3$, the CO abundance relative to total hydrogen abundance is typically ~ 10^{-4} .

This is not the case with the inflow model. For the inflow model, the transition from one stage to another is much broader and less well-defined, and the average amount of carbon monoxide is lower. For the KL region, C⁺ is most abundant even through A_V of 3, and then is overtaken by neutral carbon. CO does not become more abundant than the neutral carbon for $A_V < 10$, and even at an extinction of 10, the ratio C/CO ~ 5. Also, CO only reaches a relative abundance of ~ 10^{-5} , one order of magnitude below standard. This is in good agreement with observation for the outflow region, as well as the extended and compact ridge and the plateau.

In the core of Orion KL, the abundance of carbon monoxide is virtually the standard abundance. Indeed, the carbon chemistry for the inflow model does not match well with the observed abundance of carbon monoxide in the core of Orion KL. This is probably due to the high amount of shielding in the core, where $A_V > 20$, as well as the much higher density of $n = 10^7$ cm⁻³.

4.4.4 Inflow results: H₂O and OH

The H_2O abundance for the water in this case is somewhat predictable, because the rate of flow has become a parameter in this model. Given the violent nature of the region, water is greatly depleted,

having only a relative abundance of 2×10^{-8} , more than two orders of magnitude lower than the observed abundance of 3×10^{-6} . The water result is improved an order of magnitude by increasing the water inflow to $S = 10^{-11}$ cm⁻³ s⁻¹ or by integrating to $A_V = 20$, but these options increase either the H₂O⁺ abundance to well beyond the observed value or, if the extinction is doubled, the H₃O⁺ abundance exceeds the upper limit by an order of magnitude. The results for H₂O in the Orion KL inflow model are in Figure 4.3.

The OH abundance, connected closely to the water abundance via dissociation processes, is ~ 75 times underproduced. Nevertheless, both OH and H₂O abundances are far better with the inflow model than with a standard PDR model with $\zeta > 10^{-14}$ s⁻¹ necessary to achieve the OH⁺/H₂O⁺ ratio, which has water and OH at abundances of $\leq 10^{-10}$. Decreasing the cosmic ray ionization rate will improve results for water and OH, but will also result in much higher amounts of H₃O⁺ than is observed. Another alternative is to decrease the density to 10^3 cm⁻³ and to decrease the cosmic ray ionization. This achieves much better results for water, OH, and preserves the observed OH⁺/H₂O⁺ ratio, but the densities are inconsistent with values determined by Plume et al. (2012), though their values depend on CO and isotopologue ratios, which may be lower than typical in the outflow.

4.4.5 Inflow results: OH^+ , H_2O^+ and H_3O^+

The results for OH^+ , H_2O^+ and H_3O^+ are plotted in Figure 4.3. The model succeeds in bringing these abundances to within a factor of 3 of observation for both OH^+ and H_2O^+ , and H_3O^+ abundance is right at the observation limit. The fact that H_3O^+ hugs the limit may not be too detrimental, given that Gupta et al. (2010) argue that there may be a weak absorption line for H_3O^+ .

 OH^+ and H_2O^+ are produced at different extinctions by the reactions detailed in Table 4.4. It is interesting that Reaction (4.12) played such a major role in producing OH^+ by photodissociating water. This effect, as well as the effect of Reactions (4.13),(4.14) is more pronounced in the gas-grain model, discussed further in Section 4.5.3. The ionization of the products of the H_3O^+ destruction, OH and H_2O , provide an important channel for OH^+ production, as does the charge exchange between H^+ and OH and H_2O .

The most relevant factor for OH^+ production in this model, and in the gas-grain model, is the H/H_2 ratio. If H_2 is very abundant, then H_3O^+ is quickly formed from OH^+ and H_2O^+ , destroying



Figure 4.3: Inflow results plotted for OH⁺, H₂O⁺, H₃O⁺ and water. These results can be compared to observations of OH⁺ and H₂O⁺ at a column of ~ 10^{13} cm⁻². OH⁺ is over-abundant by a factor of 5, while H₂O⁺ falls into excellent agreement with observation. H₃O⁺ has a column right at the observational upper limit of ~ 10^{12} cm⁻². This would suggest that H₃O⁺ is right at the threshold of detection in this region. Water is underproduced by more than two orders of magnitude.

the observed species, and producing too much of the absent species. The water inflow helps the OH^+ and H_2O^+ production considerably, by encouraging a chemical environment similar to those of comets (see, for example Hjalmarson & Odin Team 2002; Hjalmarson et al. 2003). Indeed, these species have both been observed in comets, OH^+ first by Delsemme & Swings (1952) and H_2O^+ first by Herzberg & Lew (1974). The ion H_3O^+ has not been observed in comets, to the author's knowledge. Even so, the ratio of H/H_2 must be high enough to allow for OH^+ and H_2O^+ survival, as presented by Neufeld et al. (2010). It is possible that ionization from photon sources within the cloud may compensate further for a low H/H_2 ratio, and we plan to examine this in a future chapter. Currently, however, it seems that the hydroxyl and water ion abundances are most easily accomplished by high ionization rates, low densities, or a combination of the two.

4.4.6 Inflow predictions for $\mathrm{HCO^{+}}$ and $\mathrm{H_{3}^{+}}$

The best way to differentiate the inflow model from the gas-grain model is by the different predictions for HCO⁺. This species is impacted by the ionization rate, which is very different between the gas-grain PDR and inflow models. A number of HCO⁺ isotopologues, and the isotopomer HOC⁺ have been observed in Orion KL (Ziurys & Apponi 1995), but an abundance of HCO⁺ has not yet been determined. Protonated molecular hydrogen (H_3^+) has not been observed in the Orion KL region at all, though it may be useful to search for it in absorption near this region, if an appropriate background star can be found.

The inflow model predicts very high H_3^+ abundances, and a fairly low HCO⁺ abundance. The average H_3^+ fractional abundance in the Orion KL region is 7.59×10^{-8} , corresponding to an integrated column density of ~ 2 × 10¹⁵ cm⁻². This prediction is similar to the higher column densities of H_3^+ observed in Sgr B2 (Oka et al. 2005).

The HCO⁺ on the other hand is relatively low, at an average fractional abundance of 5.77×10^{-10} . This is in due to three factors: the efficiency with which it recombines with its electrons ($k_e \sim 10^{-7}$), the high electron abundance even deep within the outflow, and the low amount of carbon monoxide necessary to produce HCO⁺. It will be very useful to use HCO⁺ as a gauge for the success of this and the gas-grain model.

4.5 Gas-Grain Photodissociation Region Model

We now consider a gas-grain PDR model. For this model, we incorporate time-dependent parameters into a dynamic gas-grain chemical code (Garrod et al. 2008), spanning three distinct phases. In the first phase, AFG stars turn on. The OB stars ignite in the second phase, and the third phase evolves the chemistry from constant physical parameters. In this model, the cosmic ray and X ray ionization rates are both column-dependent and time-dependent, the impinging UV field is timedependent, and the temperature is calculated from thermal balance using the Meudon PDR model at the beginning and end of each phase, and interpolating between phases. The warm-up phases of Orion KL are discussed in Section 4.2.

The model is a gas-grain model, so it has a large network of thousands of gas-phase reactions,

and a second network of thousands of surface reactions, all of which are solved together as a series of coupled differential equations. Gas-phase species are written out as normal species (OH, H_2O , etc.), whereas surface species have a J in front of them (JOH, JH₂O, etc.).

The gas-phase and surface reactions are coupled to each other by adsorption of species onto the surface of grains, and desorption from the surface of grains back into the gas. The surface of grains is treated as a two-dimensional space, and the gas-phase is three dimensional. The difference in dimensionality provides an increased level of complexity when coupling the gas-grain and gasphase networks. Adsorption and desorption involve relations between these two spaces. The surface units (in this chapter, monolayers) and gas-phase units (cm⁻³) are related by the number of sites on the grain surface ($N_s = 10^6$ monolayer⁻¹), and the number density of dust grains (n_d). For this model, $n_d = 10^{-8}$ cm⁻³, corresponding to a fractional abundance of 10^{-12} . The conversion is made with the factor $\alpha = N_s n_d$, such that, to convert the amount of species A from monolayers (N_m) to the number density:

$$\alpha N_m(JA) \leftrightarrow n(A),$$

where α has units of monolayer⁻¹ cm⁻³. If we imagine a species, A, which only reacts with itself on grains at a rate k_{AA} (monolayer⁻¹ s⁻¹), and has adsorption and desorption rates, k_a (s⁻¹) and k_d (s⁻¹), respectively, we have the gas-phase and surface terms as:

$$\frac{dn(\mathbf{A})}{dt} = -k_a(\mathbf{A})n(\mathbf{A}) + \alpha k_d(\mathbf{J}\mathbf{A})N_m(\mathbf{J}\mathbf{A});$$
$$\frac{dN_m(\mathbf{J}\mathbf{A})}{dt} = \frac{k_a(\mathbf{A})}{\alpha}n(\mathbf{A}) - k_{AA}[N_m(\mathbf{J}\mathbf{A})]^2 - k_d(\mathbf{J}\mathbf{A})N_m(\mathbf{J}\mathbf{A})$$

The adsorption rate is typically calculated based on the cross-section of the grain (σ_d), the sticking coefficient (*s*), the Boltzmann-averaged velocity of the gas-phase molecules relative to the grains ($\langle v(A) \rangle$ for species A) and n_d , so,

$$k_a(\mathbf{A}) = sn_d\sigma_d \langle v(\mathbf{A}) \rangle;$$

for all species in our network, we take s = 1 (a species sticks whenever it hits a grain).

We consider three mechanisms for desorption when determining k_d for a species. The mechanisms are thermal desorption, photodesorption and cosmic ray/X-ray desorption. Thermal desorption, for physisorbed species (the only sort of adsorption we consider; see Garrod et al. 2008) is

the probability a certain species will have enough energy to overcome the van der Waals barrier. Photodesorption is calculated in a manner similar to photodissociation in the gas-phase, though the base rates are determined by experimental methods (Öberg et al. 2009). Cosmic ray desorption is a result of cosmic ray iron heating the grain mantles, and is based on the calculations of Leger et al. (1985).

This gas-grain network and model is applied multiple times at different A_V as a series of slabs, with radiation impinging on only one side, the edge. The slabs further from the edge are connected only by taking into account H₂ and CO abundances of the slabs closer to the edge, determining the CO and H₂ columns, and applying these columns as well as the self-shielding factors from Lee et al. (1996b), their Tables 10 and 11, to their analytical formulae (A1, A2). These self-shielding tables and formulae had already been incorporated in the gas-grain model of Garrod et al. (2008), but we have modified the model by utilizing the column-densities from multiple slabs, instead of simply assigning the single-point column-density to Lee et al. (1996b)(A1, A2).

This model was constructed mostly to explore water ice chemistry and its role in the hydroxyl and water ion formation and destruction. Water forms on the surfaces of grains much more rapidly than in the gas-phase. The high abundances of water would, after a warm-up phase, be desorbed into the gas, and act as a water inflow. One major difference is that the water, once it evaporates, is destroyed, and eventually is depleted and can no longer drive the hydroxyl ion chemistry very effectively. This is a way to explore the time dimension of the hydroxyl and water ion problem in Orion KL.

For this model, we begin with TMC-1 abundances, listed in Table 4.5, and run a single-point gas-grain model for 10^7 years at $A_V = 10$ and at the initial temperature of Phase 1. This allows the surfaces to become populated, and the surface chemistry to initiate. We use the results of this single-point model as the initial chemistry for all the slabs at the beginning of Phase 1. We then evolve the chemistry for our number of slabs over all three phases. We show the temperature as a function of depth and time, and discuss its impact on the chemistry in Section 4.5.1. The results are presented for H, H₂, H⁺, e^- and the carbon chemistry in Section 4.5.2. Section 4.5.3 contains the results for water and OH, of particular importance to understanding this model's success with the hydroxyl ion chemistry. The hydroxyl and water ions, as well as the hydronium results are discussed in Section

Species	$f(X)^1$	Species	$f(X)^1$
H_2	0.5	C_2H	1.0×10^{-8}
Н	7.5×10^{-5}	CO_2	1.3×10^{-8}
He	0.14	H_2O	3.5×10^{-8}
С	2.8×10^{-8}	HCN	1.0×10^{-8}
0	1.0×10^{-4}	HNC	$1.0 imes 10^{-8}$
Ν	1.3×10^{-5}	NH ₃	$1.0 imes 10^{-8}$
S	7.2×10^{-8}	SO_2	5.0×10^{-10}
Si	$7.8 imes 10^{-9}$	C_3H	5.0×10^{-9}
Cl	4.0×10^{-9}	C_4H	4.5×10^{-8}
Fe	3.9×10^{-10}	$c - C_3H_2$	5.0×10^{-9}
Mg	1.9×10^{-9}	HC ₃ N	1.0×10^{-8}
Na	4.7×10^{-10}	C^+	4.7×10^{-9}
Р	3.0×10^{-9}	H^+	4.2×10^{-10}
CH	1.0×10^{-8}	He ⁺	3.5×10^{-10}
CN	2.5×10^{-9}	Fe ⁺	2.6×10^{-9}
CO	7.3×10^{-5}	Mg^+	5.1×10^{-9}
CS	2.0×10^{-9}	Na ⁺	1.5×10^{-9}
N_2	4.2×10^{-6}	S^+	1.2×10^{-9}
NO	1.5×10^{-8}	Si ⁺	2.5×10^{-10}
O_2	8.1×10^{-8}	H_3^+	1.4×10^{-9}
OH	1.0×10^{-7}	HCO+	4.0×10^{-9}
S_2	1.8×10^{-9}	HCS ⁺	2.0×10^{-10}
SO	1.0×10^{-9}	N_2H^+	2.0×10^{-10}

Table 4.5: Initial fractional abundances with respect to n_H

Notes. ⁽¹⁾ $f(X) = n(X)/(n(H) + 2n(H_2))$.

4.5.4, results for shock tracers in Section 4.5.5 and surface species in Section 4.5.6. Finally, Section 4.5.7 discusses the unique predictions this model makes for HCO^+ , O_2 , H_3^+ and CH_4 in the outflow.

4.5.1 Temperature in the Gas-Grain Model

Surface species are extremely sensitive to dust temperatures. Even a temperature variation of 5 or 10 Kelvins can make the difference between a significant number of monolayers of ice enduring on grains for millions of years, and the loss of all monolayers over a few thousand years. Changes in temperature of ≥ 20 K result in completely different results for surface chemistry, and can impact gas-phase chemistry greatly. Since astronomy is in many cases an order of magnitude science, this makes determining mantle desorption rates exceptionally difficult. More difficult is the lingering

uncertainty over bonding temperatures.

The desorption energies for various species, E_d , are given in terms of Kelvins, and impact the desorption rate by a factor of $e^{-E_d/T}$, and the pre-factor for desorption rates varies. Using water as an example, because it is very relevant to the hydroxyl ion chemistry, we have $A = 10^{12} \text{ s}^{-1}$ as the rate pre-factor, so that the first-order desorption rate for water ice, κ_d is (using A and E_d values from Fraser et al. 2001):

$$\kappa_d = 10^{12} \,\mathrm{s}^{-1} \,e^{-5773\,\mathrm{K}/T}.\tag{4.20}$$

Therefore, at a temperature of 90 K, Equation (4.20) yields an average life-time for water ice on the grain-surface of $\sim 10^8$ years. For a temperature of 100 K, this drops to 10^5 years, and at 125 K, the lifetime is on the order of a single year. The rate for water desorption can change by more than an order of magnitude when the temperature increases by only 10%.

Because the dust temperature is of great importance to the surface chemistry, it is necessary to have a good grasp of surface temperatures over all ranges of time and depth. To this end, we provide density plots for temperature as a function of both time and depth for Phase 1 (Figure 4.4), Phase 2 (Figure 4.5), and Phase 3 (Figure 4.6). Applying these temperatures to our example of water ice, and considering still only thermal desorption, we would estimate that, for Phase 1, water ice exists at all extinctions greater than one. At the end of the massive heat-up in Phase 2, however, the dust temperature will mean that all water ice will be gone in the course of a thousand years for $A_V < 2$, and in less than 10^5 years for $A_V \approx 3$. It turns out that, with cosmic ray and photodesorption with such extreme UV and cosmic ray fluxes, the water is significantly depleted for $A_V < 5$, as is discussed in Section 4.5.3.

4.5.2 Gas-Grain Results similar to Inflow results

Results of the gas-grain PDR calculation for Orion KL are more complicated to present and discuss than the inflow model results, because of the added dimension of time. Since most species abundances are both depth-dependent and time-dependent, presenting results over all times and depths is not feasible. Instead, we will highlight results at various times and depths into Orion KL. In the figures and in the discussion, time-dependence will be emphasized, and the depth will be split into



Figure 4.4: Dust temperature for Phase 1 as a function of extinction and time. The temperature at this phase does not change markedly.



Figure 4.5: Dust temperature for Phase 2 as a function of extinction and time. The temperature at this phase changes rapidly, especially at $A_V < 5$.



Figure 4.6: Dust temperature for Phase 3 as a function of extinction and time. At this time, the surface chemistry deeper in the cloud settles, and surface abundances will increase again at later times ($t \gtrsim 10^5$ years).

three regions, at $A_V = 1$, $A_V = 3$ and $A_V = 10$.

The results for the gas-grain PDR model for H, H₂, H⁺, e^- , and the carbon chemistry is very similar to the inflow model, and so much of the relevant information for these species has been discussed above in Sections 4.4.1-4.4.3. The H/H₂ results are sometimes substantially different from those of the inflow model, probably due to the simplistic radiative transfer incorporated into the gas-grain PDR. At the edge, the H/H₂ fraction changes greatly with time, from 10⁻³ at the beginning of Phase 1 to 10⁴ at a million years into Phase 3. The H/H₂ ratio at the three regions is plotted in Figure 4.7.

The results for the ionization are less pronounced than for the inflow model, because the ionization rates are lower than the inflow rates at most depths. Nevertheless, the ionization fraction in Phase 3 does not get below 10^{-6} at $A_V = 10$. The ionization fraction follows closely the timedependence of the UV and cosmic ray components. H⁺ is also surprisingly abundant from 10^4 years into Phase 3, rising eventually to an abundance of ~ 10^{-5} a million years after the beginning of Phase 3. The combination of the high H/H₂ fraction and high ionization contributes to the abundance of hydroxyl and water cations.

4.5.3 Gas-Grain Results: OH and H₂O

For a plot of both gas-phase and ice water in this model, consult Figure 4.8. At $A_V = 1$, the water ice begins to evaporate from the grain, and is depleted to only a handful of molecules per grain by 10⁴ years into Phase 1. By 10⁵ years in Phase 1, virtually no water is left on the grains. At $A_V = 3$, the process takes substantially longer, with about 100 monolayers of ice enduring through Phase 1 and a tenth of Phase 2. At the end of Phase 2, only a few water molecules remain on the surface. Interestingly, in Phase 3, with the parameters held at high constant values, the water first evaporates almost entirely and then later readsorbs somewhat, ending at about a dozen monolayers at 10⁶ years. The fast desorption of water has a similar effect as the inflow, although the effect is highly time-dependent. At $t < 10^4 - 10^5$ years, much of the water has been ionized and dissociated to form OH⁺ and H₂O⁺, and these species quickly react with the molecular hydrogen to form H₃O⁺, which survives substantially longer.

Gas-phase OH follows the water desorption in Phase 3, and increases rapidly until a thousand



Figure 4.7: The H/H₂ ratio for three different extinctions as a function of time. The solid line corresponds to $A_V = 1$, the dashed line with $A_V = 3$ and the dotted line with $A_V = 10$. As the UV field and ionization rates increase over the three phases, all of the H/H₂ ratios increase. There is a curious increase of H/H₂ at $A_V = 10$ after 10^5 years into Phase 3. We are not sure why this occurs. It may relate to the simplistic radiative transfer model utilized, and the complex chemical dynamics involved over these time-scales.

years time. After this time, the OH abundance decreases, from 10^{-7} fractional abundance at 10^4 years down an order of magnitude to $\sim 10^{-8}$ fractional abundance at 10^6 years. This change precedes the OH⁺ and H₂O⁺ peaks. OH at the edge is primarily destroyed via ionization by cosmic rays and X-rays, and by charge exchange with the high number of ambient ions.

4.5.4 Gas-Grain Results: OH⁺,H₂O⁺,H₃O⁺

The results for OH^+ , H_2O^+ and H_3O^+ are plotted in terms of integrated column-densities over all three phases, in Figures 4.9 and 4.10. Integrated column density is used here for these species, in order to allow direct comparison between the model results and observation. Figure 4.9 plots results for a network without Reactions (4.12),(4.13) and (4.14). Figure 4.10 includes these reactions in the network.

The photodissociation of ions has a more substantial effect on the results than was expected, but still only influences the results by increasing OH^+ abundance by a factor of about 2, and decreasing H_3O^+ abundance by about the same amount. H_2O^+ abundance is relatively unaffected by these



Figure 4.8: Water on the surface and in the gas-phase. Gas-phase concentrations (in terms of fractional abundance; left axis) are solid lines, and surface concentrations (in terms of monolayers; right axis) are the dashed lines. The red lines are results for $A_V = 1$, the green lines for $A_V = 3$ and the blue lines for $A_V = 10$. The $A_V = 1$ ice quickly desorbs in Phase 1 and does not return, and the ice for $A_V = 10$ remains throughout the phases, decreasing somewhat at the end of Phase 3. For $A_V = 3$, the water desorbs and then, when the chemistry settles around the constant physical parameters, readsorbs, although at an order of magnitude fewer monolayers.

reactions. The photodissociation of H_2O^+ enhances its rate of destruction, but the photodissociation of H_3O^+ enhances its formation rate by about the same amount.

In this model, OH^+ , H_2O^+ and H_3O^+ all achieve a column density of ~ 10^{13} cm⁻², which for OH^+ , H_2O^+ is within a factor of two agreement with observation, and H_3O^+ is above the observation limit by a factor of five. This result is time-dependent. For all of Phase 1 and 2, and before ~ 10^4 years, H_3O^+ is the dominant species. After 10^4 years, the abundances become very close, though it is expected that, on the order of ten million years after the beginning of Phase 3, H_3O^+ will again dominate.

Results have not been calculated for greater than one million years in Phase 3, or for many different physical parameters, because of the computational intensity of these gas-grain PDR calculations. Nevertheless, they have been examined for a small range of parameters, varying the surface X-ray and cosmic ray ionization rate to $\zeta(A_V = 1) = 5 \times 10^{-16} \text{ s}^{-1}$ and the density to 10^3 cm^{-3} and 10^5 cm^{-3} . For $\zeta(A_V = 1) = 5 \times 10^{-15} \text{ s}^{-1}$ and 10^3 cm^{-3} , OH⁺ increases by a factor of five, H₂O⁺ by

a factor of three, and H_3O^+ decreases by an order of magnitude. This is largely due to the different H/H_2 ratio. For $\zeta(A_V = 1) = 5 \times 10^{-15} \text{ s}^{-1}$ and 10^5 cm^{-3} , H_3O^+ dominates, even through Phase 3. Finally, for $\zeta = 5 \times 10^{-16} \text{ s}^{-1}$, for the density range of $10^3 - 10^5 \text{ cm}^{-3}$, H_3O^+ dominates and OH^+ and H_2O^+ are depleted by about an order of magnitude.

4.5.5 Gas-Grain Results for shock tracers SO and SiO

Observation of molecules SO and SiO at fractional abundance of 10^{-7} and 10^{-8} respectively are both seen as signs of shock-driven chemistry. Gezari (1992); Kondratko et al. (1999); Wright & Plambeck (1983) discuss the observation of SiO masers and Plambeck et al. (1982) discusses SO observations. Evidence of shocks in Orion KL is discussed first by Chernoff et al. (1982). Wright et al. (1996), among others, link these two species to shocks in this region.

Our model does not incorporate shocks in any way, and as a consequence calculated fractional abundances are orders of magnitude lower than the observed abundances. The closet we come for both SO and SiO is at very early times in Phase 3 (< 10^3 y), and late times in Phase 2. Of these, at the end of Phase 2 and beginning of Phase 3, SO comes to within an order of magnitude to observation. Our results agree with much of the rest of literature in supporting the presence and important chemical role of shocks in the Orion KL outflow.

4.5.6 Gas-Grain Results for some species produced on grain surfaces

Methanol (CH₃CO), carbon dioxide (CO₂) and formaldehyde (H₂CO) are all mostly produced on the surface of grains. None of these species are included in the Meudon network, and so there are no inflow results for these molecules. All of these molecules have been observed in Orion KL. Methanol and carbon dioxide have measurable abundances in the core, and formaldehyde is observed in the outflow. Both CH₃OH and H₂CO are thought to be formed primarily by hydrogenation of CO (see Tielens & Hagen 1982; Watanabe & Kouchi 2002; Hiraoka et al. 2002). It is unknown how carbon dioxide forms, since gas-grain models consistently underproduce the species. Garrod & Pauly (2011) present a promising new theory for carbon dioxide formation, but their techniques are not incorporated into our model.

Formaldehyde is formed on dust primarily by the adsorption of carbon monoxide onto the sur-



Figure 4.9: Column densities of OH^+ (solid), H_2O^+ (dashed) and H_3O^+ (dotted) as a function of time. Note that it takes about 10^5 years after the OB stars turn on for the OH^+ , H_2O^+ and H_3O^+ columns to intersect. 114



Figure 4.10: Same as Figure 4.9, except with the Photodissociation Reactions (4.12-4.14) included. The $OH^+/H_2O^+/H_3O^+$ ratios intersect somewhat earlier, at 5×10^4 years, when these reactions are included. H_3O^+ is depleted about a factor of two hore than in Figure 4.9.

face, and then the surface reactions (see, for example Cuppen et al. 2009):

$$JCO + JH \rightarrow JHCO$$
,
 $JHCO + JH \rightarrow JH_2CO$.

The formaldehyde is mostly formed at and before Phase 1; some of it is desorbed in Phase 2, and much of the rest of it at the beginning of Phase 3. At 10^4 years, its gas-phase fractional abundance reaches 10^{-8} . The formaldehyde is rapidly destroyed by photodissociation and ion-neutral reactions, and is already depleted at 10^5 years to 8×10^{-11} . The observation of formaldehyde in the outflow supports a fractional abundance of 10^{-8} for formaldehyde. This observation coincides with the time-frame for the region, already supported by the chemistry (Mauersberger et al. 1988; Millar et al. 1991; Wakelam et al. 2004). The physical properties of the outflow recommend even lower ages, down to ~ 500 years for the high-velocity flow, and ~ 10^4 years for the low-velocity flows (Bally et al. 2011).

Methanol is formed also primarily on grain surfaces by hydrogenation of formaldehyde, via the reactions

 $JH_2CO + JH \rightarrow JH_2COH$, $JH_2COH + JH \rightarrow JCH_3OH$.

This pathway, coupled with the chaotic environment in Orion KL and the low density our model incorporates, does not result in very much methanol during Phase 3. The methanol abundance is many orders of magnitude below observation for the Core. Carbon dioxide is also orders of magnitude below the core abundance, although this is the case in standard core models as well (Ruffle & Herbst 2001; Hassel et al. 2010). The lack of methanol suggests that our model best fits the outflow and possibly the surrounding plateau only, and not core or other dense and well-shielded environments. It should be noted that methanol is not observed in as significant abundances in the outflow, although it is observed in virtually every other part of Orion KL, though the recent survey by Crockett et al. (2010).

4.5.7 Gas-Grain Predictions: O_2 , CH_4 , H_3^+ and HCO^+

The gas-grain PDR makes predictions for O₂ and methane, and the ions H⁺₃ and HCO⁺. These predictions, along with other results of the gas-grain PDR model, are listed in Table 4.6. If the outflow is young ($\leq 10^4$ y), then gas-phase methane should be quite abundant, achieving average fractional abundances of ~ 10^{-7} . If the outflow is older, then the abundance will be depleted by an order of magnitude, due to the active and strong destructive processes in the region. The ion HCO⁺ is predicted by this model to have an early time abundance of 5×10^{-8} , two orders of magnitude higher than the predicted inflow abundance. This is because the ionization fraction is lower and because there is a higher abundance of CO than in the inflow model.

Throughout Phase 1, methane exists largely on the surface, comprising a dozen monolayers of the ice. Only near the edge, at $A_V \leq 1$ is the methane depleted, where JCH₄ drops to less than a monolayer. Phase 1 molecular oxygen interestingly increases its abundance at higher temperatures on the surface of grains, likely a result of its activation and desorption energies, which may require a somewhat higher temperature for the formation of molecular oxygen on the surface. This is not entirely unexpected, given that we incorporate the surface formation rates for molecular oxygen:

$$JO + JOH \rightarrow JO_2 + JH,$$
 (4.21)

from Quan et al. (2008), and they predict the formation of molecular oxygen decreases rapidly at T < 40 K. The oxygen abundance in grain mantles at $A_V \sim 1$ is almost 10 monolayers, dropping to less than a monolayer at $A_V < 3$. At Phase 2, the temperature is too high to allow oxygen to last for long on the grain surfaces, though oxygen forms rapidly before the heat-up passes ~ 100 K. At $A_V < 5$, molecular oxygen still comprises 10^{-4} monolayers. As Phase 3 progresses, there ceases to be very much methane or molecular oxygen on the surface of grains, and, for methane, destruction in the violent gas-phase of the KL environment soon follows.

Protonated hydrogen is abundant in this model, as in the inflow model. H_3^+ is very timedependent, and if the outflow is young, H_3^+ will be as abundant or somewhat more abundant than for the inflow model. If the outflow is older, the H_3^+ fractional abundance drops an order of magnitude, from 10⁻⁷ to 10⁻⁸. This result has important implications for H_3^+ observations near very active regions, like Sgr B2 or supernovae remnants (see Oka et al. 2005; Indriolo et al. 2010); the abundance of H_3^+ , if treated as a steady-state abundance to calculate ζ may overestimate the cosmic ray ionization rate by up to an order of magnitude.

4.6 Discussion

We present results for two models, an H₂O inflow model and a gas-grain PDR model. The inflow model utilized the Meudon PDR code and its results are at steady-state. The gas-grain PDR is time-dependent, but it incorporates only very simple radiative transfer calculations, accounting for dust extinction and H₂ and CO self-shielding based on analytical formulae. For both the inflow and gas-grain code, the injection of water, whether artificially or via grain desorption, in combination with a high H/H₂ ratio, results in calculated OH⁺ and H₂O⁺ columns that agree with observation. In the case of H₃O⁺, both gas-grain and inflow models come very close to the observational limit, although the gas-grain predictions surpass this limit.

The results for water with the inflow model are disappointing. Even with the water inflow, the calculated H₂O fractional abundance is two orders of magnitude below the observed abundance. If the inflow is increased to force agreement with observation, H₂O⁺ is overproduced by more than an order of magnitude. If instead the extinction is increased, then H₃O⁺ surpasses the observational limit, and is too abundant. The fractional abundance for water agrees to within a factor of five between calculation and observation for the gas-grain PDR, if the time is $\leq 10^4$ years.

The gas-grain PDR also produced interesting results for methanol and formaldehyde. These results suggest that the Orion KL outflow may be in a transitional state with its surface chemistry, possessing high abundances of formaldehyde, and unobservable amounts of methanol. Other complex species, like ethyl cyanide, are also below the limits of observation, and are currently not seen in the outflow. The violent environment seems to demolish the surface chemistry, although some surface chemistry recovers at later times. Observational results are consistent with this interpretation.

The abundance of HCO⁺ provides the best way to distinguish between the inflow and the gasgrain PDR models. In the inflow model, because the physical parameters are even more extreme

Species	H ₂ O Inflow	Gas-Grain PDR		Observed		
-		10 ⁴ y	10 ⁵ y	10 ⁶ y	Outflow	Core
$N_{H} ({\rm cm}^{-2})$					$2.3(23)^{b}$	$3.1(23)^b$
H^+	1.68(-4)	3.88(-6)	4.63(-6)	2.01(-5)		
Н	2.22(-1)	1.91(-2)	4.02(-2)	1.65(-1)		
H_2	3.88(-1)	4.88(-1)	4.77(-1)	4.15(-1)		
C^+	4.49(-5)	1.24(-5)	1.31(-5)	1.41(-5)		
С	2.46(-5)	1.29(-5)	1.71(-5)	2.04(-5)		
CO	1.90(-6)	4.69(-5)	1.65(-5)	1.06(-5)	9.7(-6) ^c	8.0(-5) ^c
H_2^+	1.12(-9)	6.42(-11)	5.58(-11)	3.41(-11)		
$H_3^{\tilde{+}}$	7.59(-8)	1.89(-7)	3.36(-8)	1.63(-8)		
O_2	6.32(-11)	2.75(-9)	5.48(-10)	3.78(-10)		$2.1(-7)^d$
OH	1.08(-8)	1.68(-7)	8.08(-8)	8.45(-9)	$7.5(-7)^{e}$	
H_2O	1.95(-8)	8.40(-7)	1.47(-7)	1.72(-7)	$2.9(-6)^{f}$	$1.2(-5)^{f}$
OH^+	1.83(-9)	5.11(-11)	1.01(-10)	1.18(-10)	$4.3(-10)^{g}$	
H_2O^+	5.24(-10)	1.88(-10)	2.88(-10)	1.44(-9)	$4.3(-10)^{g}$	
H_3O^+	6.75(-11)	2.98(-10)	1.85(-10)	8.65(-11)	$< 2(-10)^{g}$	
CH^+	1.38(-10)	4.99(-12)	3.62(-12)	1.64(-12)		
HCO^+	5.77(-10)	4.63(-8)	3.45(-9)	1.81(-9)		
NH ₃	5.3(-13)	3.83(-10)	4.04(-11)	3.54(-12)		$1.6(-6)^{f}$
NO	3.98(-12)	5.83(-9)	1.49(-10)	4.83(-11)		$2.8(-7)^{f}$
CN	1.52(-9)	8.51(-8)	5.04(-9)	7.48(-10)		$7.9(-9)^{f}$
HNC	2.28(-11)	1.78(-8)	9.91(-11)	9.70(-12)	$1.2(-9)^{f}$	$4.4(-10)^{f}$
HCN	4.07(-11)	2.00(-8)	1.39(-10)	1.61(-11)	$7.2(-9)^{h}$	$2.6(-9)^h$
SO	4.32(-15)	1.09(-12)	2.68(-15)	6.74(-16)	$3.1(-7)^{f}$	
CO_2	i	9.65(-11)	1.41(-11)	1.14(-11)		1(-7) - 1(-5) ^j
SiO	i	1.28(-13)	2.61(-13)	1.16(-13)	$3.3(-8)^{f}$	
H_2CO	i	1.05(-8)	8.23(-11)	1.94(-11)	$1.4(-8)^{f}$	
CH_4	i	2.37(-7)	4.14(-8)	1.30(-8)		
CH ₃ OH	i	3.19(-16)	1.52(-19)	3.42(-20)		$7.9(-7)^{f}$
HC ₃ N	i	1.14(-10)	2.41(-16)	2.39(-17)		$1.8(-9)^{f}$
CH ₃ CN	i	6.11(-11)	2.19(-15)	4.54(-16)		$5.0(-9)^{f}$

Table 4.6: Average Fractional Abundances from Inflow Model and Gas-Grain PDR Model^a

Notes. ^(a) Calculated from column-densities. For species X, the average fractional abundance is $f_{AV}(X) = N(X)/N_H$

^(b) Plume et al. (2012); $N_H = N(H) + 2N(H_2)$

^(c) Lerate et al. (2006), based on column densities

^(d) Goldsmith et al. (2011); based on the column-density over the entire KL region

^(e) Goicoechea et al. (2006a)

(f) Persson et al. (2007)

^(g) Gupta et al. (2010)

^(h) Abundances calculated using HNC abundances from Persson et al. (2007) and the HCN/HNC ratios from Goldsmith et al. (1986)

(*i*) The Meudon PDR network does not include these species

^(j) Boonman et al. (2003); in this chapter, the KL region is spatially resolved, and there is a large difference between CO_2 abundances toward different parts of the core

than with the gas-grain PDR model, H_3^+ is produced in exceptionally high abundances, but HCO⁺ is destroyed due to the low amount of CO as well as the high electron fraction. For the gas-grain PDR at early times, the steady-state H_3^+ will no doubt be lower than for the inflow model, but H_3^+ is strongly time-dependent at early times, and so for < 10⁵ years, its abundance will not be simply connected to the cosmic ray ionization rate. For early times, H_3^+ is actually more abundant in the gas-grain PDR than the inflow model. HCO⁺ is orders of magnitude more abundant in the gas-grain PDR, and this seems to be the most direct prediction separating these two models. The inflow model interestingly predicts high abundances of H_2^+ , and in an environment like the Orion KL outflow, this species might be at the threshold of detection in rovibrational emission (John Black, private communication).

It is ironic that before molecular oxygen has been observed first in Orion KL (Goldsmith et al. 2011), astrochemical models consistently predicted that this species would be far more abundant than the observational constraints allowed. Now that O_2 has been observed, our model results for Orion KL have it in abundances much lower than observation. This is likely because the O_2 is contained within the core or within some dense region, and not in high abundances within the outflow.

Though both of these models have produced interesting results and decisive predictions for the Orion KL outflow, both of these models are only the first step toward dynamic modeling of violent regions like Orion KL or Sgr B2. The greatest weakness of the gas-grain PDR model is a simplistic radiative transfer, that very likely miscalculates the H/H₂ ratio, especially at $A_V \leq 3$. The Meudon PDR model utilizes comprehensive radiative transfer calculations for molecular hydrogen, but is not time-dependent, and there is much to suggest both in observation and in these models that the outflow is probably young, at ~ $10^3 - 10^4$ years, and therefore time-dependence is essential to understanding its chemistry. We plan next to incorporate the robust radiative transfer of the Meudon PDR code into a time-dependent model with an extensive gas-grain network. Eventually, the effect of ice mantles on radiative transfer should also be included. Furthermore, in a warm-up model, surface chemistry has to be solved by more sophisticated techniques than rate equations, such as the Monte-Carlo model of Vasyunin et al. (2009). Also, at $T \gtrsim 300$ K, a higher temperature network should be adopted (Harada et al. 2010).

Both the gas-grain and inflow models also oversimplify the geometry of the region, treating the low-velocity component of the plateau and blue-shifted outflow as the same chemical region, and treating both the outflow and the core as though they are two spatially disconnected and homogeneous regions. Some causal connection and heterogeneity must be incorporated into models of Orion KL and Sgr B2, especially as angular resolution improves. Incorporating heterogeneity will be vitally important when modeling chemistry near hot, excited regions in the Large Megallanic Cloud on the sub-arcsecond scale, as it will be viewed by the Atacama Large Millimeter/submillimeter Array. chapters like Boonman et al. (2003) take the first important steps toward astrochemical models of Orion KL and similar regions that properly account for the heterogeneous nature of these sources.

Once better radiative transfer calculations are incorporated into the gas-grain PDR, it may be useful to apply the gas-grain model to Sgr B2. There are many sight-lines towards Sgr B2 where OH^+ and H_2O^+ have been observed, but H_3O^+ is absent. There are also sight-lines where all three ions have been observed. It may be that the density or the age of the regions along the sight-lines is the reason for the very different chemical observations. It is important to note that H_3^+ is seen along every sight-line in Sgr B2 where OH^+ and H_2O^+ are observed.

Our understanding of Orion KL is only beginning, as the newest models have just begun to account for some of the rich complexity observers have discovered in Orion. Orion KL will remain an object of great interest for a long time, both for the outstanding mysteries of its chemistry, as well as for what it can tell us about the process of star formation. This region has many different chemical phases, a wide range of densities, and experiences high fluxes of radiation and strong shocks. There are a variety of new theoretical techniques that will have to be developed in order to come to understand this region and what it can tell us about the chemistry, its connection to the interstellar environment and star formation. This work is an early attempt to grasp at the rich complexity of Orion KL.

Chapter 5 Summary

Guided by observing the basic connections between physics and chemistry in the interstellar medium, we developed two astrochemical models, one for a typical irradiated source, the Horsehead Nebula, and another for a young and violent source, the Orion KL region. In both cases, incorporating detailed cosmic ray and UV photon calculations into determining χ and ζ helped to solve some outstanding chemical mysteries in both regions.

We incorporated both a detailed depth-dependent cosmic ray ionization rate and time-dependence of physical parameters scaled to star formation and developed new and more accurate predictions for interstellar chemistry. The predictions for the Orion KL region especially should be explored, in order to determine the usefulness of our model in its current form. Exploration into other active regions, such as Sgr B2, is a logical next step.

The cosmic ray transport model needs to be further developed, to incorporate electron transport, and to account for shocks and gravitation within the cloud itself. Eventually, the transport calculation needs to be expanded into three dimensions. It also would be useful to calculate in detail the X-ray penetration into clouds, and to determine what chemical signatures would help us distinguish X-ray from cosmic ray impact on the interstellar medium.

If these models could be improved, and rates and physical conditions both determined to much higher accuracy, chemistry in space could provide a measure both for specific physical parameters and for the age of particular interstellar environments. The provision of these constraints would afford a unique insight into the mechanisms and phases of star formation, many aspects of which are not well understood. The increased angular resolution of ALMA means that single objects will no longer appear homogeneous, and cannot be treated as single points. Two and three dimensional chemical models will eventually need to be incorporated in order to make sense of ALMA results, and to provide useful predictions for future observations at high angular resolution. These new observations, joined with robust astrophysical and chemical models, will help us to better understand interstellar chemistry, especially in young violent environments, and may provide new insights key to understanding how stars form from interstellar matter.

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Appendix A

PROPAGATION OF LOW-ENERGY COSMIC RAYS IN MOLECULAR CLOUDS: CALCULATIONS IN THREE DIMENSIONS

A.1 Introduction

Cosmic rays of energy less than 1 GeV, called low-energy cosmic rays, drive interstellar chemistry and may cause specific spectral features recently measured, such as the 6.7 keV emission line. Yet the origin and flux of low energy cosmic rays is currently unknown because the Sun's magnetic field deflects these particles, so that they cannot be directly observed. There is a great deal of uncertainty about the correct cosmic-ray flux-spectrum for low energy cosmic rays, ranging from a steep slope of ~ E^{-3} (predicting a great many low energy cosmic rays, see Nath & Biermann 1994) all the way to a positive slope of ~ E (Spitzer & Tomasko 1968, predicting very few low energy cosmic rays). A robust model of cosmic ray transport in molecular clouds is necessary in order to understand this flux-spectrum as a function of position within a molecular cloud. Modelling low energy cosmic ray streaming will provide a better understanding of interstellar chemistry and possible line emissions caused by these cosmic rays.

We model cosmic ray transport in three dimensions using a two-fluid approximation, The first fluid is the interstellar medium and the second fluid is the cosmic rays. The first fluid is modelled as a non-relativistic plasma using standard magnetohydrodynamics equations. These equations are solved using the ZEUS magnetohydrodynamics code (Stone & Norman 1992) and will be discussed in Section A.2. The second fluid is described by the collisional relativistic Boltzmann

transport equation with the ISM magnetohydrodynamics providing the external force in the form of the Lorentz Force. We describe our calculations in Section A.3. Section A.4 contains a brief discussion of our results. Section A.2 follows closely the development and notation of Landau & Lifshitz (1960) and Section A.3 proceeds at the beginning from Skilling (1975).

A.2 First Fluid: The ISM

The ISM is our first fluid, and we treat it with the standard magnetohydrodyanics (MHD) equations, describing it in terms of its velocity, \mathbf{v} (cm/s), density ρ (cm⁻³), pressure *P* (erg cm⁻³) and magnetic field \mathbf{H} (ampere cm⁻¹). We assume a non-infinite electrical conductivity, σ , and negligible thermal conductivity and viscosity. Allowing the thermal conductivity to be zero means, for instance, that we can treat our fluid as though it is isentropic. We alter the basic MHD equations in order to connect the first fluid to the second. This is done by applying Gauss's law to the cosmic ray proton and electron distribution functions in order to determine the resulting electric field:

$$\nabla \cdot \mathbf{E}_{CR} = 4\pi e \int (f_p - f_e) d^3 p, \qquad (A.1)$$

where f_p and f_e are the distribution functions for the cosmic ray protons and electrons, respectively, solved for in Section A.3, and $e = 4.8032 \times 10^{-10}$ esu is the elementary charge. We write Maxwell's Equations for the first fluid as:

$$\nabla \cdot \mathbf{H} = 0; \tag{A.2}$$

$$\frac{\partial \mathbf{H}}{\partial t} = \nabla \times (\mathbf{v} \times \mathbf{H}) - \nabla \times \mathbf{E}_{CR} + \frac{c^2}{4\pi\sigma} \nabla^2 \mathbf{H}, \tag{A.3}$$

where $c = 3 \times 10^{10}$ cm/s is the speed of light. We add to this the equation of continuity, which is unaffected by the cosmic rays, and is:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \tag{A.4}$$

and the Nevier-Stokes equation for fluid motion:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{v} = -\frac{\nabla P}{\rho} + \frac{(\nabla \times \mathbf{H}) \times \mathbf{H}}{4\pi\rho} + \frac{\mathbf{j}_{CR} \times \mathbf{H}}{c}, \tag{A.5}$$

where the cosmic ray current is determined from the distribution functions, the first moment of Equation (A.1), as:

$$\mathbf{j}_{CR} = e \int \left(f_p \frac{\mathbf{p}}{\gamma_p m_p} - f_e \frac{\mathbf{p}}{\gamma_e m_e} \right) d^3 p.$$
(A.6)

The conductivity, σ , can be estimated from the electron damping rate from collisions with the ambient medium. This damping rate, which Skilling & Strong (1976) incorporate in their cosmic ray transport calculations, is from Dalgarno & Dickinson (1968), and is:

$$\Gamma = 1.12 \times 10^{-9} \frac{n(\text{HI})}{1 \text{ cm}^{-3}} \left(\frac{T}{1000 \text{ K}}\right)^{-1/2} \text{ s}^{-1}$$
(A.7)

The conductivity can be estimated as a function of the total electric field, **E**, and electron current, which is related to the electron density, n_e , and the average velocity $\langle \mathbf{v}_e \rangle$. The conductivity is:

$$\sigma(\mathbf{x}) = \frac{en_e(\mathbf{x})}{\mathbf{E}(\mathbf{x})} \cdot \langle \mathbf{v}_e \rangle. \tag{A.8}$$

The average velocity is related to the Γ such that:

$$\langle \mathbf{v}_e \rangle = \frac{e\mathbf{E}(\mathbf{x})}{m_e} \frac{1}{\Gamma}.$$
 (A.9)

Therefore:

$$\sigma(\mathbf{x}) = \frac{e^2 n_e(\mathbf{x})}{m_e \Gamma}.$$
(A.10)

With our estimation for conductivity, we can proceed with setting up the complete set of MHD equations, Equations (A.1),(A.3),(A.4) and (A.5), into a series of equations to be solved numerically. In our case, these equations will be solved by perturbation. We start with a given magnetic field, \mathbf{H}_0 , density, ρ_0 and pressure P_0 , each perturbed so that:

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}',\tag{A.11}$$

$$\rho = \rho_0 + \rho', \tag{A.12}$$

$$P = P_0 + P'.$$
 (A.13)

We then apply Equations (A.11)-(A.13) to the MHD equations. We also note that, since the ISM is considered isentropic, we can treat the entropy, s, as being a constant, and therefore can write the

pressure in terms of the velocity of sound in the ISM, v_s . So:

$$P' = \left(\frac{\partial P}{\partial \rho}\right)_s \rho'; \tag{A.14}$$

$$\mathbf{v}_s = \left(\frac{\partial P}{\partial \rho}\right)_s^{1/2};\tag{A.15}$$

$$P' = v_s^2 \rho'. \tag{A.16}$$

The MHD equations become:

$$\nabla \cdot \mathbf{H'} = 0, \qquad \nabla \cdot \mathbf{E}_{CR} = 4\pi e \int (f_p - f_e) d^3 p, \qquad (A.17)$$

$$\frac{\partial \mathbf{H}'}{\partial t} = \nabla(\mathbf{v} \times \mathbf{H}) + \frac{c^2}{4\pi\sigma} \nabla^2 \mathbf{H}' - \nabla \times \mathbf{E}_{CR}$$
(A.18)

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{v} = -\frac{\mathbf{v}_s^2}{\rho}\nabla\rho' + \frac{(\nabla \times \mathbf{H}') \times \mathbf{H}}{4\pi\rho} + \frac{\mathbf{j}_{CR} \times \mathbf{H}}{c}.$$
(A.19)

This is the point at which ZEUS 3D discretizes and solves these equations. Only the magnetic field, density and velocity field (v_0 below) couples with the . These are applied to the equations describing the second fluid. Though the density does couple to the second fluid, the variation of ρ' from ρ_0 does not seem to impact the cosmic ray transport significantly.

A.3 Second Fluid: Cosmic Ray Transport

Cosmic rays are the second fluid. Since the second fluid is far from equilibrium, it cannot be treated by standard MHD equations, because thermodynamic quantities cannot be usefully applied to solve cosmic ray transport. Also, our second fluid has velocity fields of magnitude close to c, and as such is highly relativistic. We describe this fluid by its distribution function:

$$f(\mathbf{x}, \mathbf{p}, t) \ d^3x \ d^3p \ dt, \tag{A.20}$$

which represents the number of particles in the phase space volume d^3xd^3p located at **x**,**p** at time t + dt. We begin describing *f* with the standard Boltzmann Equation:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + \frac{\partial}{\partial \mathbf{p}} \left(f \frac{\partial \mathbf{p}}{\partial t} \right) = 0. \tag{A.21}$$

We include the Lorentz Force, and apply Lorentz transformations to the velocities, achieving the Relativistic Boltzmann Transport Equations (RBTE), sometimes called the Relativistic Vlasov Equations, after Vlasov (1938). This system of equations is:

$$\frac{\partial f_p}{\partial t} + \gamma_p \mathbf{v}_p \cdot \nabla f_p + e \left[\mathbf{E} + \frac{\gamma_p}{c} (\mathbf{v}_p \times \mathbf{B}) \right] \cdot \frac{\partial f_p}{\partial \mathbf{p}} = 0; \tag{A.22}$$

$$\frac{\partial f_e}{\partial t} + \gamma_e \mathbf{v}_e \cdot \nabla f_e - e \left[\mathbf{E} + \frac{\gamma_e}{c} (\mathbf{v}_e \times \mathbf{B}) \right] \cdot \frac{\partial f_e}{\partial \mathbf{p}} = 0, \tag{A.23}$$

where both **E** and **B** are provided by the first fluid. In the future, we will discuss the Boltzmann Equations as a single equation of the form (for Equation A.22,A.23):

$$\frac{\partial f_{\alpha}}{\partial t} + \gamma_{\alpha} \mathbf{v}_{\alpha} \cdot \nabla f_{\alpha} + \epsilon_{\alpha} e \Big[\mathbf{E} + \frac{\gamma_{\alpha}}{c} (\mathbf{v}_{\alpha} \times \mathbf{B}) \Big] \cdot \frac{\partial f_{\alpha}}{\partial \mathbf{p}} = 0, \tag{A.24}$$

where $\alpha = p, e$, and $\epsilon_{\alpha} = +1$ for $\alpha = p$ and $\epsilon_{\alpha} = -1$ for $\alpha = e$. The relativistic corrections are:

$$\gamma_{\alpha} = \left(1 - \frac{c^2 p^2}{E_{\alpha}^2}\right)^{-1/2},$$
 (A.25)

$$E_{\alpha}^2 = c^2 p^2 + E_{\alpha,0}^2, \tag{A.26}$$

$$T_{\alpha} = E_{\alpha} - E_{\alpha,0},\tag{A.27}$$

where $E_{\alpha,0}$ is the rest-energy, and $E_{p,0} = 938$ MeV and $E_{e,0} = 511$ keV. Cosmic rays are usually described by their kinetic energy, T, which for low-energy cosmic ray protons is most important for ionizing collisions when $T \sim 1$ MeV, and for low-energy electrons is most important for $T \sim 1$ keV. It should be noted that a Boltzmann transport equation must be independently solved for each species of cosmic ray.

Since the first fluid is solved in the standard way, the electric field is placed entirely in terms of the magnetic field, by the relationship:

$$\nabla \times \mathbf{H} = \frac{4\pi\sigma}{c} \Big[\mathbf{E} + \frac{1}{c} (\mathbf{v}_0 \times \mathbf{B}) \Big].$$
(A.28)

where \mathbf{v}_0 is the fluid velocity of the medium. With our fluid, $\mu \approx 1$, and therefore $\mathbf{H} \approx \mathbf{B}$, so:

$$\mathbf{E} = \frac{c}{4\pi\sigma} \nabla \times \mathbf{H} - \frac{1}{c} \mathbf{v}_0 \times \mathbf{H}.$$
 (A.29)

Applying Equation (A.29) to Equation (A.24), we obtain the more useful form of:

$$\frac{\partial f_{\alpha}}{\partial t} + \gamma_{\alpha} \mathbf{v}_{\alpha} \cdot \nabla f_{\alpha} + \epsilon_{\alpha} e \left[\frac{c}{4\pi\sigma} \nabla \times \mathbf{H} + \frac{\gamma_{\alpha}}{c} (\mathbf{v}_{\alpha} \times \mathbf{H}) - \frac{1}{c} (\mathbf{v}_{0} \times \mathbf{H}) \right] \cdot \frac{\partial f_{\alpha}}{\partial \mathbf{p}} = 0.$$
(A.30)

Equation(A.30) is valid for collisionless fluids, but cosmic rays lose significant energy from collisions with the ISM, and this must be accounted for. The following approximations will make the RBTE quasi-collisional, since they incorporate collisions with the ISM, but not collisions with other cosmic rays, an approximation that seems entirely reasonable in all conditions except possibly for in cosmic ray sources.

To approximate collisions between the ISM and the cosmic rays, we include a term from Cesarsky & Volk (1978):

$$\left(\frac{d\mathbf{p}}{dt}\right)_{\text{coll},\alpha} \left(\frac{\partial f_{\alpha}}{\partial \mathbf{p}}\right),\tag{A.31}$$

and we distinguish elastic ("el") and inelastic equations ("in"), so:

$$\left(\frac{d\mathbf{p}}{dt}\right)_{\text{coll},\alpha} = \left(\frac{d\mathbf{p}}{dt}\right)_{\text{el},\alpha} + \left(\frac{d\mathbf{p}}{dt}\right)_{\text{in},\alpha}.$$
(A.32)

We approximate the inelastic case as:

$$\left(\frac{dp}{dt}\right)_{\mathrm{in},\alpha} \approx \frac{n\sigma_{\mathrm{in}}p}{\gamma_{\alpha}m_{\alpha}}(\Delta p)_{\alpha};$$
 (A.33)

where σ_i is the inelastic scattering cross-section from Cravens et al. (1975) and other sources, listed and reviewed very well in Padovani et al. (2009). The other terms, Δp is the momentum change from each collision, also reviewed in Padovani et al. (2009) and Rimmer et al. (2012). *n* is the density of the cloud, and *m* is the mass of the cosmic ray particle, either the electron or proton mass. Elastic scattering is dealt with in a similar manner, except that the momentum is conserved over the two bodies involved in the collision, and the scattering cross-section is different.

The collisional relativistic Boltzmann Equation is:

$$\frac{\partial f_{\alpha}}{\partial t} + \gamma_{\alpha} \mathbf{v}_{\alpha} \cdot \nabla f_{\alpha} + \epsilon_{\alpha} e \left[\frac{c}{4\pi\sigma} \nabla \times \mathbf{H} + \frac{\gamma_{\alpha}}{c} (\mathbf{v}_{\alpha} \times \mathbf{H}) - \frac{1}{c} (\mathbf{v}_{0} \times \mathbf{H}) \right] \cdot \frac{\partial f_{\alpha}}{\partial \mathbf{p}} = \left(\frac{d\mathbf{p}}{dt} \right)_{\text{coll},\alpha} \left(\frac{\partial f_{\alpha}}{\partial \mathbf{p}} \right). \quad (A.34)$$

We discretize and solve this equation using a restricted Crank-Nicolson method (Crank et al. 1947). It is restricted because Equation (A.34) has only first-order terms. We solve this problem for a box of equal sides and equal momentum-steps. The number of spatial steps is equal to N_x and the number of momentum steps is N_p . We discretize f in terms of n_i , k_i and m. The index i = 1, 2, 3 for x, y, z, and $n_i = 0, 1, ..., N_x$, $k_i = 0, 1, ..., N_p$. The value of m = 0, 1, 2, ... is equal to the time-step. Each step is divided into parts such that, for a box of volume L^3 and cosmic rays of momentum range P, the step-size for each variable is:

$$\Delta x = \frac{L}{N_x}, \quad \Delta p = \frac{P}{N_p}.$$
(A.35)

The distribution function is thus transformed into:

$$f_{\alpha}(\mathbf{x}, \mathbf{p}, t) \to f_{\alpha}(n_i, k_i, m).$$
 (A.36)

The values for **x**, **p** in Equation (A.34) are determined entirely by the values n_i and k_i . For a particular component of the position, $x_i = n_i \Delta x$. We can now discretize the differentials of f by taking steps in n_i,k_i ; see Figure A.1. We make not only of the shifted discrete phase-space variables, and of the time-step. We discretize the position-differentials as:

$$\frac{\partial f_{\alpha}}{\partial x_{i}} = \frac{1}{4\Delta x} \Big\{ [f_{\alpha}(n_{i}+1,m+1) - f_{\alpha}(n_{i}-1,m+1)] + [f_{\alpha}(n_{i}+1,m) - f_{\alpha}(n_{i}-1,m)] \Big\},$$
(A.37)

and the momentum differential is discretized as:

$$\frac{\partial f_{\alpha}}{\partial p_i} = \frac{1}{4\Delta p} \Big\{ [f_{\alpha}(k_i+1,m+1) - f_{\alpha}(k_i-1,m+1)] + [f_{\alpha}(k_i+1,m) - f_{\alpha}(k_i-1,m)] \Big\},$$
(A.38)

and the time differential is:

$$\frac{\partial f_{\alpha}}{\partial t} = \frac{1}{2\Delta t} [f_{\alpha}(m+1) - f_{\alpha}(m)].$$
(A.39)

This method of discretization is stable regardless of the size of Δx , Δp and Δt . Unless the size of the time-step is:

$$\Delta t < \frac{\Delta x}{c},\tag{A.40}$$

the solution will not be predictable and will not typically match even the qualitative behavior of the system. If the inequality in Equation (A.40) is upheld, then the order of error can be calculated, and is:

$$\mathcal{E} = O(\Delta t^2) + 3O(\Delta x^2) + 3O(\Delta p^2). \tag{A.41}$$



Figure A.1: A stencil of the Crank-Nicolson equation, showing the shifts, in this case, for a onedimensional time-dependent system (courtesy of Wikipedia). The stencil for this problem would be more extensive, since we are solving an equation in a 6 + 1 dimensional phase-space.

The above equation only expresses the order of error from the Crank Nicolson discretization. Depending on the environment, the error might be much higher, depending on the accuracy of the many other approximations we have made, especially Equations (A.10) and (A.31).

We now discretize the coefficients in Equation (A.34). Since relativistic corrections are explicit in the equation, the velocity can be represented as:

$$\mathbf{v}_{\alpha} = \frac{\mathbf{p}}{m_{\alpha}},\tag{A.42}$$

and therefore the second coefficient on the l.h.s. of Equation (A.34) can be written as:

$$\mathbf{v}_{\alpha} \cdot \nabla = \frac{1}{m_{\alpha}} \left(p_i \frac{\partial}{\partial x_i} \right). \tag{A.43}$$

For Equation (A.43) and following, we use the Einstein summation rule, where the repeated *i* index is summed over the values 1,2 and 3. The magnetic field is likewise discretized, and **H** is broken up into H_1 , H_2 and H_3 for the magnetic field magnitude in the *x*, *y* and *z* directions respectively. These magnitudes, H_i , depend only on the position, and not the momentum. Using the Levi-Civita Symbol:

$$\varepsilon_{ijk} = \begin{cases} +1 & \text{if } (i, j, k) \text{ is } (1, 2, 3), (3, 1, 2) \text{ or } (2, 3, 1), \\ -1 & \text{if } (i, j, k) \text{ is } (1, 3, 2), (3, 2, 1) \text{ or } (2, 1, 3), \\ 0 & \text{if } i = j \text{ or } j = k \text{ or } k = i, \end{cases}$$
(A.44)

the parts in the third term on the l.h.s. of Equation (A.34) are discretized as

$$(\nabla \times \mathbf{H}) \cdot \frac{\partial f_{\alpha}}{\partial \mathbf{p}} = \varepsilon_{ijk} \left(\frac{\partial}{\partial x_j} H_k \right) \frac{\partial f_{\alpha}}{\partial p_i}.$$
 (A.45)

and:

$$(\mathbf{v}_{\alpha} \times \mathbf{H}) \cdot \frac{\partial f_{\alpha}}{\partial \mathbf{p}} = \varepsilon_{ijk} (\mathbf{v}_{\alpha,j} H_k) \frac{\partial f_{\alpha}}{\partial p_i}, \tag{A.46}$$

where:

$$H_i(x_j) \to H_i(n_j);$$
 (A.47)

$$\frac{\partial H_i}{\partial x_j} = \frac{H_i(n_j + 1, m) - H_i(n_j - 1, m)}{2\Delta x};$$
(A.48)

$$v_{\alpha,i}H_j = \frac{p_i}{m_\alpha}H(n_j),\tag{A.49}$$

and the $\partial f_{\alpha}/\partial \mathbf{p}$ terms in Equations (A.45),(A.46) are discretized following Equation (A.38). The quantity $\mathbf{v}_0 \times \mathbf{H}$ is determined entirely from the first fluid.

We can group the factors into differential variable terms, and can then define the new values in terms of previously-determined values. We then compose an $N_x \times N_x$ matrix for each possible value of n_3, k_i at each time-step *m*. The method of generating and inverting these matrices is computationally intensive, and we will discuss run-times for our parallelized code later. With this goal in mind, we parametrize Equation (A.34) in terms of Equations (A.36)-(A.46), and define the terms:

$$A_i \equiv \frac{\gamma_\alpha p_i \Delta t}{2m_\alpha \Delta x},\tag{A.50}$$

$$B_1 \equiv \frac{\epsilon_{\alpha} \Delta t}{2\Delta p} \left[\frac{c}{4\pi\sigma} \left(\frac{\partial H_3}{\partial x_2} - \frac{\partial H_2}{\partial x_3} \right) + \frac{\gamma_{\alpha}}{cm_{\alpha}} (p_2 H_3 - p_3 H_2) - \frac{1}{c} (\mathbf{v}_0 \times \mathbf{H})_1 + \left(\frac{dp_1}{dt} \right)_{\text{coll}} \right], \quad (A.51)$$

$$B_2 \equiv \frac{\epsilon_\alpha \Delta t}{2\Delta p} \left[\frac{c}{4\pi\sigma} \left(\frac{\partial H_1}{\partial x_3} - \frac{\partial H_3}{\partial x_1} \right) + \frac{\gamma_\alpha}{cm_\alpha} (p_3 H_1 - p_1 H_3) - \frac{1}{c} (\mathbf{v}_0 \times \mathbf{H})_2 + \left(\frac{dp_2}{dt} \right)_{\text{coll}} \right], \quad (A.52)$$

$$B_{3} \equiv \frac{\epsilon_{\alpha} \Delta t}{2\Delta p} \left[\frac{c}{4\pi\sigma} \left(\frac{\partial H_{2}}{\partial x_{1}} - \frac{\partial H_{1}}{\partial x_{2}} \right) + \frac{\gamma_{\alpha}}{cm_{\alpha}} (p_{1}H_{2} - p_{2}H_{1}) - \frac{1}{c} (\mathbf{v}_{0} \times \mathbf{H})_{3} + \left(\frac{dp_{3}}{dt} \right)_{\text{coll}} \right].$$
(A.53)

Equation (A.34) can be rewritten in terms of A_i and B_i as:

$$2(\Delta t)\frac{\partial f_{\alpha}}{\partial t} + A_i\frac{\partial f_{\alpha}}{\partial x_i} + B_i\frac{f_{\alpha}}{\partial p_i} = 0, \qquad (A.54)$$

Which is discretized by Equations (A.36)-(A.46) and becomes the relations:

$$0 = f_{\alpha}(m+1) - f_{\alpha}(m) +A_{i}[f_{\alpha}(n_{i}+1,m+1) - f_{\alpha}(n_{i}-1,m+1) + f_{\alpha}(n_{i}+1,m) - f_{\alpha}(n_{i}-1,m)] (A.55) +B_{i}[f_{\alpha}(k_{i}+1,m+1) - f_{\alpha}(k_{i}-1,m+1) + f_{\alpha}(k_{i}+1,m) - f_{\alpha}(k_{i}-1,m)].$$

We know all values of f at m, and use them to solve for the unknown values of f at m + 1. We place all f at m on one side of the equation, and f at m + 1 at the other side. For particular values n_2, n_3, k_i , we can place the A_i values into a matrix, M, and we solve the equation:

$$\mathbf{MF} = \mathbf{D} \tag{A.56}$$

where:

$$\mathbf{F} = \begin{pmatrix} f_{\alpha}(0, n_{2}, n_{3}, k_{i}, m+1) \\ f_{\alpha}(1, n_{2}, n_{3}, k_{i}, m+1) \\ f_{\alpha}(2, n_{2}, n_{3}, k_{i}, m+1) \\ \vdots \\ f_{\alpha}(N_{x}, n_{2}, n_{3}, k_{i}, m+1) \end{pmatrix},$$
(A.57)

and:

$$\mathbf{D} = \begin{pmatrix} d_{\alpha}(0, n_{2}, n_{3}, k_{i}, m) \\ d_{\alpha}(1, n_{2}, n_{3}, k_{i}, m) \\ d_{\alpha}(2, n_{2}, n_{3}, k_{i}, m) \\ \vdots \\ d_{\alpha}(N_{x}, n_{2}, n_{3}, k_{i},) \end{pmatrix}.$$
(A.58)

The elements in **D** are:

$$d_{\alpha}(n_{i},k_{i},m) = A_{1}[f(n_{1}-1,m) - f(n_{1}+1,m)] + A_{i>1}[f(n_{1},n_{i}-1,m) - f(n_{1},n_{i}+1,m)] + B_{i}[f(k_{i}-1,m) - f(k_{i}+1,m)].$$
(A.59)

The matrix of coefficients, a sparse block-diagonal matrix, can be split into a tridiagonal component (M_0) and a block-diagonal component (M'):

$$\mathsf{M} = \mathsf{M}_0 + \mathsf{M}'. \tag{A.60}$$

The matrix M', though not necessarily tridiagonal, is still very sparse. The values of $f(0, k_i, m)$ and $f(N_x, k_i, m)$ for all values of *m* are boundary-values, and are defined as parameters. All values of $f(n_i, k_i, 0)$ are defined as initial conditions, where when $0 < n_i < N_x$, $f(n_i, k_i, 0) = 0$, and $f(0, k_i, 0)$ and $f(N_x, k_i, 0)$ are boundary conditions. The boundary values are defined, for $n_j = 0, N_x$:

1

$$b_i(k_i, m) = f_\alpha(n_i, k_i, m)_{n_i=0},$$
 (A.61)

$$b_{\rm f}(k_i, m) = f_{\alpha}(n_i, k_i, m)_{n_i = N_x}.$$
 (A.62)

The tri-diagonal matrix is:

$$\mathsf{M}_{0} = \begin{pmatrix} b_{\mathrm{i}} & A_{1} & 0 & \cdots & 0 \\ -A_{1} & 1 & A_{1} & \cdots & 0 \\ 0 & -A_{1} & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & b_{\mathrm{f}} \end{pmatrix}.$$
 (A.63)

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The block-diagonal matrix depends on all the other values, $n_{i>1}$, k_i , m, and different values will be populated depending on the value of these discrete variables. For example, if $n_2 = 0$, $n_3 = k_1 = 1$, $k_2 = k_3 = 2$ then:

$$\mathsf{M}' = \begin{pmatrix} 0 & -A_3 - B_1 & 0 & 0 & \cdots & 0 \\ A_2 & 0 & -B_2 - B_3 & 0 & \cdots & 0 \\ 0 & A_3 + B_1 & 0 & 0 & \cdots & 0 \\ 0 & 0 & B_2 + B_3 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 0 \end{pmatrix}.$$
 (A.64)

For each value n_2 , n_3 , k_i at time-step *m*, we determine a matrix M and solve the equation by inverting



Figure A.2: Flow-chart for the RBTE and ZEUS calculations.

the matrix. This brings Equation (A.55) to:

$$\mathbf{F} = \mathbf{M}^{-1}\mathbf{D}.\tag{A.65}$$

Once we have solved for all f at m + 1, we take $f(m + 1) \rightarrow f(m)$, and repeat the process for the next time-step. At the end of each time-step, we apply the distribution function f(m + 1) to the ZEUS code as an input to determine the cosmic ray current and charge-density, Equations (A.1) and (A.6). ZEUS is used to determine **H** for the next time-step, to update the A_i and B_i factors. This essentially makes these factors time-dependent. Figure A.2 gives a flow-chart for the steps in this calculation.

For the size of the box, $L \times L \times L$, we use L = 0.1 parsecs, which is somewhat large for a dense cloud. We take $N_x = N_p = 100$. We ideally calculate for time-steps necessary to reach a steady state, although the computational intensity of these calculations may limit the number of time-steps, as a practical problem. Given the box size and N_x , $\Delta x \approx 6 \times 10^{15}$ cm. The momentum-size, Δp corresponds to a ΔT , and has to span a range of many orders of magnitude. This is achieved, at some loss of accuracy, by determining ΔT logarithmically, based on the energy T at the given k_i . For protons this provides a minimum $T_p(k_i = 0) = 10$ eV. We reach a $T_p(k_i = N_p) = 10$ GeV. This leaves us ten momentum-steps for each order of magnitude. So, for $T_p = 1$ GeV, $\Delta T_p = 100$ MeV, and for protons.

The number of momentum-steps and position-steps leads to about 312 million (100×100) matrices to be inverted. Since, for our first-order Equation (A.34), the resulting matrices, M, are always tridiagonal, the inversion takes about 10^{-4} seconds of runtime, using one graphics processor core. We utilize a graphics card with 240 processor cores in parallelto invert these matrices quickly. We utilize the pycoda package for Python in order to efficiently parallelize the graphics card. The runtime for a single time-step then is ~ 70 minutes. The ZEUS code require about 30 minutes to solve for the magnetic field in our relatively simple plasma, so the total computational time for a single time-step is about 90 minutes. Therefore we can calculate the three-dimensional cosmic ray distribution for about 20 time-steps over the course of two days. Because this is too intensive to reach steady-state, we present here results for calculations reduced to two dimensions. We are hopeful that, with future access of a supercomputer, the three-dimensional calculations can be realistically undertaken, and three-dimensional solutions can be obtained for a variety of boundary conditions.

A.4 Results in terms of the Ionization Rate

It is useful for astrochemists, and also conceptually advantageous, to represent the two-dimensional results for the cosmic ray distribution in terms of a cosmic ray ionization rate, ζ which is the rate at which hydrogen atoms are ionized by cosmic rays. This can be achieved mathematically by converting the distribution function to a position-dependent flux-density as the number of particles per square centimeter per second entering the cloud, j(E). The direction into the cloud will here be represented as $\hat{\mathbf{n}}_{c}$, and:

$$j(E) dE = \left(\frac{f_p}{\gamma_p m_p} + \frac{f_e}{\gamma_e m_e}\right) \mathbf{p} \cdot \mathbf{\hat{n}_c} d^3 p.$$
(A.66)

To derive a position-dependent ionization rate from the flux-density, we use Equations 2.2-eqn:total. We performed the calculations for $f(x, y, p_x, p_y)$. For both calculations, the flux at the boundary is



Figure A.3: ζ as a function of depth into the cloud for an isotropic flux at the boundary from Nath & Biermann (1994) with a minimum energy of 1 MeV.

taken from Nath & Biermann (1994). For the first case, the flux is isotropic and there is a lowenergy cutoff for the initial flux-density of 1 MeV (of course, the flux density inside the cloud can extend down to 10 eV). In the second case, the initial flux extends down to 10 eV but impinges only on one side. The other side has the same initial flux-density, but with the 1 MeV cutoff.

For the first case, the cosmic ray ionization rate extends from about 7.5×10^{-17} s⁻¹ at the center to 2×10^{-16} s⁻¹ at the edges. This difference is too small to accurately detect, given that chemical tracers are the best current way to determine the cosmic ray ionization rate, and are accurate only to within a factor of 2 or 3 (see McCall et al. 2003; Indriolo et al. 2007; Le Petit et al. 2006, for a review). In the second case, however, the ionization rate spans two orders of magnitude, and should definitely be within detection capability, provided that sources can be found near the sites of cosmic ray production and with angular resolution capable of achieving length-scales of about 10-100 AU.



Figure A.4: ζ as a function of depth into the cloud for an isotropic flux at the boundary from Nath & Biermann (1994) with a minimum energy of 1 MeV on the right side, and 10 eV on the left side.

A.5 Discussion and Future Work

To more thoroughly examine the ionization of cosmic rays, we need to treat electrons as well as protons. The cross-sections have already been included in the code, and the electron cosmic ray streaming will be calculated simultaneously with the proton cosmic rays as a logical next step. Eventually turbulence and self-gravitation will be incorporated in the calculations.

There are many other questions such a model may answer beyond the cosmic ray ionization rate, such as what are the dominant magnetic effects on low energy cosmic rays. Candidates include magnetic mirroring (discussed in Cesarsky & Volk 1978), Alfvén weaves (Skilling & Strong 1976), and gravitational and turbulence-driven effects. Eventually, Fermi acceleration and shock-driven acceleration will be added to the model, so that the origin and range of these low energy cosmic rays can be theoretically explored.

The main problem that this code addresses now is the question of the cosmic ray ionization rate, and why it has the value that it does, connecting it with a flux-spectrum that depends on cloud geometry, composition, and physical properties like density and electromagnetic properties. At the end of his 2006 review, Alex Dalgarno stated that "The interesting question may be not why are [cosmic ray ionization rates] so different but why are they so similar" (Dalgarno 2006). The preliminary results of this study suggest that a combination of geometry and magnetic field effects may provide the answer to both questions.