STRUCTURE AND EXCITON COUPLING
IN JET-COOLED BICHROMOPHORES

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ABSTRACT

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The spectroscopy and exciton coupling in a series of conformationally flexible bichromophoric molecules have been investigated in a supersonic jet. The investigated molecules are: 1,2-diphenylethane (DPE), 1,2-bis(4-methylphenyl)ethane (M2DPE), 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (THDC), cis and trans isomers of 1,2-diphenylcyclopropane (DPCP), 2-phenylindane (2PI), and 2-(4-fluorophenyl)indane (2FPI). Resonant enhanced two-photon ionization (R2PI) spectra of these compounds and many of their deuterated isotopomers have been recorded for the first time. The observed spectral features have been assigned. The experimental results are compared with the predictions of the dipole-dipole based Förster theory, and the supramolecular model of bichromophoric molecules with identical chromophores.

Analysis of the experimental data is facilitated by the spectral analysis of the single chromophore analogues of the investigated bichromophoric molecules. These include ethylbenzene-d0, α-ethylbenzene-d1, cis and trans isomers of 1-methyl-2-phenylcyclopropane, and 2-methylindane.

The molecular structures and other properties of the investigated molecules in their ground and exited singlet states have been computed at various levels of theory. The calculations predict energetic preference of localized electronic excitation of most of the investigated molecules, suggesting weak inter-chromophore interactions in the excited states. Transition density surfaces indicate that the lowest excited singlet states of most of the investigated molecules have Lb ππ* character.

Two conformers of DPE, M2DPE, THDC, and 2-methylindan have been observed. The rest of the investigated molecules are found to exist in a single conformation. The S2 ← S0 transitions of both anti and gauche conformers of DPE, the anti conformer of M2DPE, the chair
conformer of THDC, and the trans isomer of DPCP are forbidden. However, the $S_2 \leftarrow S_0$ transitions of the asymmetrically deuterated isotopomers are observed, which allows for the estimation of the exciton splittings in these bichromophores.

The exciton splittings are ca. three times higher in the more compact $C_2$ symmetric gauche conformers of DPE and $M_2$DPE than in the $C_{2h}$ symmetric anti conformers. The experimental exciton splittings of DPE conformers are higher than those of the corresponding $M_2$DPE conformers. Dipole-dipole based Förster theory predicts higher splittings in $M_2$DPE conformers, and incorrect ordering of the excited states of the anti conformers of DPE and $M_2$DPE. The exciton splitting in the $C_2$ symmetric twist-boat conformer of THDC is seven times higher than that of the $C_{2h}$ symmetric chair conformer. The exciton splittings in THDC conformers are substantially larger than those of the structurally similar conformers of DPE and $M_2$DPE.

Experimental evidence is provided in support of the conjugated nature of cyclopropyl ring. The trans isomer of DPCP has $C_2$ symmetry. The spectrum of trans-DPCP is devoid of $6a^1$ and $6b^1$ like transitions. The cis isomer of DPCP is asymmetric. The $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of cis-DPCP are localized on the bisected and perpendicular phenyl rings, respectively. The $S_2 \leftarrow S_0$ minimum is calculated to lie just 60 cm$^{-1}$ below the transition state along the phenyl torsional coordinates; hence, $S_2 \leftarrow S_0$ vibronic transitions are not observed in the spectrum of cis-DPCP. The $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of 2PI and 2FPI are found to be completely localized on the ortho-xylyl and phenyl (4-fluorophenyl) chromophores, respectively.
This dissertation is dedicated to my relatives, friends, and neighbors.
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INTRODUCTION

The major objectives of this work are to study the structure and intramolecular exciton coupling in a series of conformationally flexible bichromophoric molecules. The investigated compounds contain identical or nearly identical chromophores, and are closely related to 1,2-diphenylethane (DPE). All correspond to the case of two chromophores with small transition dipole moments and at small interchromophore separation.

Supersonic jet techniques coupled with resonant-enhanced two-photon ionization spectroscopy are employed to obtain mass-selective vibrationally resolved electronic spectra of the isolated molecules. Analysis of the spectra provides information about the structures and relative populations of the ground state conformations, structural changes that occur upon electronic excitation to the excited singlet states, and exciton couplings. The spectra of selectively deuterated bichromophores often provide an unambiguous assignment of the observed spectral bands to electronic origins and vibrational modes. Therefore, synthesis of various deuterated isotopomers of the bichromophores is an integral part of this work.

Ab initio computations of the ground and excited electronic states of the investigated bichromophoric molecules provide information about the equilibrium geometries of the molecules in their ground and excited singlet states, relative stabilities of various conformations, vibrational frequencies, vertical and adiabatic electronic excitation energies, transition dipole moments, transition densities, electronic coupling energies, etc. The experimental results are compared with the predictions of electronic structure calculations and theoretical models of exciton coupling.
CHAPTER 1. BACKGROUND AND RESEARCH METHODOLOGIES.

1.1. Electronic energy transfer

Electronic energy transfer (EET) is a process whereby an electronically excited chromophore (energy donor) transfers its excitation energy to another chromophore (energy acceptor) at a finite rate. The energy donor and the acceptor may be identical or different chromophores, and may or may not be connected by a bridge. EET occurs in condensed and gas phases at a wide range of inter-chromophore distances (1 Å to more than 50 Å), and on timescales from femtoseconds to milliseconds.\(^1\)\(^2\) EET plays a very important role in photosynthesis wherein the light energy absorbed by plants is transmitted to the reaction centers to initiate photosynthesis.\(^3\) The working mechanism of several organic light emitting diodes and other optoelectronic devices is based on EET between different segments of the active materials.\(^4\) EET is the basis of the so-called spectroscopic ruler used to measure distances between different chromophores in biological systems.\(^5\)

Some of the experimental manifestations of EET in bichromophoric molecules with non identical chromophores include: observation of acceptor-like emission upon photoexcitation of the donor chromophore, broadening of the absorption bands, and reduction of the excited state lifetime of the donor chromophore.\(^1\)\(^2\)\(^6\)\(^7\) EET in bichromophoric molecules with identical chromophores is manifested by exciton splittings and/or shifts of the absorption bands of a bichromophore when compared with the absorption bands of the individual chromophores (monomers).\(^8\)\(^13\) This dissertation mostly focuses on the less studied bichromophoric molecules (dimers) with identical chromophores.
EET is mediated by electronic interactions between the excited donor and acceptor chromophores. The electronic coupling energy, $V$, is the measure of these interactions. The rate constant for EET in bichromophoric molecules with non identical chromophores is proportional to $V^2$.

**1.2. Exciton Coupling**

Electronic interactions in the excited states of bichromophoric molecules are conveniently categorized into three cases. In the strong coupling case, the electronic coupling energy is larger than the reorganization energies (frequencies of intramolecular vibrations) of the excited chromophores. In this case the electronic excitation energy is delocalized over the entire bichromophoric molecule. The electronic coupling energy is comparable to the frequencies of intramolecular vibrations in the intermediate coupling case. In the weak coupling case, the electronic coupling energy is substantially smaller than the reorganization energies of the excited chromophores. The electronic excitation energy is thus essentially localized on a single chromophore. Experimental determination of exciton splittings in weakly coupled bichromophoric molecules requires high spectral resolution because of the small magnitudes of the electronic coupling energies. This dissertation focuses on weakly coupled bichromophoric molecules.

In the weak coupling case, the excited vibronic states of bichromophores incorporating two identical chromophores, $A$ and $B$, are formed by the exciton interactions of two chromophore localized vibronic states, $\phi_A^\ast \chi^\ast(Q_A)\phi_B^0 \chi_\omega^0(Q_B)$ and $\phi_B^\ast \chi_\omega^\ast(Q_B)\phi_A^0 \chi^0(Q_A)$, and described by the wavefunction, 

$$\phi_\pm = c_A \phi_A^\ast \chi^\ast(Q_A)\phi_B^0 \chi_\omega^0(Q_B) \pm c_B \phi_B^\ast \chi_\omega^\ast(Q_B)\phi_A^0 \chi^0(Q_A) \quad (1.1)$$
where $\phi_A$ and $\phi_B$ are the chromophore localized electronic wavefunctions, $\chi_r(Q_A)$, and $\chi_{\omega}(Q_B)$ - are the chromophore localized vibrational wavefunctions, $c_A$ and $c_B$ are constants that depend on nuclear coordinates, and reflect the contribution of chromophore localized vibronic states to the formation of exciton states. If the interactions involve degenerate vibronic states of identical chromophores, then $c_A = c_B = 1/\sqrt{2}$, and the vibronic excitation is equally shared (delocalized) by the two chromophores. As the degeneracy of the chromophore localized vibronic states is lifted, $c_A$ and $c_B$ will have different values. Complete localization occurs when $c_A = 0$ and $c_B = 1$ or $c_A = 1$, and $c_B = 0$.

A sketch of the excited state potential energy surface of a weakly coupled bichromophoric molecule (dimer) with identical chromophores is displayed in Figure 1.1. The first excited singlet state is characterized by a double-minimum potential energy surface; the minima of which correspond to the global minimum geometries of the locally excited chromophores. Each degenerate pair of monomer localized vibronic states splits into two exciton states. The spectroscopically accessible exited states are delocalized vibronic states that spread over the two identical chromophores. The observed exciton splitting, $2V_{vv}$, of the vibronic bands is composed of the purely electronic and vibrational components. The vibrational component is determined by the Franck-Condon factor of the vibronic transition (FC$_{vv}$).
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The electronic component, $V$, is composed of terms describing the Coulombic, exchange, and through-bond mediated interactions of the interacting chromophores.\textsuperscript{1, 2, 11-13, 17-21} The electronic component, $V$, can be estimated from the experimental data using equation 1.2.

$$V = \frac{V_{vv}}{FC_{vv}} \quad (1.2)$$

The excitation energies of two exciton states that are formed by the coupling of the lowest vibronic states of two equivalent chromophores, $A$ and $B$, are: $E_{S_1} = E_{0A} - V_{00}$, and $E_{S_2} = E_{0A} + V_{00}$. $E_{0A}$ is the $0^0$ transition energy of the equivalent chromophores ($E_{0A} = E_{0B}$), the exciton splitting is equal to $2V_{00}$. However, if the two chromophores are not equivalent (assuming $E_{0A}$ is greater than $E_{0B}$ by $\delta$), i.e. $E_{0A} - E_{0B} = \delta$, then, the energy gap between the two exciton states, $\Delta E$, is given by:\textsuperscript{22, 23}

$$\Delta E = \sqrt{\delta^2 + 4V_{00}^2} \quad (1.3)$$

Coulombic interactions between the transition charge densities of the interacting chromophores do not require overlap of the electronic wavefunctions of the donor and the acceptor chromophores; therefore, they are operative at all distances.\textsuperscript{1, 2, 18} The electronic matrix element for Coulombic interactions, $V_{Col}$, is often expanded in a multipole series.

$$V_{Col} = V_{d-d} + V_{d-q} + V_{d-o} + V_{q-o} + \ldots \ldots \quad (1.4)$$

The first term of the expansion, $V_{d-d}$, accounts for the interaction between the transition dipole moments of the chromophores. Forster theory is solely based on the dipole-dipole part of the multipole expansion. The dipolar coupling energy, $V_{d-d}$, depends on the magnitudes of the transition dipole moments of the interacting chromophores ($\mu_1$ and $\mu_2$), their relative orientations as determined by the orientation factor, $\kappa$, and also on their center-to-center distance, $R$.\textsuperscript{1}
\[ V_{d-d} = \frac{\mu_1 \mu_2}{R^3} \kappa \]  

(1.5)

\[ \kappa = 2\cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos\varphi \]  

(1.6)

The geometrical parameters, \( R, \theta_1, \theta_2 \) and \( \varphi \) are defined in Fig. 1.2. For bichromophores with identical chromophores, such that \( \mu_1 = \mu_2 \), \( V_{d-d} \) can be expressed in terms of the oscillator strength, \( f \), and the transition energy, \( v_0 \), of the individual chromophores (monomers).\(^{11}\)

\[ V_{d-d} = \frac{(1.070685 \times 10^{10}) f}{v_0 R^3} \kappa \]  

(1.7)

\textbf{Figure 1.2} Definitions of the geometrical parameters used for calculating the orientation factor, \( \kappa \), equation 1.6.

The transition dipole moments (TDMs) for the \( S_1 \leftarrow S_0 \) and \( S_2 \leftarrow S_0 \) electronic transitions of a bichromophoric molecule are derived from the in-phase and out-of-phase vector sum of the
monomer $S_i \leftarrow S_0$ transition dipole moments, $\mu_i$ and $\mu_2$. The relative intensities of the $S_i \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions can be expressed in terms of the geometrical parameters, $\theta_1, \theta_2$ and $\varphi$.

$$\frac{I_{S_i}}{I_{S_2}} = \frac{\sqrt{((\cos\theta_1 - \cos\theta_2)^2 - (\sin\theta_1 + \sin\theta_2 \cos\varphi)^2 + (\sin\theta_1 \sin\varphi)^2)}}{\sqrt{((\cos\theta_1 + \cos\theta_2)^2 - (\sin\theta_1 + \sin\theta_2 \cos\varphi)^2 + (\sin\theta_2 \sin\varphi)^2)}}$$  (1.8)

The extreme cases of the dipole-dipole interactions in symmetric bichromophoric molecules (dimers) occur when the two transition dipoles are coplanar and parallel or perpendicular to one another as shown in Figure 1.3. In the case of parallel displaced orientations of two coplanar localized transition dipoles (Figure 1.3a), the dipolar coupling destabilizes the in-phase combination of the transition dipoles. Hence, only the $S_2 \leftarrow S_0$ transition is one-photon allowed, as the out of phase combination is zero. J-aggregates are typical examples of parallel displaced bichromophores, their absorption bands are shifted to the blue of the absorption bands of the individual chromophores. H-aggregates belong to the second case, here the coplanar transition dipoles are in head to tail orientation (Figure 1.3b). The in-phase combination of the dipoles is stabilized. Therefore, the $S_0 \rightarrow S_1$ transition is one photon allowed, while the $S_0 \rightarrow S_2$ transition is forbidden. The last extreme case of the dipole-dipole interactions occurs when two coplanar transition dipoles are perpendicular to one another (Figure 1.3c). This results in $V_{d-d} = 0$; hence, no exciton splitting will be observed at all.

Forster theory has been very successful in describing EET and exciton coupling in several bichromophoric systems; it even forms the basis of the spectroscopic ruler. However, several investigations have shown the failure of the theory to describe electronic interactions at very close inter-chromophore separations, and also in the case of very weak and forbidden electronic
transitions.\textsuperscript{2} Better results could be obtained by taking into account the higher multipole terms of equation 1.4, exchange and through-bond coupling energies.\textsuperscript{1, 11, 19, 26}

Dexter exchange interactions originate from the requirement that a wavefunction must be antisymmetric when two electrons are exchanged. Exchange interactions require overlap of the electronic wavefunctions of the interacting chromophores, and decay exponentially with inter-chromophore distance.\textsuperscript{2, 21} Exchange interactions are usually important in the case of very weak and forbidden electronic transitions (e.g. triplet-triplet EET), and also at very small inter-chromophore distance.\textsuperscript{2, 20, 21}

EET and exciton coupling in aromatic bichromophores can also be mediated by the aliphatic bridge between the aromatic chromophores.\textsuperscript{1, 2, 11, 19, 20, 26} Through-bond mediated interactions also decay exponentially with the number of bonds in the bridge, and decreases with increase in the energy gap between chromophore localized $\pi (\pi^*)$ orbitals and the bridge localized $\sigma (\sigma^*)$ orbitals.
Figure 1.3 Dipole-dipole interactions in symmetric bichromophores (dimers).
Both through-space (Coulombic and exchange) and through-bond interactions contribute collectively to the total electronic coupling energies. However, the coupling mechanisms reinforce or oppose each other depending on their signs; for example, Coulombic and exchange coupling terms usually have opposing signs. Clearly, there exists a strong dependence of the electronic coupling energy on the molecular structures of bichromophoric systems, regardless of which mechanisms dominate the coupling. Most of the research work on EET and exciton coupling is performed in condensed phases where solvent and crystal lattice effects, as well as possible interactions between several neighboring chromophores often make it difficult or impossible to explore structure-electronic coupling energy relationship. These problems can be avoided by performing the experiments in a supersonic jet using covalently linked bichromophoric molecules with well defined structures.

1.3 The lowest excited electronic states of benzene derivatives.

According to the Platt’s notation, the lowest excited electronic states of benzene and its derivatives are usually called \( L_b \) and \( L_a \) states. The transition densities from the ground state of aromatic chromophores to the \( L_b \) and \( L_a \) states are located on bonds and atoms, respectively. The \( L_b \) state of benzene and its derivatives is lower in energy (\( S_1 \) state); the \( S_2 \) state is \( L_a \). The energy gap between the two states is ca. 9000 cm\(^{-1}\). The surfaces of the transition densities for the \( S_1 \leftarrow S_0 \) and \( S_2 \leftarrow S_0 \) transitions of benzene and toluene are depicted in Figure 1.4.

The six fold symmetry of benzene causes complete cancellation of the transition densities for the \( S_1 \leftarrow S_0 \) and \( S_2 \leftarrow S_0 \) transitions of benzene. Therefore, electronic transitions from the ground state to the lowest excited states of benzene are electric dipole forbidden. However, these states gain their intensities as a result of vibronic coupling with the higher excited states.
Cancellation is not complete in most benzene derivatives such as toluene because of the lowered symmetry. Hence, the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions are electric dipole allowed. The cancellation is more profound for the $L_b$ states. Therefore, the $L_b$ states have substantially lower oscillator strength than the $L_a$ states. The transition dipole moments for the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of benzene derivatives that have an axis or plane of symmetry about the point of substitution are polarized along the long and short molecular axes, respectively.\textsuperscript{27-29} The orientations of the transition dipole moments for the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of toluene are illustrated in Figure 1.4e and 1.4f. As with most alkylbenzenes, the $L_b$ state is polarized along the short axis; the $L_a$ state is polarized along the long axis.
Figure 1.4 Transition density surfaces for the: (a) $S_1 \leftarrow S_0$ transition of benzene, (b) $S_2 \leftarrow S_0$ transition of benzene, (c) $S_1 \leftarrow S_0$ transition of toluene, and (d) $S_2 \leftarrow S_0$ transition of toluene. The orientations of the transition dipole moments for the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of toluene are shown in (e) and (f), respectively.
1.4 Isotope effect

According to the Born-Oppenheimer approximation, vibrational and electronic wavefunctions are independent; hence isotopic substitution has no effect on electronic structure. In this work an isotope effect is used to assign the electronic origins of different conformers, exciton states, and vibrational modes. In the harmonic oscillator model, the frequency of a vibrational mode, $\nu$, is calculated according to equation 1.9.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (1.9)$$

The reduced mass, $\mu$, increases upon deuteration. The force constant, $k$, is invariant to deuterium substitution, but depends on the strength of the chemical bonds that are associated with the vibrational mode. Therefore, replacement of hydrogen atoms with deuterium atoms leads to the decrease in the frequencies of all vibrational modes involving the substituted hydrogen atoms. This leads to the decrease in the zero point energies of the ground and excited electronic states. The $C_{sp2}-C_{sp2}$ bond length of aromatic compounds increases by about 0.003 Å upon photoexcitation to the $S_1$ state. The force constants are therefore, smaller than in the $S_1$ state. This leads to the blue-shift of the electronic origins of aromatic compounds upon deuteration. For example, the electronic origins of p-toluene-$d_1$ and toluene-$d_5$ are blue-shifted by 30.7 cm$^{-1}$ and 165.9 cm$^{-1}$, respectively.

Reliable assignment of vibronic transitions of bichromophoric molecules to electronic origins can be very difficult and ambiguous because transitions to some of the close lying excited states are often symmetry forbidden. The best way of spectral analysis is by comparison with the spectra of selectively deuterated isotopomers of the investigated bichromophores. At least one of the isotopomers must be of lower symmetry, thereby rendering the forbidden transitions of the
symmetric isotopomers weakly (or sometimes strongly) allowed, depending on the size of the perturbation introduced by the asymmetric deuteration.\textsuperscript{10, 14, 22, 25, 32, 33}

It has been reported that isotopic substitution has much higher effect on the frequencies of vibronic transitions than on the relative $0_0$ transition energies of conformers.\textsuperscript{34} Therefore, electronic origins of conformers can be distinguished from vibronic bands based on the observed isotope effects. A conclusion about the molecular symmetry of bichromophoric molecules can be drawn by spectral analysis of asymmetrically deuterated isotopomers. This strategy is extensively used in this work to assign transitions of the gauche and anti conformers of DPE. The same strategy is used to assign the symmetries of the investigated bichromophoric molecules.

1.5 Electronic spectroscopy in supersonic jets

Supersonic jet laser spectroscopy is one of the most powerful techniques for studying the structure and dynamics of molecules in the gas phase.\textsuperscript{35, 36} In a supersonic jet, molecules are cooled to their lowest vibrational states in the ground electronic state. This ensures that all electronic transitions are from the zero point energy level of the ground state. Thermal broadening of spectral bands is effectively eliminated. The fact that molecules are cooled to as low as 1K in a supersonic jet allows one to investigate instable and rapidly inter-converting species such as clusters and conformers.\textsuperscript{35, 36}

Electronic spectroscopy in supersonic jets involves interaction of the jet-cooled molecules with electromagnetic radiation energetic enough to excite the molecules to their excited electronic states. Many molecules fluoresce upon electronic excitation; a fluorescence
excitation and dispersed fluorescence spectra can be recorded by detecting the total and dispersed fluorescence, respectively.\textsuperscript{36}

By applying a relatively high laser power, the electronically excited molecule can also absorb another photon to form a molecular ion. In other words the first photon is used to excite the molecule to the excited electronic state, and the second photon is used to softly ionize the excited molecule. This can only happen if the ionization energy of the molecule is lower than the energy of two photons. Electronic spectrum is obtained by recording the number of molecular ions (ion current) as a function of the excitation laser energy. The obtained spectrum is called one color resonant-enhanced two-photon ionization spectrum, often abbreviated as \((1+1)\) R2PI or simply R2PI spectrum. If the ionization energy of the molecule is higher than the energy of the two photons, the excitation and the ionization photons must differ in energy, and the resulting spectrum is called two color resonant-enhanced two-photon ionization (R2PI) spectrum.\textsuperscript{36}

One color, resonant-enhanced two-photon ionization (R2PI) detection is used in this work because the ionization potentials of the investigated molecules are less than twice the electronic excitation energies to their lowest singlet states. R2PI technique has the additional advantage of mass selectivity, which allows one to obtain clean spectra, free from clusters and impurities. Spectra of several compounds can be obtained from the same sample.

The schematic diagram of the supersonic jet spectrometer is shown in Figure 1.5. The third harmonic (355 nm, 10 ns) of a Q-switched Nd:YAG laser operating at 10 Hz repetition rate is used to pump a dye laser. Both coumarin 500 and coumarin 540 A laser dyes are used to cover the spectral region of interest. Tunable UV laser photons (250-280 nm) are generated by frequency doubling of the output of the dye laser in a KDP crystal.
The molecular beam apparatus is composed of two differentially pumped expansion and ionization chambers. The ionization chamber houses the time of flight mass spectrometer. The required vacuum of about $10^{-3}$ Torr is achieved in the expansion chamber by using a 9-in. vapor diffusion pump. The required high vacuum ($\sim 10^{-7}$ Torr) in the ionization chamber is achieved by using a liquid nitrogen trap 6-in. diffusion pump.

The sample source is located inside the expansion chamber. Small amount of sample placed on a piece of cotton inside the sample holder is heated by an electric heater in order to increase the vapor pressure of the sample. The temperature of the sample holder is monitored with a thermocouple. The heated sample is seeded in a monoatomic carrier gas (helium, argon or neon) at 1 – 3 atm, and then expands into the expansion chamber from a 1-mm pulsed nozzle. The gas pulses are produced by a pulse valve of varying duration. Delay generator is used to synchronize the events of valve opening and laser firing. The desired degree of cooling is usually achieved by varying the delay time between pulsed valve opening and Nd:YAG laser firing.

The free jet in the expansion chamber is skimmed by a 1-mm skimmer, and the resulting molecular beam in the ionization chamber is perpendicularly crossed by a frequency doubled, Nd:YAG pumped dye laser beam. The first absorbed photon resonantly excites the isolated cold molecule to the first excited singlet state, absorption of the second photon by the excited molecule leads to the soft ionization of the excited molecules. The molecular ions produced are then detected and mass analyzed using a time of flight mass spectrometer. R2PI spectra are obtained by scanning the dye laser at a
Figure 1.5 Schematic diagram of the supersonic jet spectrometer used in the present work.
sweep rate of 0.01-0.1 Å/s. R2PI spectra are measured using a boxcar integrator interfaced with a computer.

Analysis of the obtained vibrationally resolved electronic spectra can be very difficult and ambiguous. The analysis is facilitated by comparison with the spectral features of closely related isotopically labeled molecules, and electronic structure calculations.

1.6 Jet spectroscopy of bichromophores with identical chromophores

Several bichromophoric systems (covalently linked dimers, hydrogen bonded dimers, and vander Waals dimers) have been studied in a supersonic jet with different goals. Oftentimes, the main purpose of these studies is to obtain information about the ground state structures of vander Waals and hydrogen bonded dimer. These include benzene dimer,$^{10,22,33}$ anthracene dimer,$^{37}$ p-aminobenzoic acid dimer,$^{38}$ anthranilic acid dimer,$^{15}$ etc. In most cases the structures of the dimers are proposed by analyzing the magnitude of the observed exciton splittings, and the relative intensity of the two exciton states that result from the electronic coupling of two monomeric excited states. The analysis is facilitated by recording the electronic spectra of at least two selectively deuterated dimers, one of which is asymmetrically deuterated. For example, Schlag et al. and Bernstein et al. proposed different geometries of benzene dimer by analyzing the spectra of three isotopomers of the dimer (d₀-d₀, d₀-d₆, and -d₆-d₆)$^{10,22,33}$

Another purpose of investigating bichromophoric systems is to characterize their lowest excited singlet states. The excited state of a bichromophore is usually regarded as being localized on one chromophore if the electronic coupling energy is very small, such that a small perturbation introduced by replacing one or more hydrogen atoms with deuterium atoms will lead to two localized vibronic transitions.$^{10,22,23,25,32,35}$ Delocalized excited state is characterized
by the similar appearance of the electronic spectra of symmetrically and asymmetrically
deuterated isotopomers of a bichromophore. Sakota et al. recently studied the electronic spectra
of several deuterated isotopomers of 7-azaindole dimer,32 two electronic origins were observed
in the spectra of some of the singly deuterated isotopomers that are assigned to the localized excitation of the deuterated and undeuterated halves of the dimers; it was thus concluded that 7-
azaindole dimer is weakly coupled dimer. The electronic excitation energy in 2-pyridone dimer
was found to be delocalized over the two chromophores because it was not possible to assign any peak to the electronic origin of either the deuterated or undeuterated half of the asymmetrically deuterated dimer.23 The spectrum of the asymmetric dimer is slightly different from those of the symmetric dimers owing to the symmetry lowering, which renders some forbidden transitions (including the $S_0 \rightarrow S_1$ origin) in the symmetric dimers weakly allowed.

The work of Levy et al. on spirobifluorenes reveals the absence of electronic couplings in
spirobifluorenes because of the perpendicular relative orientations of the monomeric transition
dipole moments.25 All vibronic bands in the spectrum of 9,9'-bifluorenyl appear as doublets
because of the exciton interactions between the two fluorene units.16 The splittings are found to be proportional to the Franck-Condon factors of the corresponding vibronic transitions in the spectrum of fluorene.

1.7 Electronic structure calculations

All methods of electronic structure calculations are based on the approximate solutions of
the Schrödinger equation, $H\Psi = E\Psi$. Presently, a large number of computational methods are
implemented in many software packages. The choice of a suitable method is dictated by the required accuracy of the computed data, and the availability of computational resources.

Hatree-Fock self consistent field method (HF) is the simplest and cheapest ab initio electronic structure method for treating molecules in their ground states. Very good geometries and vibrational frequencies are often obtained from HF calculations. However, HF method doesn’t yield satisfactory results if non-bonded dispersion interactions play an important role in determining molecular structure.\(^\text{39}\)

Configuration interaction singles (CIS) method is a version of HF method, designed for the excited electronic states.\(^\text{40}\) CIS often predicts very accurate geometries and frequencies of valence excited states of electronically excited aromatic molecules.\(^\text{41}\) The $C_{\text{sp2}}-C_{\text{sp2}}$ bond lengths in benzene are predicted to increase by 0.0028 Å in the CIS optimized $S_1$ state when compared with the HF optimized $S_0$ values. This result is consistent with what was obtained from the Franck-Condon analysis of the vibronic bands in the absorption spectrum of benzene, and also from the analysis of the rotationally resolved electronic spectrum of benzene.\(^\text{30}\) Both experimental approaches indicate that the $C_{\text{sp2}}-C_{\text{sp2}}$ bond lengths increase by ca. 0.0035 Å upon excitation to the $S_1$ state. The CIS predicted geometry of phenylacetylene is essentially similar to that predicted by the more advanced CASSCF method.\(^\text{42}\)

Besides structural information, other important computational observables relevant to this work are the transition charge densities and the corresponding transition dipole moments. The transition dipole moments as predicted by the CIS method are not expected to be quantitatively accurate because CIS method doesn’t obey the Thomas-Reiche-Kuhn dipole sum rule, which states that the sum of transition dipole moments must be equal to the number of electrons.\(^\text{40}\) However, analyses of the rotationally resolved electronic spectra of several derivatives of
benzene have shown that the CIS predicted orientations of transition dipole moments are often very accurate.\textsuperscript{43} The orientation of transition dipole moment is conformation-dependent; hence, electronic spectra of conformationally flexible molecules are often analyzed with the support of the CIS computations.\textsuperscript{43}

The major drawback of both HF and CIS methods is lack of electron correlation, the consequence of which includes: the failure of the HF method to treat non-bonded interactions,\textsuperscript{39} overestimation of vibrational frequencies by both HF and CIS methods,\textsuperscript{48} and overestimation of the electronic excitation energies by the CIS method.\textsuperscript{40}

The other commonly used electronic structure methods that somehow include electron correlation are the density functional theory (DFT), and the second-order Møller–Plesset perturbation (MP2) methods. DFT calculations are generally faster than MP2 calculations. However, DFT methods do not treat non-bonded dispersion interactions well.\textsuperscript{44, 45} Several functionals are being developed, the hybrid Becke-3–Lee–Yang–Parr (B3LYP) is one of the most popular functionals today.\textsuperscript{45} MP2 method often overestimates conjugation,\textsuperscript{46} and often predicts conformational relative energies that are opposite to the predictions of the HF and DFT methods.\textsuperscript{47} MP2 method gives very good description of hydrogen-bonded and vander Waals clusters.\textsuperscript{44}

Most electronic structure methods overestimate vibrational frequencies owing to the neglect of anharmonicity, lack of electron correlations, and the use of finite basis sets. Therefore, the calculated frequencies are often scaled before comparison with the experimental data is made. The scaling factors are available in the literature.\textsuperscript{48}

In the present work, extensive electronic structure calculations were performed at the HF, MP2, DFT(B3LYP), and CIS levels of theory as implemented in Gaussian 98 and Gaussian 03
suites of programs. The default convergence criteria for optimizations and single point energy calculations were employed.

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CHAPTER 2. CONFORMATION-DEPENDENT EXCITON COUPLINGS IN 1,2-DIPHENYLETHANE AND 1,2-BIS(4-METHYLPHENYL)ETHANE

2.1 Introduction

1,2-Diphenylethane (DPE) plays an important role in the development of fossil fuel processing technologies, serving as a model compound for methylene connecting links between aromatic segments of coal and other fossil materials. The structure of DPE has been the subject of several investigations. Ab initio calculations of DPE at various levels of theory with different basis sets predict that the anti and gauche conformers are the only two stable conformers. The HF and DFT geometries of each conformer are essentially the same. The anti conformer is 2.5 – 3.6 kJ/mol lower in energy than the gauche conformer at the HF and DFT levels. However, high level correlated computations (MP2, MP3, MP3, MP4) predicted a more stable, by 0.6 – 6.5 kJ/mol, gauche conformer. Analysis of the gas phase electron diffraction data of DPE reveals the predominance (85 %) of the anti conformer. X-ray studies show that only the anti conformer is present in the crystal. The presence of the anti conformer in the crystal was also confirmed by IR and Raman spectroscopy. In the liquid phase, the anti conformer was found to be more stable (2.5 ± 0.5 kJ/mol) than the gauche conformer by measuring the temperature dependence of the relative intensities of two band pairs in the liquid phase Raman spectra. The two band pairs were assigned to the anti and gauche conformers, respectively.

DPE is a typical example of bichromophoric molecules with identical chromophores. The two phenyl chromophores are linked by ethylene bridge. McClure studied the electronic spectrum of DPE at low temperature in a crystal, and found no exciton splitting of the electronic origin. However, four peaks of equal intensity in the region of the $6a_0^1$ and $6b_0^1$ transitions of
toluene were observed. By analyzing the four peaks, he predicted an exciton splitting of $45 \pm 14$ cm$^{-1}$ in DPE. It should be noted that McClure’s analysis is for the anti conformer. The fact that the absorption spectra of DPE and toluene exhibit similar vibronic structure suggests that DPE can be treated as a weakly coupled dimer of toluene.$^{7,8}$ Therefore, the absorption spectrum of DPE can be analyzed within the framework of the weak coupling regime of exciton theory.$^{8}$

The major aims of this work were to investigate the conformational preferences of DPE, and the exciton coupling of the lowest excited singlet states of DPE, under the isolated conditions of supersonic expansions. In order to accomplish these tasks, eight deuterated isotopomers of DPE have been synthesized. Mass selective vibrationally resolved electronic spectra of DPE isotopomers have been analyzed with the support of ab initio calculations. The substituent effects on the exciton coupling have been investigated by analyzing the spectra of 1,2-bis(4-methylphenyl)ethane (M$_2$DPE) and two deuterated isotopomers of M$_2$DPE. The structures of the investigated isotopomers of DPE and M$_2$DPE are shown in Figure 2.
Figure 2.1 Investigated isotopomers of DPE and M₂DPE.
2.2 Experimental

2.2.1 Synthesis

**DPE-d\textsubscript{0}**

Most of the isotopomers of DPE and M\textsubscript{2}DPE were synthesized by Wurtz coupling of the appropriate deuterium labeled benzylbromides and benzylbromide-d\textsubscript{0}.\textsuperscript{17} The typical procedure of Wurtz coupling is described for the synthesis of DPE-d\textsubscript{0}. Benzylbromide-d\textsubscript{0} (10 mmol) and CuCl\textsubscript{2} (1 mmol) were dissolved in a mixed solvent of THF (20 ml) and water (20 ml). Manganese (30 mmol) was then added slowly to the mixture while stirring. The reaction mixture was stirred under N\textsubscript{2} for 16 hours. The reaction was quenched with HCl (3 M, 30 ml) and extracted with dichloromethane. The yield of DPE-d\textsubscript{0} is about 95 %.

The deuterated isotopomers of DPE were also prepared following the same procedure; 10 mmol of benzylbromide-d\textsubscript{0} was replaced by a mixture of 5 mmol of benzylbromide-d\textsubscript{0} and 5 mmol of benzylbromide-d\textsubscript{n}. This produces a mixture, which if statistical would be 1.25 mmol of DPE-d\textsubscript{0}, 2.5 mmol of the asymmetrically deuterated isotopomer and 1.25 mmol of the symmetrically deuterated isotopomer.

**α-DPE-d\textsubscript{2} and α,α’-DPE-d\textsubscript{4}**

A statistical mixture of DPE-d\textsubscript{0}, α-DPE-d\textsubscript{2}, and α,α’-DPE-d\textsubscript{4} was prepared by coupling benzylbromide-d\textsubscript{0} (5 mmol) and α-benzylbromide-d\textsubscript{2} (5 mmol). The latter was made in two steps. α-Benzylalcohol-d\textsubscript{2} was first synthesized by refluxing a mixture of methylbenzoate (13 mmol) and LiAlD\textsubscript{4} (7 mmol) in THF (30 ml) for 15 hours. Reaction of α-benzyl alcohol-d\textsubscript{2} (11 mmol) with 7 mmol of PBr\textsubscript{3} in dichloromethane (20 ml), at 20 °C for two hours yielded α-benzylbromide-d\textsubscript{2}.
**M$_2$DPE-d$_0$, α- M$_2$DPE-d$_2$, and α,α’-M$_2$DPE-d$_4$**

A statistical mixture of M$_2$DPE-d$_0$, α- M$_2$DPE-d$_2$, and α,α’-M$_2$DPE-d$_4$ was similarly (as for α-DPE-d$_2$, and α,α’-DPE-d$_4$) prepared by coupling 4-methylbenzylbromide-d$_0$ and 4-methylbenzylbromide-α-d$_2$. The latter was prepared by reducing 4-methylbenzoate with LiAlD$_4$, and subsequent bromination of the obtained alcohol with PBr$_3$.

**DPE-d$_5$ and DPE-d$_{10}$**

Phenylmagnesium bromide-d$_5$ was prepared by Grignard reaction of bromobenzene-d$_5$ (12 mmol) and magnesium (16 mmol) in THF (12 ml), at 40 °C for three hours. 3 g of crushed dry ice was then added to the Grignard reagent. The reaction mixture was stirred for 30 mins to yield benzoic acid-d$_5$. Benzylalcohol-d$_5$ was prepared by refluxing a mixture of benzoic acid-d$_5$ and LiAlH$_4$ in THF for 15 hours. Treatment of the benzylalcohol-d$_5$ with PBr$_3$ in dichloromethane at 20 °C for two hours yielded benzylbromide-d$_5$. A statistical mixture of DPE-d$_0$, DPE-d$_5$, and DPE-d$_{10}$ was made by coupling of benzylbromide-d$_5$ (5 mmol) and benzylbromide-d$_0$ (5 mmol).

**p-DPE-d$_2$**

Bis-(p-bromophenyl)-1,2-diphenylethane was first made by coupling of p-bromobenzylbromide following the same procedure as for DPE-d$_0$. p-DPE-d$_2$ was then synthesized by quenching the Grignard reagent prepared from bis-(p-bromophenyl)-1,2-diphenylethane (9 mmol) and magnesium (23 mmol) in refluxing THF (25 ml), with 2ml of D$_2$O.
p-DPE-d$_1$

p-DPE-d$_1$ was synthesized in three steps: a mixture of sodium methoxide (12 mmol), p-bromobenzaldehyde (12 mmol), and diethylbenzylphosphonate (12 mmol) in 50ml of DMF was stirred at room temperature for 24 hours. 50 ml of cold water was then added to the reaction mixture, filtration of the resulting suspension yielded 8 mmol of p-bromostilbene. The Grignard reagent prepared from 8 mmol of p-bromostilbene and 12 mmol of magnesium in refluxing THF (15 ml), was quenched with 1 ml of D$_2$O to yield p-stilbene–d$_1$. p-DPE-d$_1$ was obtained by refluxing a mixture of p-stilbene–d$_1$ (5 mmol), iodine (4 mmol), and hypophosphorous acid (50 %, 20 mmol) in refluxing 25 ml of acetic acid under N$_2$ for 24 hours.

α-DPE-d$_1$ and α,α’-DPE-d$_2$

A statistical mixture of DPE-d$_0$, α-DPE-d$_1$, and α,α’-DPE-d$_2$ was prepared by stirring 5 mmol of meso-1,2-dibromo,1,2-diphenylethane and 50 mmol of magnesium in a mixture of MeOD (7 ml), MeOH (3 ml), and dry THF (4 ml), under reflux conditions for 20 hours. Pure α,α’-DPE-d$_2$ was also made by reducing 3 mmol of trans-stilbene with 30 mmol of magnesium in a mixture of MeOD (6 ml) and THF (3 ml).

α-Ethylbenzene-d$_1$

α-Ethylbenzene-d$_1$ was made by stirring a mixture of (1-bromoethyl)-benzene (6 mmol) and magnesium (20 mmol) in 6ml of MeOD under reflux conditions for 20 hours.

The isotopic purity of all the synthesized compounds was checked by GC/MS analysis.
2.2.2 Spectroscopy

The supersonic jet apparatus used in this work has been described in chapter 1. The carrier gas (He or Ne) at 1-3 atm is passed through a heated sample reservoir containing the sample (at 20 °C for ethylbenzene, 100 °C for DPE, and 120 °C for M2DPE). Mass selectivity of the used apparatus permits the spectra of DPE-d_0, α-DPE-d_1, and α,α'-DPE-d_2 to be obtained from the same sample. Similarly, the spectra of α-DPE-d_2 and α,α'-DPE-d_4, as well as those of DPE-d_5 and DPE-d_10 were obtained using a mixed sample of DPE-d_0/α-DPE-d_2/α,α'-DPE-d_4 and DPE-d_0/DPE-d_5/DPE-d_10, respectively. The same applies to the mixed sample of M_2DPE-d_0, α-M_2DPE-d_2, and α,α'-M_2DPE-d_4. The use of the mixed samples is in fact good for the analysis of the experimental data. Accurate relative transition energies of closely related symmetric and asymmetric isotopomers are required for the calculations of exciton coupling energies.

2.3 Results and Analysis

2.3.1 Ab initio calculations

Ground state optimized geometries and harmonic frequencies were calculated at the Hartree-Fock (HF) level of theory. Single point energy calculations were performed at the MP2 level. Configuration interaction singles (CIS) method was used to compute vertical excitation energies, and optimize the excited state geometries of the investigated molecules. Vertical excitation energies and oscillator strengths were computed using the HF optimized S_0 geometries. The calculations were performed using 6-311G(d,p) basis set.

Some selected S_0 geometrical data and relative energies of DPE and M_2DPE are reported in Table 2.1. The CIS/6-311G(d,p) computed S_1 ← S_0 and S_2 ← S_0 vertical excitation energies together with their oscillator strengths, and adiabatic S_1 ← S_0 excitation energies of the two
stable conformers of DPE and M₂DPE are compiled in Table 2.2. Adiabatic excitation energies are the differences in the total energies of the CIS optimized S₁ minima and the HF optimized S₀ minima. The minimum energy S₁ structures of the anti and gauche conformers of DPE and M₂DPE are displayed in Figure 2.2. Also shown in the Figure are the orientations of the transition dipole moments (TDMs) for the localized S₁ ← S₀ transitions, and the Cₛᵖ²-Cₛᵖ² bond lengths of the aromatic chromophores.

2.3.1.1 DPE

It is well known that S₁ ← S₀ excitation of benzene derivatives is accompanied by the expansion of the aromatic chromophores; the Cₛᵖ²-Cₛᵖ² bond lengths increase by about 0.035 Å in the S₁ states with respect to the Cₛᵖ²-Cₛᵖ² bond lengths in the S₀ states. Upon electronic excitation of bichromophoric molecules with identical chromophores, the electronic excitation energy can either be essentially localized on one of the chromophores or delocalized over the two chromophores. Delocalized excitation occurs in the strong coupling regime, where the electronic coupling energy is substantially larger than the relaxation energy of the excited chromophores. However, if the coupling energy is very small, the electronic excitation energy will essentially localize on one chromophore.
Table 2.1 Calculated $S_0$ geometrical data and relative energies of the two stable conformers of DPE and M$_2$DPE.

<table>
<thead>
<tr>
<th></th>
<th>DPE</th>
<th>M$_2$DPE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gauche</td>
<td>Anti</td>
</tr>
<tr>
<td>$\text{C}<em>{\text{sp}3}-\text{C}</em>{\text{sp}3}$, (Å)</td>
<td>1.544</td>
<td>1.541</td>
</tr>
<tr>
<td>$\text{C}<em>{\text{sp}2}-\text{C}</em>{\text{sp}3}$, (Å)</td>
<td>1.514</td>
<td>1.513</td>
</tr>
<tr>
<td>$\text{C}<em>{\text{sp}2}-\text{C}</em>{\text{sp}2}$, (Å)</td>
<td>1.386</td>
<td>1.386</td>
</tr>
<tr>
<td>$\text{C}<em>{\text{sp}3}-\text{C}</em>{\text{sp}3}-\text{C}_{\text{sp}2}$, (degrees)</td>
<td>114.4</td>
<td>112.7</td>
</tr>
<tr>
<td>$\text{C}<em>{\text{sp}2}-\text{C}</em>{\text{sp3}}-\text{C}<em>{\text{sp3}}-\text{C}</em>{\text{sp3}}$, (degrees)</td>
<td>68.0</td>
<td>180.0</td>
</tr>
<tr>
<td>$E_{\text{rel}}$, (cm$^{-1}$)</td>
<td>0</td>
<td>-316</td>
</tr>
<tr>
<td>$\text{MP2/6-311G(d,p)// HF/6-311G(d,p)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{\text{rel}}$, (cm$^{-1}$)</td>
<td>0</td>
<td>327</td>
</tr>
</tbody>
</table>

$^a$Average values.

In an attempt to model delocalized excitation, geometrical optimizations of the $S_1$ and $S_2$ states of the two stable conformers of DPE were performed under the constraints of their ground state symmetries ($C_2$ for the gauche and $C_{2h}$ for the anti). Subsequent harmonic frequency calculations on the optimized symmetric $S_1$ states of both conformers yielded one imaginary frequency, which involves expansion of one of the rings and contraction of the other. Therefore,
the optimized symmetric S\textsubscript{1} states of both conformers are transition states along a ring expansion (breathing) coordinate of the S\textsubscript{1} potential energy surface. No imaginary frequency appears in the results of the frequency calculations on the optimized symmetric S\textsubscript{2} states. The C\textsubscript{sp2}-C\textsubscript{sp2} bond lengths in the optimized symmetric S\textsubscript{1} and S\textsubscript{2} states are longer than the HF computed S\textsubscript{0} bond lengths by about 0.015 Å. The energy gaps between the optimized symmetric S\textsubscript{1} and S\textsubscript{2} states of the gauche and anti conformers are 84 cm\textsuperscript{-1} and 12 cm\textsuperscript{-1}, respectively. These energy gaps are very similar to the gaps between the vertical S\textsubscript{1} ← S\textsubscript{0} and S\textsubscript{2} ← S\textsubscript{0} excitation energies listed in Table 2.2, indicating similar geometries of the symmetric S\textsubscript{1} and S\textsubscript{2} states.

In order to locate the local minima on the S\textsubscript{1} potential energy surface, the S\textsubscript{1} states of the gauche and anti conformers were optimized under the constraints of C\textsubscript{1} and C\textsubscript{s} symmetries, respectively. The results of frequency calculations on the optimized low symmetry S\textsubscript{1} states do not include any imaginary frequency. The optimized structures of the S\textsubscript{1} minima shown in Figure 2.2 reveal the localized nature of the optimized excited states. The C\textsubscript{sp2}-C\textsubscript{sp2} bond lengths of only one of the two phenyl chromophores increased by ca. 0.028 Å relative to the HF computed C\textsubscript{sp2}-C\textsubscript{sp2} bond lengths in the S\textsubscript{0} state. Also shown in Figure 2.2 are the orientations of the transition dipole moments (TDMs) for the localized S\textsubscript{1} ← S\textsubscript{0} transition. The TDM of the anti conformer is short axis polarized; i.e. lies perpendicular to the long axis of the excited phenyl ring. However, the TDM of the gauche conformer forms an angle of 33 \degree with the short axis of the excited phenyl ring. The calculated orientations of the TDMs of the gauche and anti conformers of DPE are similar to the observed orientations of the TDMs for the S\textsubscript{1} ← S\textsubscript{0} transitions of the gauche and trans conformers of n-propylbenzene, respectively.\textsuperscript{21}
The results of the CIS optimizations are consistent with the potential energy surface of weakly coupled bichromophores in the $S_1$ state, the sketch of which is shown in Figure 1.1. The energy gaps between the optimized low symmetric $S_1$ minima and the symmetric $S_1$ maxima of the gauche and anti conformers are 511 cm$^{-1}$ and 480 cm$^{-1}$, respectively. Thus, at the CIS/6-311G(d,p) level of theory, the barriers in the $S_1$ potential energy surfaces of the gauche and anti conformers are 511 cm$^{-1}$ and 480 cm$^{-1}$, respectively. The calculations support the assumption that DPE is a weakly coupled bichromophore.

Table 2.2 Calculated vertical $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transition energies ($E_1$ and $E_2$, cm$^{-1}$) with their oscillator strengths ($f_1$ and $f_2$), and localized $S_i \leftarrow S_0$ adiabatic excitation energies ($E_{ad}$, cm$^{-1}$) of DPE and M$_2$DPE.

<table>
<thead>
<tr>
<th></th>
<th>$E_1$</th>
<th>$f_1$</th>
<th>$E_2$</th>
<th>$f_2$</th>
<th>$E_2-E_1$</th>
<th>$E_{ad}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DPE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gauche</td>
<td>49782</td>
<td>0.0053</td>
<td>49896</td>
<td>0.0001</td>
<td>86</td>
<td>48780</td>
</tr>
<tr>
<td>Anti</td>
<td>49858</td>
<td>0.0000</td>
<td>49868</td>
<td>0.0045</td>
<td>10</td>
<td>48825</td>
</tr>
<tr>
<td><strong>M$_2$DPE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gauche</td>
<td>49069</td>
<td>0.0116</td>
<td>49146</td>
<td>0.0041</td>
<td>77</td>
<td>47792</td>
</tr>
<tr>
<td>Anti</td>
<td>49076</td>
<td>0.0000</td>
<td>49099</td>
<td>0.0187</td>
<td>23</td>
<td>47956</td>
</tr>
</tbody>
</table>
Figure 2.2 Minimum energy $S_1$ structures of (a) gauche DPE, (b) anti DPE, (c) gauche M2DPE, and (d) anti M2DPE. The angles show the computed orientations of transition dipole moments (TDMs) for the localized $S_1 \leftarrow S_0$ transitions.

2.3.1.2 M2DPE

The $S_0$ geometries and relative energies of the gauche and anti conformers of M2DPE reported in Table 2.1 are very similar to those of the corresponding DPE conformers. The $C_{2h}$ symmetric anti conformer of M2DPE is 309 cm$^{-1}$ more stable than the $C_2$ symmetric gauche
conformer at the HF level. Single point MP2 energy calculations on the HF optimized geometry reverses the relative stabilities of the conformers, predicting a more stable (by 330 cm\(^{-1}\)) gauche conformer. The \(S_1 \leftarrow S_0\) transitions of the two conformers of M\(_2\)DPE are also predicted to be localized as illustrated in Figure 2.1. The TDM of the anti conformer is short axis polarized. Whereas, the TDM of the gauche conformer is rotated by 67 \(^{\circ}\) from the short axis of the excited phenyl chromophore.

2.3.2 Resonant enhanced two-photon ionization (R2PI) spectra

The observed \(0^0\) transition energies of all isotopomers of DPE and M\(_2\)DPE are listed in Table 2.3.

2.3.2.1 R2PI spectrum of DPE–d\(_0\)

The spectra of DPE-d\(_0\) and n-propylbenzene shown in Figure 2.3 resemble one another in the sense that the two molecules absorb in the same region and exhibit similar vibronic features. The electronic spectrum n-propylbenzene has been analyzed by several research groups\(^{21-23}\) the electronic origin of the gauche conformer of n-propylbenzene is red-shifted by 49 cm\(^{-1}\) relative to that of the anti conformer. The first intense peak in the spectrum of DPE-d\(_0\) occurs at 37481.5 cm\(^{-1}\), scanning to the red of this peak didn’t reveal additional features.
Table 2.3 List of the observed $0^J_0$ transition frequencies of the investigated isotopomers of DPE and M$_2$DPE.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Gauche</th>
<th>Anti</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_1 \leftarrow S_0$</td>
<td>$S_2 \leftarrow S_0$</td>
</tr>
<tr>
<td>DPE-d$_0$</td>
<td>37481.5</td>
<td>37547.5</td>
</tr>
<tr>
<td>$\alpha$-DPE-d$_1^a$</td>
<td>37482.7</td>
<td>37548.4</td>
</tr>
<tr>
<td>$\alpha$,$\alpha'$-DPE-d$_2^a$</td>
<td>37484.2</td>
<td>37550.5</td>
</tr>
<tr>
<td>$\alpha$-DPE-d$_2$</td>
<td>37486.1</td>
<td>37498.7</td>
</tr>
<tr>
<td>$\alpha$,$\alpha'$-DPE-d$_4^a$</td>
<td>37492.4</td>
<td>37554.2</td>
</tr>
<tr>
<td>p-DPE-d$_1^b$</td>
<td>37512.2</td>
<td>37578.1</td>
</tr>
<tr>
<td>$d_o^* - d_i$</td>
<td>37487.1</td>
<td>37548.9</td>
</tr>
<tr>
<td>$d_i^* - d_o$</td>
<td>37516.4</td>
<td>37580.5</td>
</tr>
<tr>
<td>p-DPE-d$_2$</td>
<td>37512.2</td>
<td>37578.1</td>
</tr>
<tr>
<td>DPE-d$_5^b$</td>
<td>37489.2</td>
<td>37549.8</td>
</tr>
<tr>
<td>$d_o^* - d_s$</td>
<td>37654.6</td>
<td>37716.1</td>
</tr>
<tr>
<td>$d_s^* - d_o$</td>
<td>37647.3</td>
<td>37713.7</td>
</tr>
<tr>
<td>M$_2$DPE-d$_0$</td>
<td>36779.4</td>
<td>36787.5</td>
</tr>
<tr>
<td>$\alpha$- M$_2$DPE-d$_2$</td>
<td>36782.7</td>
<td>36793.1</td>
</tr>
<tr>
<td>$\alpha$,$\alpha'$-M$_2$DPE-d$_4$</td>
<td>36788.6</td>
<td>36796.8</td>
</tr>
</tbody>
</table>

$^a$Display more than one $S_i \leftarrow S_0$ electronic origin for the gauche conformer. $^b$Localized excitation of the deuterated and undeuterated halves.
Figure 2.3 R2PI spectra of (a) n-propylbenzene, and (b) DPE-d_0. Assignments of the vibronic features of n-propylbenzene were taken from ref. 23.

Laser power saturation experiments were performed in order to assign transitions of various DPE conformers. Shown in Figure 2.4 are the R2PI spectra of DPE-d_0 obtained at three different laser powers; as the laser power is increased the relative intensities of all spectral bands increase significantly; the only exception is the band at 37547.5 cm\(^{-1}\). Therefore, the bands at 37547.5 cm\(^{-1}\) and 37481.5 cm\(^{-1}\) are electronic origins of two different conformers. Tentative
assignment of the two origins is made by comparison with the electronic spectrum of n-propylbenzene. The first intense peak at 37481.5 cm$^{-1}$ is assigned to the $0_0^0$ transition of the gauche conformer. The peak at 37547.5 cm$^{-1}$ is assigned to the $0_0^0$ transition of the anti conformer. The three peaks between the assigned origins are fundamental transitions of low frequency vibrational modes of the gauche conformer (See section 2.3.2.3).

Figure 2.4 R2PI spectra of DPE-d$_0$ in the origin region recorded using a relative laser fluences of (a) $\times$12, (b) $\times$5 and (c) $\times$1
2.3.2.2 R2PI spectra of α-DPE-d₁ and α,α’-DPE-d₂

The first four bands in the spectrum of α-DPE-d₁ shown in Figure 2.5b appear as doublets. The deuterium atom in the gauche conformer α-DPE-d₁ can be located in two inequivalent positions with the same probability; hence, the appearance of the doublets is caused by the two configurations of the gauche conformer of α-DPE-d₁. The two origins of α-DPE-d₁ are blue-shifted by 1.2 cm⁻¹ and 3.3 cm⁻¹ from the origin of the gauche conformer of DPE-d₀. The spectrum of β-ethylbenzene-d₁ also features two origins; however, the first origin is more intense than the second and is blue-shifted by about 1 cm⁻¹ with respect to the 0₀₀ band of ethylbenzene-d₀; the second origin is blue shifted by about 3 cm⁻¹ from the 0₀₀ band of ethylbenzene-d₀. The origin of such deuterium effect can be understood by examining the distance between the center of the phenyl rings and β-hydrogens. Two of the β-hydrogens in ethylbenzene are located at 3.81 Å from the center of the phenyl ring, and the other one is at 4.77 Å from the ring center. The two β-hydrogens of the gauche conformer of DPE are located at 3.77 Å and 4.78 Å from the center of either one of the two equivalent rings. On the other hand, the two β-hydrogens of the anti conformer are equidistant from the center of either one of the two equivalent rings; hence they are equivalent. Similar argument will predict the vibronic features of the gauche conformer of α,α’-DPE-d₂ to appear as triplets (Figure 2.5a). The two origins of the anti conformer of α,α’-DPE-d₂ overlap, suggesting negligible differences between the two configurations.

The spectra of ethylbenzene-d₀ and α-ethylbenzene-d₁ displayed in Figure 2.6a and 2.6b are characterized by a single electronic origin, indicating that the two α hydrogens of ethylbenzene are equivalent. The origin of α-ethylbenzene-d₁ is blue-shifted by 3.4 cm⁻¹ with respect to that of α-ethylbenzene-d₀ due to the zero point energy changes in the S₀ and S₁ states upon deuteration.
Figure 2.5 R2PI spectra of (a) $\alpha,\alpha'$-DPE-d$_2$, (b) $\alpha$-DPE-d$_1$ and (c) DPE-d$_0$ in the origin region.

Except for the splittings of the vibronic bands, the spectra of $\alpha$-DPE-d$_1$ and $\alpha,\alpha'$-DPE-d$_2$ are very similar to the spectra of DPE-d$_0$. Therefore, the electronic excitation is delocalized in DPE-d$_0$, $\alpha$-DPE-d$_1$ and $\alpha,\alpha'$-DPE-d$_2$ in the sense that it is impossible to tell which half of the
molecules is excited. The spectra of α-DPE-d₁ and α,α'-DPE-d₂ provide the strongest evidence in support of the assignments of the observed vibronic bands to the gauche and anti conformers.

Figure 2.6 0₀ bands in the R2PI spectra of (a) α-ethylbenzene-d₀, and (b) α-ethylbenzene-d₁.

2.3.2.3 R2PI spectra of p-DPE-d₂, α-DPE-d₄ and DPE-d₁₀

The R2PI spectra of the symmetrically deuterated α-DPE-d₄, p-DPE-d₂, and DPE-d₁₀ are displayed in Figure 2.7a, 2.8a, and 2.9a, respectively. The spectra of DPE-d₀ and the symmetrically deuterated isotopomers are qualitatively identical because the symmetric deuteration conserves the symmetry of the molecule. Table 2.5 summarizes the frequencies of
the observed vibronic bands in the spectra of the symmetric isotopomers, their isotope effects, and proposed assignments. The isotope effects, IE, were calculated as the percentage decrease in the frequencies of the observed vibronic bands in the spectra of the symmetric isotopomers with respect to the frequencies of the corresponding bands in the spectrum of DPE-d\textsubscript{0} using the expression:

$$\text{IE} = \frac{\nu_{dn} - \nu_{d0}}{\nu_{d0}} \times 100\%$$

where $\nu_{d0}$ and $\nu_{dn}$ are the frequencies of the observed vibronic bands relative to the origin of the gauche conformers of DPE-d\textsubscript{0} and DPE-d\textsubscript{n}, respectively. As seen in Table 2.5, the peaks that correlate with the peaks at 28.2 cm\textsuperscript{-1}, 37.6 cm\textsuperscript{-1}, and 43.3 cm\textsuperscript{-1} in the spectrum of DPE-d\textsubscript{0} have an associated isotope effect. Therefore, the three peaks are fundamental transitions of low frequency vibrations.\textsuperscript{26} The proposed assignments of the vibronic bands reported in the last column of Table 2.5 were made by comparison with the HF calculated vibrational modes in the S\textsubscript{0} state (Table 2.4).

It is well known that isotopic substitution has much higher effect on vibronic bands than on electronic origins of conformers; hence, electronic origins can be distinguished from vibronic bands based on the observed isotope effects.\textsuperscript{26} The peak at 66.0 cm\textsuperscript{-1} in the spectrum of DPE-d\textsubscript{0} exhibits very small isotope effect in the spectra of the symmetrically ring deuterated isotopomers, supporting its assignment as the origin of the anti conformer.
Table 2.4 HF/6-311G(d,p) calculated lowest frequency vibrational modes of the gauche conformers of DPE and M₂DPE.

<table>
<thead>
<tr>
<th>Mode</th>
<th>DPE</th>
<th>M₂DPE</th>
<th>Approximate description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequencies, cm⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>30.8</td>
<td>26.1</td>
<td>Symmetric torsion about Cₓsp-Cₓsp bonds + torsion about Cₓsp-Cₓsp bonds</td>
</tr>
<tr>
<td>B</td>
<td>32.8</td>
<td>34.3</td>
<td>Asymmetric torsion about Cₓsp-Cₓsp bonds</td>
</tr>
<tr>
<td>C</td>
<td>46.4</td>
<td>40.2</td>
<td>Symmetric flapping of aromatic rings</td>
</tr>
<tr>
<td>M1</td>
<td>--</td>
<td>18.8</td>
<td>Asymmetric methyl torsion</td>
</tr>
<tr>
<td>M2</td>
<td>--</td>
<td>20.2</td>
<td>Symmetric methyl torsion</td>
</tr>
</tbody>
</table>

Table 2.5 Assignment of the lowest frequency vibronic transitions of the symmetric isotopomers of DPE.\(^a\)

<table>
<thead>
<tr>
<th>DPE-d₀</th>
<th>α,α’-DPE-d₄</th>
<th>p-DPE-d₂</th>
<th>DPE-d₁₀</th>
<th>Assignment(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ν_d₀)</td>
<td>(ν_{dn})</td>
<td>IE, %</td>
<td>(ν_{dn})</td>
</tr>
<tr>
<td></td>
<td>28.2</td>
<td>28.1</td>
<td>-0.4</td>
<td>27.7</td>
</tr>
<tr>
<td></td>
<td>37.6</td>
<td>37.6</td>
<td>0.0</td>
<td>37.4</td>
</tr>
<tr>
<td></td>
<td>43.3</td>
<td>43.4</td>
<td>0.2</td>
<td>42.8</td>
</tr>
<tr>
<td></td>
<td>66.0</td>
<td>61.8</td>
<td>-6.4</td>
<td>65.9</td>
</tr>
<tr>
<td></td>
<td>70.9</td>
<td>70.8</td>
<td>-0.1</td>
<td>70.1</td>
</tr>
<tr>
<td></td>
<td>79.4</td>
<td>79.7</td>
<td>0.4</td>
<td>78.8</td>
</tr>
<tr>
<td></td>
<td>85.6</td>
<td>85.3</td>
<td>-0.4</td>
<td>84.5</td>
</tr>
</tbody>
</table>

\(^a\)Wavenumbers are relative to the origin transition of the gauche conformer of each isotopomer (Table 2.3). \(^b\)Vibrational modes are described in Table 2.4.
2.3.2.4 R2PI spectra of α-DPE-d₂, p-DPE-d₁, and DPE-d₅

The spectra of asymmetrically deuterated isotopomers of DPE displayed in Figure 2.7b, 2.8b, and 2.9b, respectively have been recorded with the sole purpose of estimating the magnitudes of the exciton coupling energies, and the relative ordering of the exciton states in DPE conformers (See section 2.4.2). The spectra of p-DPE-d₁ and DPE-d₅ are more complicated than those of the other isotopomers. The complexity can be related to the lowering of the molecular symmetry and change in the nature of the excited states.

Four distinct electronic origins appear in the spectrum of p-DPE-d₁ at similar frequencies as those of the 0⁰₀ bands of the gauche and anti conformers of DPE-d₀ and p-DPE-d₂. Therefore, the excitation is localized on the undeuterated (d₀⁺ – d₁) and deuterated (d₀ – d₁⁺) halves of the anti and gauche conformers of p-DPE-d₁. Similarly, Figure 2.9b illustrates the localized nature of the electronic excitation in DPE-d₅.

Three fundamental transitions of low frequency vibrations occur at 24.9 cm⁻¹, 38.2 cm⁻¹, and 42.8 cm⁻¹ from the d₀⁺ – d₁ origin of the gauche conformer of p-DPE-d₁; three weaker peaks also appear at 28.5 cm⁻¹, 39.8 cm⁻¹, and 42.4 cm⁻¹ from the origin of the d₀ – d₁⁺ half of the gauche conformer. The frequencies of the three fundamentals are close to those observed in DPE-d₀; therefore, the low frequency vibrational modes of p-DPE-d₁ are similar to those of the symmetric isotopomers (Table 2.5).

Only two fundamentals are found to be built off the origins of the d₀⁺ – d₅ and d₅⁺ – d₀ halves of the gauche conformer of DPE-d₅. The fundamentals appear at 31.1 cm⁻¹ and 40.9 cm⁻¹ from the d₀⁺ – d₅ origin, with their combination at 71.7 cm⁻¹; and also at 30.0 cm⁻¹ and 41.7 cm⁻¹ to the blue of the d₅⁺ – d₀ origin, with their combination at 70.8 cm⁻¹. The distinct vibrational
activity of DPE-d₅ may be caused by the stronger perturbation of the vibronic structure of DPE induced by the five deuterium atoms owing to the large energy gap between the zero order vibronic states, leading to more localized excitation than in p-DPE-d₁. The fundamental at ca. 41 cm⁻¹ from the two localized electronic origins of the gauche conformer of DPE-d₅ is similar to the third lowest frequency fundamental of the symmetrical isotopomers, so it can be assigned to the flapping of the phenyl rings. The fundamental transitions at 31.1 cm⁻¹ and 30.0 cm⁻¹ from the origins of the $d_0^* - d_5$ and $d_5^* - d_0$ halves, respectively, are most likely due to localized phenyl torsions. Localized phenyl torsion of the deuterated half will have lower frequency because of the larger reduced mass. The higher frequency of this mode for the $d_0^* - d_5$ half indicates that the phenyl torsion is mainly localized on the excited aromatic ring. The assignment of the vibronic features of DPE-d₅ is further supported by the results of the CIS frequency calculations on the optimized non symmetric gauche conformer in the S₁ state. The frequencies of the first two modes are 27.4 cm⁻¹ and 31.7 cm⁻¹. The first and second modes are associated with the localized phenyl torsions of the unexcited and excited phenyl rings, respectively. The third lowest frequency mode (41.3 cm⁻¹) involves flapping of the two phenyl rings.
Figure 2.7 R2PI spectra of (a) $\alpha,\alpha'$-DPE-d$_4$, (b) $\alpha$-DPE-d$_2$, and (c) DPE-d$_0$ in the origin region.
**Figure 2.8** R2PI spectra of (a) p-DPE-d$_2$, (b) p-DPE-d$_1$, and (c) DPE-d$_0$ in the origin region.

Two localized electronic origins of each conformer are clearly seen in the spectrum of p-DPE-d$_1$. 
Figure 2.9 R2PI spectra of (a) DPE-d₁₀, (b) DPE-d₅, and (c) DPE-d₀ in the origin region.

Two localized electronic origins of each conformer are clearly seen in the spectrum of DPE-d₅.
2.3.2.5 R2PI spectra of M2DPE-d0, α-M2DPE-d2, and α-M2DPE-d4

Figure 2.10 features the spectra of M2DPE-d0, α-M2DPE-d2, and α-M2DPE-d4. Laser power saturation experiments were performed in order to assign vibronic features of the gauche and anti conformers. The \(0^0\) transitions of the gauche and anti conformers of M2DPE-d0 occur at 36779.4 cm\(^{-1}\) and 36833.0 cm\(^{-1}\), the two origins are red shifted by 702 cm\(^{-1}\) and 714 cm\(^{-1}\) relative to the \(0^0\) transitions of the corresponding DPE-d0 conformers. These shifts are similar to the reported red-shifts of ca. 723 cm\(^{-1}\) of the electronic origins p-n-propyltoluene conformers relative to those of n-propylbenzene conformers.\(^{22}\) Apart from the red-shifts of the electronic origins, the major difference between the spectra of M2DPE-d0 and DPE-d0 is the appearance of a number of very weak vibronic bands in the spectrum of M2DPE-d0 and its isotopomers. These weak vibronic features appear in the supersonic expansions of both helium and neon with the same relative intensities; hence, they are not due to hot bands or clusters. Most of the weak bands are certainly associated with methyl torsions. The fundamental transition of the methyl rotor occurs at 16 cm\(^{-1}\) above the \(0^0\) transition of the gauche conformer of M2DPE-d0; this can be compared with the observed frequency of 15.5 cm\(^{-1}\) for the \(0a_1 \rightarrow 3a_1\) transition of the methyl rotor in the gauche conformer of p-n-propyltoluene.\(^{22}\) The proposed assignments of the observed vibronic features in the spectra of M2DPE-d0, α-M2DPE-d2, and α-M2DPE-d4 are summarized in Table 2.6. The assignments were made by comparison with the HF calculated S\(_0\) vibrational modes listed in Table 2.4.
Figure 2.10 R2PI spectra of (a) \( \alpha,\alpha' \)-M\(_2\)DPE-d\(_4\), (b) \( \alpha \)-M\(_2\)DPE-d\(_2\) and (c) M\(_2\)DPE-d\(_0\) in the origin region.
**Table 2.6** Assignment of the low frequency vibronic transitions of M2DPE-d₀, α-M2DPE-d₂, and α,α′-M2DPE-d₄.ᵃ

<table>
<thead>
<tr>
<th>M₂DPE-d₀</th>
<th>α,α′-M₂DPE-d₄</th>
<th>α- M₂DPE-d₂</th>
<th>Assignmentᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>8.1</td>
<td>10.4</td>
<td>S₂ ← S₀ origin (gauche conformer)</td>
</tr>
<tr>
<td>16.0</td>
<td>15.8</td>
<td>16.0</td>
<td>Methyl rotor</td>
</tr>
<tr>
<td>21.0</td>
<td>20.9</td>
<td>21.0</td>
<td>A₀*</td>
</tr>
<tr>
<td>32.8</td>
<td>33.1</td>
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<td>B₀*</td>
</tr>
<tr>
<td>37.3</td>
<td>37.6</td>
<td>37.4</td>
<td>C₀*</td>
</tr>
<tr>
<td>39.7</td>
<td>37.5</td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>42.1</td>
<td>41.9</td>
<td>42.5</td>
<td>A₀⁺</td>
</tr>
<tr>
<td>53.6</td>
<td>49.4</td>
<td>50.6</td>
<td>S₁ ← S₀ origin (anti conformer)</td>
</tr>
<tr>
<td>(53.6)ᶜ</td>
<td>54.2</td>
<td></td>
<td>B₀ A₀⁺</td>
</tr>
<tr>
<td>58.4</td>
<td>58.6</td>
<td></td>
<td>A₀⁺ C₀⁺</td>
</tr>
<tr>
<td>63.4</td>
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<td>B₀⁺</td>
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<tr>
<td>70.8</td>
<td>71.0</td>
<td></td>
<td>B₀⁺ C₀⁺</td>
</tr>
</tbody>
</table>

ᵃWavenumbers are relative to the origin transition of the gauche conformer of each isotopomer (Table 2.3).ᵇVibrational modes are described in Table 2.4.ᶜOverlap with the 0₀ band of the anti conformer.
2.4 Discussion

2.4.1 Conformer distribution and structural details

The relative abundance of the two conformers of DPE was estimated by integrating the areas under the Franck-Condon envelope of each conformer in the origin region. A gauche/anti conformer ratio of 4.15 was thus estimated. The Boltzmann distribution law was then used to estimate the relative energy, \( \Delta E = E_{\text{Gauche}} - E_{\text{Anti}} \), of the two conformers. The pre-expansion temperature of 373 K was used, the degeneracy factor of the gauche conformer was taken as twice that of the anti conformer. The estimated value of \( \Delta E \) is 189 cm\(^{-1}\) (2.3 kJ/mol). This value is consistent with the results of high level correlated ab initio calculations which predicted the gauche conformer to be more stable by 1.0 – 1.6 kJ/mol.\(^2\) On the other hand, present results do not agree with the conclusions drawn from the analysis of the electron diffraction data.\(^4\) The latter analysis found more stable anti conformer (by 5 kJ/mol). Several assumptions have been made when estimating the gauche/anti population ratio:\(^27\) the two conformers have the same line strengths in the origin region, the line strength and of the gauche conformer is distributed over the origin band and the three active low frequency vibronic bands, the two conformers have similar ionization efficiencies, and the absence of conformer relaxation in the supersonic expansion.

The observation of a single electronic origin of the gauche and anti conformers in the spectra of the symmetric isotopomers can be taken as evidence of the symmetry equivalency of the two phenyl rings of both conformers. Further evidence is provided by the spectra of p-DPE-d\(_1\) and DPE-d\(_5\), which feature two localized electronic origins for the deuterated and undeuterated halves of both conformers. If the rings were not symmetry equivalent, two
electronic origins in the vicinity of the $0_0^0$ bands of the deuterated and undeuterated halves, respectively, of each conformer would have been observed.

**2.4.2 Exciton couplings in DPE**

As apparent in Figures 8 and 9, the electronic origin transitions of the symmetric isotopomers are located to the red of the origin transitions of the corresponding asymmetric isotopomers. Similar types of shifts were also observed in the spectra of benzene dimers. The $0_0^0$ transition energies of the homodimers ($h_6:h_6$ and $d_6:d_6$) of benzene are less than those of the corresponding heterodimer ($h_6:d_6$). The exciton coupling energy, $V_{00}$, and zero point energy shifts, $\Delta$, are estimated following the procedure described by Baum et al. using the observed $0_0^0$ transition energies of DPE-$d_0$ and a pair of two closely related symmetric and asymmetric isotopomers. The procedure is based on the assumption that exciton interactions do not occur in the asymmetric isotopomers; hence, the observed shifts of the $0_0^0$ bands of the asymmetric isotopomers relative to the origins of the symmetric isotopomers are caused by the exciton interactions in the symmetric isotopomers, and zero point energy changes of both symmetric and asymmetric isotopomers in the ground and excited states upon deuteration. For example, the shift of the $0_0^0$ band of DPE-$d_0$ relative to the $d_0^*-d_5^-$ origin of the asymmetric DPE-$d_5$, 7.7 cm$^{-1}$ = $\Delta-V_{00}$, and the shift of the $d_5^*-d_0^-$ origin of the asymmetric DPE-$d_5$ relative to the DPE-$d_{10}$ origin, 7.3 cm$^{-1}$ = -$\Delta-V_{00}$. The estimated values of $\Delta$ and $V_{00}$ obtained using this approach are reported in Table 2.7. For both anti and gauche conformers, $V_{00}$ has a negative sign, indicating that the assigned origins in the spectra of the symmetric isotopomers are for the $S_1 \leftarrow S_0$ transitions,
which is consistent with the blue-shifts of the localized electronic origins of p-DPE-d$_1$ and DPE-d$_5$ with respect to those of p-DPE-d$_2$ and DPE-d$_{10}$, respectively.

Table 2.7 Exciton coupling energies, $V_{00}$ (cm$^{-1}$), and zero point energy shifts, $\Delta$ (cm$^{-1}$), calculated according to the procedure outlined in ref. 31.

<table>
<thead>
<tr>
<th>Pair of isotopomers</th>
<th>Gauche</th>
<th>Anti</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_{00}$</td>
<td>$\Delta$</td>
</tr>
<tr>
<td>DPE-d$_0$/p-DPE-d$_1$/p-DPE-d$_2$</td>
<td>-4.9</td>
<td>0.7</td>
</tr>
<tr>
<td>DPE-d$_0$/DPE-d$<em>5$/DPE-d$</em>{10}$</td>
<td>-7.5</td>
<td>0.2</td>
</tr>
<tr>
<td>M$_2$DPE-d$_0$/M$_2$DPE-d$_2$/M$_2$DPE-d$_4$</td>
<td>-3.9</td>
<td>-0.6</td>
</tr>
</tbody>
</table>

The $S_2 \leftarrow S_0$ origins of the gauche and anti conformers of DPE are forbidden in the spectra of the symmetric isotopomers of DPE. The lower symmetry of the two conformers of $\alpha$-DPE-d$_1$ and $\alpha$-DPE-d$_2$ can render transitions that are strictly forbidden in the symmetric isotopomers weakly allowed. A small peak at 11.9 cm$^{-1}$ from the second origin of the gauche conformer of $\alpha$-DPE-d$_1$ can be assigned as the $S_2 \leftarrow S_0$ origin of the gauche conformer, responsible for the second origin. The larger blue shift of the second origin implies larger perturbation of the vibronic structure induced by the single deuterium atom in $\alpha$ position than in the case of the first origin, and this may lead to a weakly allowed $S_2 \leftarrow S_0$ origin of the more
perturbed gauche conformer that is responsible for the second origin. A number of very weak bands at the blue side of the anti conformer origin in the spectrum of DPE-d₀ have been assigned to combinations and overtones of the three active low frequency fundamentals of the gauche conformer. Similar bands also appear in the spectra of α-DPE-d₁ and α-DPE-d₂, the intensity of the peak at 70.8 cm⁻¹ from the gauche origin of DPE-d₀ increased significantly in the spectrum of α-DPE-d₁. The plausible interpretation of the enhanced intensity of this peak in the spectrum of α-DPE-d₁ is that the peak is due to two overlapping transitions, a combination (43 + 28 cm⁻¹) of the gauche conformer fundamentals and the $S_{2} ← S_{0}$ origin of the anti conformer, with the latter being the dominant contributor to the enhanced intensity because the peak is not split. Two weak bands appear at 12.6 cm⁻¹ and 8.2 cm⁻¹ to the blue of the $0^{0}_{0}$ bands of the gauche and anti conformers, respectively, in the spectrum of α-DPE-d₂. The two bands which have no counterparts in the spectra of the symmetric isotopomers are assigned as the $S_{2} ← S_{0}$ origins of the two conformers, accordingly.

The electronic origins of ring deuterated toluenes are blue-shifted by an average of 33 cm⁻¹ per deuterium,³² the isotope effect on the $0^{0}_{0}$ energies is additive. Therefore, one would expect the $0^{0}_{0}$ bands of the gauche and anti conformers of DPE-d₁₀ to blue-shift by about 330 cm⁻¹ relative to the $0^{0}_{0}$ bands of the corresponding DPE-d₀ conformers. However, the origins of DPE-d₁₀ conformers are blue-shifted by ca. 166 cm⁻¹. Similarly, the origins of the gauche and anti conformers of p-DPE-d₂ are blue-shifted by ca. 31 cm⁻¹ relative to those of the corresponding DPE-d₀ conformers. The observed blue-shifts of DPE-d₅ and p-DPE-d₂ are essentially equal to the blue-shifts of the origins of toluene-d₅ (165.9 cm⁻¹) and p-toluene-d₁ (30.7 cm⁻¹) relative to the origin of toluene-d₀.³² Therefore, the deuterium effect on the $0^{0}_{0}$ energies of the symmetric
isotopomers of DPE is equally shared by the two exciton states of the symmetrical isotopomers; in other words the allowed exciton state goes with one half of the deuterium effect, the other half goes with the forbidden exciton state.

Asymmetric deuteration perturbs the vibronic structure of bichromophores. The perturbation can be characterized by the detuning energy, $\delta$, (equation 1.3). By definition, the detuning energy, $\delta$, of the asymmetrically deuterated isotopomers of DPE is the interval between the $0^0_0$ transition energies of toluene-d$_0$ (the presumed monomer of DPE) and the appropriate toluene-d$_n$. For example, $\delta$ of p-DPE-d$_1$ is equal to the difference in the $0^0_0$ transition energies of toluene-d$_0$ and p-toluene-d$_1$, $\Delta E$ is the observed energy gap between the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ origins of p-DPE-d$_1$. Alternatively, $\delta$ can be taken as the difference in the $0^0_0$ transition energies of DPE-d$_0$ and p-DPE-d$_2$. Generally, $\Delta E$ is the energy gap between the observed energies of the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ origins of the asymmetrically deuterated isotopomers; $\delta$ is the difference in the $0^0_0$ transition energies of DPE-d$_0$ and the appropriate symmetric DPE-d$_n$. The experimental values of $\delta$ and $\Delta E$ are listed in Table 2.8. As the perturbation increases, the intensity of the $S_2 \leftarrow S_0$ origins increases relative to the intensity of the $S_1 \leftarrow S_0$ origins. In the limit of complete delocalization ($\delta = 0$, $\Delta E = 2V_{00}$), the $S_2 \leftarrow S_0$ transitions of the symmetric isotopomers of DPE conformers are forbidden. The $S_2 \leftarrow S_0$ origins of $\alpha$-DPE-d$_2$ are weakly allowed because of the perturbation induced by the asymmetric deuteration. Apparently, this perturbation is not enough to cause complete localization of the vibronic excitation ($\delta \leq \Delta E$). In the limit of complete localization ($\delta \sim \Delta E$), the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ origins have comparable intensities as seen in the spectra of DPE-d$_5$ and p-DPE-d$_1$. 
Table 2.8 Experimental values of δ and ΔE.

<table>
<thead>
<tr>
<th>Pair of isotopomers</th>
<th>Gauche</th>
<th></th>
<th>Anti</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔE</td>
<td>δ</td>
<td>ΔE</td>
<td>δ</td>
</tr>
<tr>
<td>DPE-d₀/α-DPE-d₂/α,α’-DPE-d₄</td>
<td>12.6</td>
<td>10.9</td>
<td>8.2</td>
<td>6.7</td>
</tr>
<tr>
<td>DPE-d₀/p-DPE-d₁/ p-DPE-d₂</td>
<td>29.3</td>
<td>30.7</td>
<td>31.6</td>
<td>30.6</td>
</tr>
<tr>
<td>DPE-d₀/DPE-d₅/DPE-d₁₀</td>
<td>165.4</td>
<td>165.8</td>
<td>166.3</td>
<td>166.2</td>
</tr>
<tr>
<td>M₂DPE-d₀/α-M₂DPE-d₂/α,α’-M₂DPE-d₄</td>
<td>10.4</td>
<td>9.2</td>
<td>7.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The above analyses of the experimental data yield average exciton splittings, 2V₀₀, of 12.0 cm⁻¹ and 4.3 cm⁻¹ for the gauche and anti conformers, respectively. A Franck-Condon factor (FC₀₀) of 0.25 was estimated for toluene by dividing the area under the 0⁰ band to that under the whole Lₐ band of the room temperature absorption spectrum of toluene. Equation 1.2 was then used to estimate the experimental values of V. The obtained values of V are 24.0 cm⁻¹ and 8.6 cm⁻¹ for the gauche and anti conformers, respectively.

The Forster model of energy transfer has been described in chapter 1. Herein, equation 1.7 is used to calculate the dipole-dipole coupling energies, Vₐ-d. The parameters used for the calculations, and the obtained values of Vₐ-d are listed in Table 2.9. The two localized TDMs of the anti conformer lie on the same plane, and are parallel to each other. The in-phase combination of the localized TDMs is higher in energy than the out-of-phase combination. The latter combination of two identical but opposing TDMs is zero. Thus, the dipole-dipole model
predicts allowed \( S_2 \leftarrow S_0 \) transition and forbidden \( S_1 \leftarrow S_0 \) transition of the anti conformer. The two localized TDMs of the gauche conformer are essentially parallel (owing to the 33° rotation of the localized TDMs from short axes of the excited phenyl rings of the gauche conformer); hence, equation 1.8 predicts the \( S_1 \leftarrow S_0 \) transition to be 48 times more intense than the \( S_2 \leftarrow S_0 \) transition.

The dipole-dipole model underestimates the magnitudes of V in both conformers. The results of the dipole-dipole model qualitatively agree with the predictions of the supramolecular model. According to the latter model, the electronic coupling energy, V, is equal to the half of the energy gap between the calculated \( S_1 \leftarrow S_0 \) and \( S_2 \leftarrow S_0 \) vertical excitation energies of a bichromophore with identical chromophores. The intensities of the \( S_1 \leftarrow S_0 \) and \( S_2 \leftarrow S_0 \) transitions are proportional to their oscillator strengths.\(^{10, 13, 14, 34, 35}\) As seen in Table 2.2, the computed \( S_2 \leftarrow S_0 \) transition of the gauche conformer is 53 times weaker than the \( S_1 \leftarrow S_0 \) transition; the \( S_1 \leftarrow S_0 \) transition of anti conformer is forbidden. The supramolecular model also suggests that the electronic coupling energy is about nine times higher in the gauche conformer (43 cm\(^{-1}\)) than in the anti conformer (5 cm\(^{-1}\)). Thus, the supramolecular model underestimates the coupling in the anti conformer, and overestimates it in the gauche conformer. Both supramolecular and dipole-dipole models predict incorrect ordering of the \( S_1 \leftarrow S_0 \) and \( S_2 \leftarrow S_0 \) transitions of the anti conformer.
Table 2.9 Parameters used for calculating $V_{d-d}$, and the obtained values of $V_{d-d}$ of the conformers of M$_2$DPE and M$_2$DPE.\textsuperscript{a,b}

<table>
<thead>
<tr>
<th></th>
<th>$R$, Å</th>
<th>$\varphi$, °</th>
<th>$\theta_1$, °</th>
<th>$\theta_2$, °</th>
<th>$\kappa$</th>
<th>$\nu_0$, cm$^{-1}$</th>
<th>$f$</th>
<th>$V_{d-d}$, cm$^{-1}$</th>
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<tr>
<td><strong>DPE</strong></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Gauche</td>
<td>4.96</td>
<td>0.0</td>
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<td>132.5</td>
<td>-1.3</td>
<td>37484</td>
<td>0.0031</td>
<td>-9.1</td>
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<td>6.60</td>
<td>9.3</td>
<td>90.0</td>
<td>90.0</td>
<td>1.0</td>
<td>37484</td>
<td>0.0031</td>
<td>3.1</td>
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<tr>
<td><strong>M$_2$DPE</strong></td>
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<tr>
<td>Gauche</td>
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<td>69.9</td>
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<td>-13.1</td>
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<td>90.0</td>
<td>1.0</td>
<td>36733</td>
<td>0.0059</td>
<td>5.9</td>
</tr>
</tbody>
</table>

$\textsuperscript{a}$The geometrical parameters, $R$, $\theta_1$, $\theta_2$ and $\varphi$ are defined in Fig. 1.2. $\textsuperscript{b}$The values of $\nu_0$ and $f$ were taken from ref. 38 for toluene and p-xylene. $\textsuperscript{c}$Localized TDMs form an angle of 30 ° with the short axes of the excited rings. $\textsuperscript{d}$Localized TDMs form an angle of 60 ° with the short axes of the excited rings.

Through-bond exciton interactions generally depend on the number of $\sigma$ bonds between the chromophores, and the energy gap between the aromatic ring localized $\pi\pi^*$ states and aliphatic bridge localized $\sigma\sigma^*$ states.\textsuperscript{11-13,15,34,35} These parameters are expected to be similar in both gauche and anti conformers. For instance, the calculated value of the through-bond coupling energy that influences the length of the central $C_{sp^3}-C_{sp^3}$ bond of DPE is 0.3 eV for both conformers of the molecule.\textsuperscript{36} The small effects of orbital overlap dependent exciton interactions can be inferred from the calculated molecular orbitals. Out of the eight molecular orbitals (HOMO-3 To LUMO+3) that make dominant contributions to the vertical $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of the two conformers, only the LUMO of the gauche conformer extends over the two phenyl rings. The higher values of the observed and calculated exciton couplings in the gauche conformer
relative to those in the anti conformer are certainly caused the differences in the inter-
cromophore distances, \( R \), and the relative orientations of the phenyl chromophores.

### 2.4.2 Exciton couplings in M\(_2\)DPE

The peak at 8.1 cm\(^{-1}\) to the blue of the \( S_0^0 \) band of the gauche conformer of M\(_2\)DPE-d\(_0\) is assigned as the \( S_2 \leftrightarrow S_0 \) origin of the gauche conformer. This assignment is supported by the similarity in the values of the observed and calculated exciton splittings, \( 2V_{00} \). The latter were calculated according to the procedure described above for DPE, the results are listed in the last row of Table 2.7. The electronic origins of the \( S_2 \leftrightarrow S_0 \) and \( S_2 \leftrightarrow S_0 \) transitions of the anti and gauche conformers of \( \alpha\)-M\(_2\)DPE-d\(_2\) are separated by 7.5 cm\(^{-1}\) and 10.4 cm\(^{-1}\), respectively. A FC\(_{00}\) of 0.25 was also estimated for p-xylene (the presumed monomer of M\(_2\)DPE) by dividing the area of under the \( S_0^0 \) band to that under the whole L\(_b\) band of the room temperature absorption spectrum of p-xylene. Equation 1.2 was then used to estimate the experimental values of the electronic coupling energy, \( V \). The estimated values of \( V \) of the gauche and anti conformers of M\(_2\)DPE are 16.2 cm\(^{-1}\) and 6.4 cm\(^{-1}\), respectively.

The calculated values of \( V_{d-d} \) of M\(_2\)DPE conformers are higher than those of the corresponding DPE conformers. The supramolecular model also predicted higher exciton coupling in the anti conformer of M\(_2\)DPE than in the anti conformer of DPE. However, the experimental exciton splittings are slightly higher in DPE conformers. Therefore, the predictions of the two theoretical models are not consistent with the experimental results.

The observation of allowed \( S_2 \leftrightarrow S_0 \) origin of the gauche conformer of M\(_2\)DPE can be rationalized by the computed orientations of the localized TDMs. Unlike in the gauche
conformer of DPE where the localized TDMs are essentially parallel such that the antisymmetric vector sum of the TDMs almost vanishes, the localized TDMs of the gauche conformer of M₂DPE is rotated by 67 °; hence both \( S_1 \leftarrow S_0 \) and \( S_2 \leftarrow S_0 \) transitions have non zero TDMs. Equation 1.8 predicts slightly more intense (by a factor of 1.2) \( S_2 \leftarrow S_0 \) transition of the gauche conformer of M₂DPE. It has been reported that the computed orientations of TDM in toluene changes by up to ± 32 ° upon rotation of the methyl group.\(^{37}\) Therefore, the orientations of the localized TDMs of M₂DPE conformers may not be as accurate as those of DPE. Nevertheless, the experimental results are reasonably explained by the computed orientations of the localized TDMs.

In spite of the similar geometrical structures and symmetries of M₂DPE and DPE in the ground and excited states, methyl substitution perturbs the electronic structure of the aromatic chromophores, red-shifting their excitation energies and rendering the \( S_2 \leftarrow S_0 \) transition of the gauche conformer weakly allowed. It is interesting to note that the CIS calculations captured these perturbations well, predicting about 900 cm\(^{-1}\) red-shift of M₂DPE conformers relative to the corresponding DPE conformers, more intense transitions of M₂DPE, and substantially lower \( S_2 \leftarrow S_0 \) \( / S_1 \leftarrow S_0 \) intensity ratio for the gauche conformer of M₂DPE than for the gauche conformer of DPE.
2.5 Conclusions

The observed splittings of the first four bands in the spectra of α-DPE-d₁ and α,α′-DPE-d₂ provide unambiguous evidence in support of the assignments of the observed vibronic bands to the gauche and anti conformers. A gauche/anti conformer ratio of 4.15 was estimated at 100 °C, leading to the energy difference, E_{anti} – E_{gauche} of 189 cm⁻¹. The spectra of p-DPE-d₁ and DPE-d₅ feature two localized electronic origins for the deuterated and undeuterated halves of the gauche and anti conformers, respectively. Therefore, the two phenyl rings of both gauche and anti conformers are symmetry equivalent.

The symmetric isotopomers and slightly perturbed asymmetric isotopomers (α-DPE-d₁, α-DPE-d₂) have identical low frequency vibronic structure, whereas DPE-d₅ exhibits different activity in the low frequency vibronic transitions. The three low frequency vibronic transitions of the gauche conformers of the symmetric isotopomers and the slightly perturbed asymmetric isotopomers of DPE and M₂DPE have been assigned with the support of HF/6-311G(d,p) calculated S₀ frequencies. On the other hand, assignment of the localized vibronic transitions of the gauche conformer of DPE-d₅ is assisted by the CIS/6-311G(d,p) calculated frequencies of the optimized non symmetric gauche conformer in the S₁ state.

CIS/6-311G(d,p) calculations predicted a double minimum S₁ potential energy surface along the ring breathing coordinate, and energetic preference of localized S₁ ← S₀ excitation of both conformers of DPE and M₂DPE. The calculations support the assumption that the two molecules are weakly coupled bichromophores. The exciton splittings in the gauche and anti conformers of DPE and M₂DPE have been estimated by analyzing the frequencies of the 0₀ transitions of closely related pair of deuterated isotopomers. The calculated values of Vₐ·d of M₂DPE conformers are higher than those of the corresponding DPE conformers. However, the
experimental exciton splittings are slightly higher in DPE conformers. The \( S_2 \leftarrow S_0 \) transitions of both gauche and anti conformers of DPE, as well as the anti conformer of M\(_2\)DPE are forbidden. However, the \( S_2 \leftarrow S_0 \) transition of the gauche conformer of M\(_2\)DPE is weakly allowed. The observation of allowed \( S_2 \leftarrow S_0 \) transition of the gauche conformer of M\(_2\)DPE and forbidden \( S_2 \leftarrow S_0 \) transitions of DPE conformers was rationalized by the computed orientations of the localized transition dipole moments. Both supramolecular and dipole-dipole models predicted incorrect ordering of the \( S_1 \leftarrow S_0 \) and \( S_2 \leftarrow S_0 \) transitions of the anti conformers of DPE and M\(_2\)DPE.

### 2.6 References


CHAPTER 3. MOLECULAR STRUCTURE AND EXCITON COUPLING
IN 5,6,11,12-TETRAHYDRODIBENZO[a,e]CYCLOOCTENE.

3.1 Introduction

The conformations of 5,6,11,12-tetrahydrodibeno[a,e]cyclooctene (THDC), also known as [2.2]-orthocyclophane, have been extensively investigated by X-ray and NMR techniques.\textsuperscript{1-3} Previous theoretical studies of THDC have been limited to molecular mechanics and density functional theory (DFT) calculations.\textsuperscript{3, 4} The calculations predicted three stable ground state conformers. The structures of the three stable conformers are displayed in Figure 3.2. The twist-boat (TB) and chair (C) conformers have been observed using NMR techniques in solution.\textsuperscript{1, 3} X-ray studies show that only the C conformer is present in the crystal.\textsuperscript{2} The conformations of THDC have not been studied in the gas phase.

The photophysical properties of THDC have been reported by Longworth et al.\textsuperscript{5} THDC absorbs and fluoresces in the same spectral region as 1,2-diphenylethane and other alkylbenzenes. However, the fluorescence of THDC is unstructured, and has a small quantum yield. The authors concluded that the interaction of the two aromatic rings of THDC in the excited state is weak, and the molecule undergoes geometrical changes upon electronic excitation.\textsuperscript{5} The fact that the interaction of two aromatic rings in the excited state is weak suggests that one can treat THDC as a weakly coupled dimer of o-xylene; hence its excited states can be related to o-xylene like excited states via exciton theory. The excited states of bichromophoric molecules (dimers) are, in the first approximation, the in-phase and out-of-phase linear combinations of the excited states of the interacting chromophores.\textsuperscript{6-8} The scope of exciton
theory is to relate the excited states of bichromophores to those of the constituent chromophores.\textsuperscript{6-9}

In this work, THDC and its two deuterated isotopomers have been synthesized. The structures of the synthesized isotopomers are shown in Figure 3.1. The gas-phase electronic spectra of the THDC isotopomers have been recorded for the first time in a supersonic jet. Analysis of the experimental data in combination with ab initio electronic structure calculations provides information about the equilibrium geometries of THDC conformers in the ground and excited singlet states, the relative populations of the conformers in the gas phase, and the exciton coupling energies.

![Figure 3.1 Investigated isotopomers of THDC.](image-url)
3.2 Experimental

3.2.1 Synthesis

**THDC-d\(_0\)**

A modified procedure of Boudjouk et al. was used to synthesize THDC in 80 % yield.\(^{10}\) The procedure involves sonication of \(\alpha,\alpha'\)-dibromoxylene (7.6 mmol) and lithium granules (30 mmol) in 15 ml of THF under argon atmosphere. After three hours of sonication at room temperature, the reaction mixture was cooled to ca. 0 °C. 20 ml of cold water was then slowly added to destroy the remaining unreacted lithium granules. The organic layer was extracted with diethylether. The crude product was purified by column chromatography on silica gel (petroleum ether) to give pure THDC-d\(_0\).

**THDC-d\(_4\) and THDC-d\(_8\)**

A statistical mixture of THDC-d\(_0\), THDC-d\(_4\) and THDC-d\(_8\) was synthesized by coupling of \(\alpha,\alpha'\)-dibromoxylene-d\(_4\) (4 mmol) and \(\alpha,\alpha'\)-dibromoxylene-d\(_0\) (4 mmol) following the same procedure as for THDC-d\(_0\). \(\alpha,\alpha\)-Dibromoxylene-d\(_4\) was synthesized in two steps. A mixture of phthalic acid-d\(_4\) (5.8 mmol) and LiAlH\(_4\) (6.5 mmol) in 20 ml of THF was refluxed for 15 hours to yield \(\alpha,\alpha'\)-benzenedimethanol-d\(_4\). Reaction of \(\alpha,\alpha'\)-benzenedimethanol-d\(_4\) (5 mmol) with 1.5 equivalent of PBr\(_3\) in 20 ml of dichloromethane at 20 °C for two hours yielded \(\alpha,\alpha'\)-dibromoxylene-d\(_4\).

The identity of the compounds was confirmed by GC/MS analysis.
3.2.2 Spectroscopy

The supersonic jet spectrometer used has been described in chapter 1. The sample of THDC isotopomers was heated to 140 °C, and seeded in a helium carrier gas at a backing pressure of 3 atm.

3.3 Results and Discussion

3.3.1 Ab initio Calculations

Ground state optimizations were carried out at the Hartree-Fock (HF), density functional theory (DFT) with the B3LYP functional, and second-order Møller–Plesset perturbation (MP2) levels of theory. Configuration interaction singles (CIS) method was used for computing the vertical excitation energies, and optimizations of the excited singlet states. The computations were performed using the 6-31+G(d) basis set. HF optimized $S_0$ geometries were used for the calculations of the vertical excitation energies.

The calculated $S_0$ relative energies of the three stable conformers of THDC are presented in Table 3.1. The T conformer is predicted to be the highest in energy by the HF, DFT, and MP2 methods. Therefore, the T conformer may not be observed in the jet experiments owing to negligible Boltzmann factors at 140 °C. The MP2 calculations predicted more stable TB conformer. Whereas, the C conformer is predicted to the most stable at the HF and DFT levels. The major differences between the MP2 and HF/DFT geometries are in the $C_{sp^2}-C_{sp^3}-C_{sp^3}$ angles and the $C_{sp^2}-C_{sp^3}-C_{sp^3}-C_{sp^2}$ dihedrals of the TB conformer, which are lower in the MP2 geometry by up to 3° and 7°, respectively. The differences between the MP2 and HF/DFT results are attributed the fact that the MP2 method accounts for the non-bonded intramolecular dispersion interactions between the $\pi$ electron clouds of the aromatic rings. These interactions are
particularly important in the TB conformer, where the aromatic rings are closer and partially overlapping.\textsuperscript{11, 12}

**Table 3.1** Relative energies (in cm\(^{-1}\)) of the three stable conformers of THDC at various levels of theory with 6-31G+(d) basis set.

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Symmetry</th>
<th>HF</th>
<th>DFT</th>
<th>MP2</th>
<th>MP2//HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB</td>
<td>C(_2)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>C(_{2h})</td>
<td>-294</td>
<td>-314</td>
<td>983</td>
<td>488</td>
</tr>
<tr>
<td>T</td>
<td>D(_2)</td>
<td>1064</td>
<td>910</td>
<td>2333</td>
<td>1867</td>
</tr>
</tbody>
</table>

The boat (B) conformation corresponds to a transition state between two equivalent TB conformers, as the single imaginary frequency that is associated with torsions about the central C\(_{sp3}\)-C\(_{sp3}\) bonds implies. The DFT and MP2 calculated barrier heights are 2.4 kcal/mol and 3.0 kcal/mol, respectively. The calculated barriers are significantly lower than the barrier of about 7 kcal/mol estimated from NMR studies in CD\(_2\)Cl\(_2\) solution.\textsuperscript{3} The disagreement between the theoretical results of the isolated molecules and solution experiments can be attributed to the possibility of better stabilizing interactions of the polar solvent with the less symmetric TB conformer than with the more compact C\(_{2v}\) symmetric transition state.
Figure 3.2 MP2/6-31+G(d) optimized ground state structures of the (a) Chair (C), (b) Twist-Boat (TB), (c) Twist (T), and (d) Boat (B) conformers of THDC. The boat conformation corresponds to a transition state between two equivalent TB conformers.

Full geometric optimizations of the first excited singlet states of the C and TB conformers without any symmetry constraints were carried out. The optimized structures are confirmed to be local minima by the subsequent normal mode analyses. The results indicate that only one of the aromatic rings is significantly affected by the $S_1 \leftrightarrow S_0$ electronic excitation, as evidenced by the average increase in the $C_{sp2}-C_{sp2}$ bond lengths of only one aromatic ring by ca. 0.026 Å with
respect to the HF $S_0$ values. Electronic excitation to the $S_1$ state is predicted to be accompanied by the lowering of molecular symmetry of the C and TB conformers from $C_{2h}$ and $C_2$ in the $S_0$ state to $C_s$ and $C_1$, respectively, in the $S_1$ state.

The transition charge density surfaces for the localized $S_1 \leftarrow S_0$ transitions are displayed in Figure 3.3a and 3.3b. The surfaces reveal the $L_b$ nature of the optimized $S_1$ states (nodes on atoms), and the localized nature of the electronic excitation. These results indicate weak interactions between the two aromatic chromophores in the excited singlet states; therefore, the electronic spectrum of THDC can be analyzed within the framework of the weak coupling case of exciton theory.

The $S_1$ states of the C and TB conformers were also optimized under the constraints of $C_{2h}$ and $C_2$ symmetry of C and TB conformers, respectively. A single imaginary frequency appears in the results of the subsequent frequency calculations of both conformers. The imaginary frequency is associated with the expansion of one aromatic ring and contraction of the other. Therefore, the symmetric conformers are transition states along the aromatic ring breathing coordinate of the $S_1$ potential energy surface. The energy gaps between the optimized low symmetry $S_1$ minima and the symmetric $S_1$ maxima of the C and TB conformers are 543 cm$^{-1}$ and 252 cm$^{-1}$, respectively.
Figure 3.3 Transition density surfaces for the localized $S_1 \leftarrow S_0$ transitions of the (a) C, and (b) TB conformers. The computed orientations of the transition dipole moments (TDMs) for the localized $S_1 \leftarrow S_0$ transitions are shown in (c) and (d).
Table 3.2 Calculated vertical $S_1 \leftrightarrow S_0$ and $S_2 \leftrightarrow S_0$ excitation energies ($E_1$ and $E_2$, cm$^{-1}$) with their oscillator strengths ($f_1$ and $f_2$), and localized $S_1 \leftrightarrow S_0$ adiabatic excitation energies ($E_{ad}$, cm$^{-1}$) of the TB and C conformers.

<table>
<thead>
<tr>
<th>Conformer</th>
<th>$E_1$</th>
<th>$f_1$</th>
<th>$E_2$</th>
<th>$f_2$</th>
<th>$E_2-E_1$</th>
<th>$E_{ad}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB</td>
<td>48440</td>
<td>0.0051</td>
<td>48807</td>
<td>0.0016</td>
<td>367</td>
<td>47635</td>
</tr>
<tr>
<td>C</td>
<td>48713</td>
<td>0.0042</td>
<td>48772</td>
<td>0.0000</td>
<td>59</td>
<td>47809</td>
</tr>
</tbody>
</table>

3.3.2 R2PI Spectra of THDC-d$_0$ and THDC-d$_8$

The spectra of THDC-d$_0$ obtained at two different laser powers are presented in Fig. 3.4a and 3.4b. The first band in the spectrum of DPE-d$_0$ appears at 36956.3 cm$^{-1}$, scanning to the red of this peak didn’t reveal additional spectral features. Therefore, the band at 36956.3 cm$^{-1}$ can be assigned to the electronic origin of one conformer. The relative intensity of the peak at 37147.9 cm$^{-1}$ did not increase when high laser power is used, indicating that the peak is an electronic origin of another stable ground state conformer.$^{14}$ The two electronic origins can be assigned by comparison with spectrum of 1,2-diphenylethane discussed in the previous chapter. The electronic origin of the compact gauche conformer of 1,2-diphenylethane is redder than that of the extended anti conformer. The first intense peak at 36956.3 cm$^{-1}$ is thus assigned to the electronic origin of the TB conformer, and the peak at 37147.9 cm$^{-1}$ is assigned to the origin of the C conformer.
Further evidence in support of the presence of only two conformers is provided by the spectrum of THDC-d₈, shown in Fig. 3.5a, which is qualitatively similar to that of THDC-d₀, as both have the same symmetry. The electronic origins of the TB and C conformers are however, blue-shifted by 130.1 cm⁻¹ and 130.8 cm⁻¹, respectively, due to the changes of zero point vibrational energies in the ground and excited states upon deuteration. Listed in Table 3.3 are the frequencies of the observed bands in the spectra of THDC-d₀ and THDC-d₈, the isotope effects
in THDC-d₈, and the proposed assignments of the vibronic transitions. The isotope effects, IE, were calculated as the percentage decrease of the frequencies of the vibronic bands in the spectrum of THDC-d₈ with respect to the frequencies of the corresponding bands in the spectrum of THDC-d₀ using the expression:

\[
IE = \frac{\nu_{d₈} - \nu_{d₀}}{\nu_{d₀}} \times 100\%
\]

As seen in Table 3.3, the band at 37147.9 cm⁻¹ has a negligible isotope effect, confirming its assignment to the electronic origin of the C conformer. All other bands have isotope effects of at least 3%.

Adiabatic excitation energy is the difference in the total energies of the CIS optimized S₁ minimum and the HF optimized S₀ minimum of each conformer. The energy gap between the adiabatic excitation energies of the C and TB conformers is 174 cm⁻¹ is very close to the energy gap of 191.6 cm⁻¹ between the electronic origins of the two conformers. Indeed, a linear correlation between the CIS calculated adiabatic excitation energies and the observed energies of 0⁰ transitions of a series of polycyclic aromatic compounds was recently reported by Sotoyoma et al.
**Figure 3.5** R2PI spectra of (a) THDC-d$_8$, (b) THDC-d$_4$, and (c) THDC-d$_0$

Two localized electronic origins of each conformer are seen in the spectrum of THDC-d$_4$. 
THDC has 90 normal modes, listed in Table 3.4 are the calculated frequencies and approximate descriptions of the five lowest frequency modes of the TB conformer in the S\textsubscript{0} and S\textsubscript{1} states. A progression with a fundamental frequency of 28.5 cm\textsuperscript{-1} is built off of the origin of the TB conformer. The first two calculated lowest frequency modes differ significantly in frequency (40 cm\textsuperscript{-1} vs. 79 cm\textsuperscript{-1} in the S\textsubscript{1} state). Therefore, the plausible assignment for the 28.5 cm\textsuperscript{-1} fundamental is to the lowest frequency mode, labeled v\textsubscript{1} in Table 3.4. This mode involves symmetric flapping (butterfly motion) of the two aromatic rings. The peak at 114.4 cm\textsuperscript{-1} can be assigned to mode v\textsubscript{3} or v\textsubscript{4} based on the similar values of the observed and calculated frequencies. This mode appears in combination with mode v\textsubscript{1} at 143.8 cm\textsuperscript{-1}. Similarly, the very weak band at 176.3 cm\textsuperscript{-1} can be assigned to mode v\textsubscript{5}. The peak at 100.0 cm\textsuperscript{-1} is not associated with an overtone or combination band; hence, it is tentatively assigned to the S\textsubscript{2} ← S\textsubscript{0} origin of the TB conformer.

Most of the low frequency modes of the C conformer are non-totally symmetric; hence, they are not expected to be active in the one-photon spectrum.

The appearance of a progression in the flapping mode with the first member being more intense than the electronic origin indicates structural changes in the excited state. The changes would then involve the four C\textsubscript{sp2}-C\textsubscript{sp3}-C\textsubscript{sp3} angles. CIS calculations predicted a slight but noticeable decrease (by ~0.7°) in the values of the C\textsubscript{sp2}-C\textsubscript{sp3}-C\textsubscript{sp3} angles in the localized S\textsubscript{1} state of the TB conformer relative to the HF S\textsubscript{0} values. THDC does not form intramolecular excimer even at room temperature, an indication that face-to-face arrangement of the aromatic rings is not achieved in the excited states.\textsuperscript{5} This observation can be rationalized by the present findings that most of the geometrical rearrangements are associated with the flapping mode.
Table 3.3  Assignment of the observed bands in the R2PI spectra of THDC-d$_0$ and THDC-d$_8$

<table>
<thead>
<tr>
<th></th>
<th>THDC-d$_0$</th>
<th></th>
<th>THDC-d$_8$</th>
<th></th>
<th></th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition energy</td>
<td>Vibrational energy, $\nu_{d0}$ (cm$^{-1}$)</td>
<td>Transition energy</td>
<td>Vibrational energy, $\nu_{d8}$ (cm$^{-1}$)</td>
<td>Isotope effect, ($%$)</td>
<td>Assignment</td>
<td></td>
</tr>
<tr>
<td>36956.3</td>
<td>0.0</td>
<td>37086.4</td>
<td>0.0</td>
<td></td>
<td></td>
<td>$S_1 \leftarrow S_0$ origin of the TB</td>
</tr>
<tr>
<td>36984.8</td>
<td>28.5</td>
<td>37113.3</td>
<td>26.9</td>
<td>-5.6</td>
<td>$v_1$</td>
<td></td>
</tr>
<tr>
<td>37012.7</td>
<td>56.4</td>
<td>37139.4</td>
<td>53.0</td>
<td>-6.0</td>
<td>2$v_1$</td>
<td></td>
</tr>
<tr>
<td>37039.7</td>
<td>83.4</td>
<td>37164.9</td>
<td>78.5</td>
<td>-5.9</td>
<td>3$v_1$</td>
<td></td>
</tr>
<tr>
<td>37056.3</td>
<td>100.0</td>
<td>37183.2</td>
<td>96.8</td>
<td>-3.1</td>
<td>$S_1 \leftarrow S_0$ origin of the C conformer</td>
<td></td>
</tr>
<tr>
<td>37065.7</td>
<td>109.4</td>
<td>37189.3</td>
<td>102.9</td>
<td>-5.9</td>
<td>4$v_1$</td>
<td></td>
</tr>
<tr>
<td>37070.7</td>
<td>114.4</td>
<td>37197.3</td>
<td>110.9</td>
<td>-3.1</td>
<td>$v_3$ or $v_4$</td>
<td></td>
</tr>
<tr>
<td>37100.1</td>
<td>143.8</td>
<td>37225.4</td>
<td>139.0</td>
<td>-3.3</td>
<td>$v_3$ (or $v_4$)+ $v_1$</td>
<td></td>
</tr>
<tr>
<td>37132.6</td>
<td>176.3</td>
<td>37257.4</td>
<td>171.0</td>
<td>-3.0</td>
<td>$v_5$</td>
<td></td>
</tr>
<tr>
<td>37147.9</td>
<td>191.6</td>
<td>37278.7</td>
<td>192.3</td>
<td>0.4</td>
<td>$S_1 \leftarrow S_0$ origin of the C conformer</td>
<td></td>
</tr>
</tbody>
</table>
### Table 3.4 Calculated lowest frequency vibrational modes of the TB conformer.

<table>
<thead>
<tr>
<th>Mode</th>
<th>S0</th>
<th>S1</th>
<th>Approximate description</th>
</tr>
</thead>
<tbody>
<tr>
<td>v1</td>
<td>47</td>
<td>42</td>
<td>40</td>
</tr>
<tr>
<td>v2</td>
<td>95</td>
<td>88</td>
<td>79</td>
</tr>
<tr>
<td>v3</td>
<td>139</td>
<td>127</td>
<td>124</td>
</tr>
<tr>
<td>v4</td>
<td>149</td>
<td>139</td>
<td>127</td>
</tr>
<tr>
<td>v5</td>
<td>178</td>
<td>163</td>
<td>173</td>
</tr>
</tbody>
</table>

The relative abundance of the TB and C conformers was estimated by integrating the area under the origin peak of the C conformer, and the areas under the whole vibronic envelope of the TB conformer in the origin region of the R2PI spectrum. The estimated TB: C population ratio is 9.1:1; thus 90% of THDC exists in the TB conformation at 413 K, the C conformer constitutes the remaining 10%. The Boltzmann distribution law was then used to determine their relative energy, $\Delta E = E_C - E_{TB}$. The statistical weight of 2 for the TB conformer, and the pre-expansion temperature of 413 K were used in the calculations. The estimated value of $\Delta E$ is 435 cm$^{-1}$, in good agreement with the single point MP2 energy of 488 cm$^{-1}$. The latter is about half of the MP2 relative energy on MP2 geometries (Table 3.1). It was concluded from NMR experiments in CD$_2$Cl$_2$ solution that THDC exists as a mixture of the TB (88 %) and C (12 %) conformers. Therefore, the TB conformer predominates in the gas and liquid phases.
3.3.3 Exciton couplings

CIS calculations suggest that it is energetically more favorable for the electronic excitation energy to be localized on one of the two equivalent chromophores of THDC. In reality, however, it is not possible to selectively excite one of the two equivalent chromophores. What actually happens is that the excitation energy is equally shared between the two chromophores via exciton coupling. The strength of the exciton coupling is determined by the electronic coupling energy, $V$.6-9,17,18

The spectrum of THDC-d$_4$ presented in Figure 3.5b was recorded with the purpose of obtaining experimental exciton coupling energies of the C conformer, and confirming the assignment of the $S_2 \leftarrow S_0$ transition of the TB conformer. The C and TB conformers of THDC-d$_4$ have $C_s$ and $C_1$ symmetries, respectively. Listed in Table 3.5 are the frequencies of the observed spectral features of THDC-d$_4$, and their proposed assignments. A four-membered progression with a fundamental frequency of 28.4 cm$^{-1}$ also appears in the spectrum of THDC-d$_4$, indicating similar geometrical structures of all isotopomers of THDC in the ground and excited states.
Table 3.5 Assignment of the observed bands in the R2PI spectrum of THDC-d$_4$.

<table>
<thead>
<tr>
<th>Transition energy, (cm$^{-1}$)</th>
<th>Vibrational energy, $\nu_{d4}$ (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>36993.2</td>
<td>0.0</td>
<td>$S_1 \leftarrow S_0$ origin ($d^+_0 - d_4$), TB conformer</td>
</tr>
<tr>
<td>37021.6</td>
<td>28.4</td>
<td>$\nu_1$</td>
</tr>
<tr>
<td>37049.2</td>
<td>56.0</td>
<td>$2\nu_1$</td>
</tr>
<tr>
<td>37076.1</td>
<td>82.9</td>
<td>$3\nu_1$</td>
</tr>
<tr>
<td>37102.4</td>
<td>109.2</td>
<td>$4\nu_1$</td>
</tr>
<tr>
<td>37151.4</td>
<td>158.2</td>
<td>$S_2 \leftarrow S_0$ origin ($d^+_0 - d_4$), TB conformer</td>
</tr>
<tr>
<td>37154.6</td>
<td>161.4</td>
<td>$S_1 \leftarrow S_0$ origin ($d^+_0 - d_4$), C conformer</td>
</tr>
<tr>
<td>37167.2</td>
<td>174.0</td>
<td></td>
</tr>
<tr>
<td>37169.3</td>
<td>176.1</td>
<td></td>
</tr>
<tr>
<td>37181.3</td>
<td>188.1</td>
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</tr>
<tr>
<td>37187.0</td>
<td>193.8</td>
<td></td>
</tr>
<tr>
<td>37196.3</td>
<td>203.1</td>
<td></td>
</tr>
<tr>
<td>37205.0</td>
<td>211.8</td>
<td></td>
</tr>
<tr>
<td>37217.6</td>
<td>224.4</td>
<td></td>
</tr>
<tr>
<td>37224.6</td>
<td>231.4</td>
<td></td>
</tr>
<tr>
<td>37286.7</td>
<td>293.5</td>
<td>$S_2 \leftarrow S_0$ origin ($d^+_0 - d_4$), C conformer</td>
</tr>
</tbody>
</table>
Four localized electronic origins are identified in the spectrum of THDC-d₄. The four origins are associated with the localized excitations of the deuterated and undeuterated halves of the C and TB conformers, as shown in Figure 3.5b. The $S_2 \leftarrow S_0$ transitions are localized on the deuterated halves; while the $S_1 \leftarrow S_0$ transitions are localized on the undeuterated halves. It is not possible to tell which of the two identical halves of THDC-d₀ or THDC-d₈ is excited because the excitation energy is delocalized over the two equivalent aromatic chromophores.

The method of Baum et al. was used to estimate the exciton splittings, $2V_{00}$, in THDC conformers. The observed $0_0^0$ transition energies of THDC-d₀ and THDC-d₈ (Table 3.4), and the localized $0_0^0$ transition energies of THDC-d₈ (Table 3.5) were used in the calculations. The estimated values of $2V_{00}$ in the TB and C conformers are -101.9 cm⁻¹ and -14.7 cm⁻¹, respectively. These results support the assignment of the band at 100.0 cm⁻¹ in the spectrum of THDC-d₀ to the $S_2 \leftarrow S_0$ origin of the TB conformer. The negative sign of $V_{00}$ indicates that the assigned origins in the spectra of the symmetric isotopomers are for the $S_1 \leftarrow S_0$ transitions, consistent with the blue-shift of the localized origins of THDC-d₄ relative to the corresponding origins of THDC-d₀ and THDC-d₈. The electronic coupling energy, $V$, was calculated using equation 1.2. A Franck-Condon factor, $FC_{0-0}$, of 0.25 was estimated by dividing the area of under the $0_0^0$ band to that under the whole $L_b$ band of the room temperature absorption spectrum of o-xylene. The experimental values of $V$ are 200.0 cm⁻¹ and 29.4 cm⁻¹ for the TB and C conformers, respectively.

The zeroth-order excited states are no longer degenerate in THDC-d₄. Thus, there exists a possibility of resonance and/or near resonance interactions between the vibronic states that are more or less localized on the undeuterated half of THDC-d₄ with those localized on the
deuterated half, and vice versa. This, together with the lower symmetry of THDC-d₄ may lead to a different vibronic activity in the spectrum of THDC-d₄. The bands at 114.4 cm⁻¹ and 143.8 cm⁻¹ above the S₁ ← S₀ origin of THDC-d₀ have no counterparts in the spectrum of THDC-d₄. This makes the proposed assignment of the two bands in the spectra of the symmetrical isotopomers uncertain. Alternatively, the two bands can be assigned to some low frequency modes with frequencies of 14.4 cm⁻¹ and 43.8 cm⁻¹ in the S₂ state of the TB conformer. Nonetheless, the previous assignments seem to be more reasonable because a mode with a small frequency of 14.5 cm⁻¹ seems unlikely.

The transition dipole moments (TDMs) for the localized S₁ ← S₀ transitions of the C and TB conformers form angles of 90 ° and 86 ° with the long axes of the excited aromatic rings, respectively, as shown in Figures 3.3c and 3.3d. The dipole-dipole coupling energies, V_d-d, and the relative intensities of the S₁ ← S₀ and S₂ ← S₀ transitions were calculated using equations 1.7 and 1.8. The input data used for calculating V_d-d, and the obtained values of V_d-d are listed in Table 3.6. Equation 1.8 predicted allowed S₁ ← S₀ transition and forbidden S₂ ← S₀ transition of the C conformer. The S₁ ← S₀ transition of the TB conformer is calculated to be eleven times more intense than the S₂ ← S₀ transition. The dipole-dipole model significantly underestimates the magnitudes of the electronic coupling energies of both conformers. The failure of the dipole-dipole model is most likely caused by the close proximity of the two aromatic chromophores, and very small value of the oscillator strength of the presumed monomer of THDC, o-xylene.
Table 3.6 Parameters used for calculating $V_{d-d}$, and the obtained values of $V_{d-d}$ of the conformers of THDC.$^a$

<table>
<thead>
<tr>
<th></th>
<th>$R$, Å</th>
<th>$\varphi$, °</th>
<th>$\theta_1$, °</th>
<th>$\theta_2$, °</th>
<th>$\kappa$</th>
<th>$\nu_0$, cm$^{-1}$</th>
<th>$f$</th>
<th>$V_{d-d}$, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$^b$</td>
<td>5.91</td>
<td>0.0</td>
<td>13.6</td>
<td>166.4</td>
<td>-1.83</td>
<td>37308</td>
<td>0.0036</td>
<td>-9.2</td>
</tr>
<tr>
<td>TB$^b$</td>
<td>4.48</td>
<td>8.1</td>
<td>52.4</td>
<td>52.4</td>
<td>1.28</td>
<td>37308</td>
<td>0.0036</td>
<td>14.7</td>
</tr>
</tbody>
</table>

$^a$The values of $\nu_0$ and $f$ for o-xylene were taken from ref. 25.

$^b$TDM vectors form an angle of 90° and with the long axes of the aromatic rings.

According to the supramolecular model of bichromophores with identical chromophores,$^{17,20-22}$ the electronic coupling energy, $V$, is equal to the half of the energy gap between the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ vertical excitation energies. The intensities of the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions are proportional to their oscillator strengths. The computed vertical excitation energies and transition dipole moments for the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of the C and TB conformers are listed in Table 3.2. The $S_1$ and $S_2$ states of the C conformer have $B_u$ and $A_g$ symmetries, respectively; hence the $S_2 \leftarrow S_0$ transition of the C conformer is one-photon forbidden. The calculated energy gap between the two states is 59 cm$^{-1}$. The $S_1$ and $S_2$ states of the TB conformer have $B$ and $B'$ symmetries, respectively. Both $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions in the TB conformer are predicted to be allowed by the CIS calculations, the former being ca. three times more intense than the latter. The energy gap between the $S_2$ and $S_1$ states of the TB conformer is 367 cm$^{-1}$. Thus, at the CIS/6-31+G(d) level of theory, the electronic coupling energies in the C and TB conformers are 29.5 cm$^{-1}$ and 183.5 cm$^{-1}$, respectively. These values are essentially equal to the experimental coupling energies of 200 cm$^{-1}$ and 29.4 cm$^{-1}$. However,
it should be noted that the results of the supramolecular model are very sensitive to the level of theory employed,\textsuperscript{17, 20-22} hence the good agreement with the experimental results could be accidental.

The large difference in the coupling energies of the two conformers is attributed to trough-space interactions. Effective orbital overlap between the two rings of the compact TB conformer is possible. Through-bond interactions generally depend on the number of $\sigma$ bonds between the chromophores, and the energy gap between the aromatic ring localized $\pi\pi^*$ states and aliphatic bridge localized $\sigma\sigma^*$ states;\textsuperscript{23} these parameters are expected to be similar in both the C and TB conformers. For instance, the values of the through-bond coupling that influences the length of the central $C_{sp3}$-$C_{sp3}$ of DPE is calculated to be 0.3 eV for both gauche and anti conformers of the molecule.\textsuperscript{24}

### 3.4 Conclusions

90\% of THDC exists in the twist boat (TB) conformation at 413 K, the chair conformer constitutes the remaining 10 \%. Most of the vibronic activity in the spectrum of THDC is associated with the symmetric flapping of the aromatic rings of the TB conformer. The $S_2 \leftrightarrow S_0$ transition of the C conformer is forbidden. The estimated exciton splittings in the spectra of C and TB conformers are 14.7 cm$^{-1}$ and 101.9 cm$^{-1}$, respectively. The observed exciton splitting of the TB conformer is 100 cm$^{-1}$. CIS/6-31+G(d) calculations predicted a double minimum $S_1$ potential energy surface along the ring breathing coordinate, and energetic preference of localized $S_1 \leftrightarrow S_0$ excitation of both conformers. The electronic coupling energies predicted by the dipole-dipole based exciton model are substantially smaller than the experimental couplings. The supramolecular model predicted electronic coupling energies that are very close to the
experimental coupling energies. The $S_2 \leftarrow S_0$ transition of the C conformer is predicted to be forbidden by the dipole-dipole and the supramolecular models.

3.5 References


4.3 Introduction

A large number of experimental and theoretical investigations of cyclopropyl-group containing compounds has revealed the conjugative properties of cyclopropyl ring. Phenylcyclopropanes incorporate two distinct unsaturated systems, the phenyl chromophore and the cyclopropyl ring, adjacent to each other. The structure and properties of phenylcyclopropanes are expected to be strongly influenced by the electronic interaction of the two unsaturated systems. Particularly interesting are 1-methyl-2-phenylcyclopropane (MPCP) and 1,2-diphenylcyclopropane (DPCP). These molecules undergo cis-trans photoisomerization, and have their first singlet absorption bands at ca. 260 nm where alkylbenzenes absorb. The cis and trans isomers of DPCP (cDPCP and tDPCP) do not fluoresce at room temperature, but do so at 77 K, an indication of a barrier to some radiationless transitions that cannot be reached at lower temperatures. On the other hand, the vapor phase fluorescence quantum yield of the trans isomer of MPCP (tMPCP) is higher than that of the closely related alkylbenzenes. Several mechanisms have been proposed to explain the photochemical and photophysical properties of MPCP and DPCP.

The dihedral angles, $\tau_1$ and $\tau_2$, as defined in Figure 4.1, are the most important structural parameters that can be used to qualitatively estimate the extent of electronic interaction between the cyclopropyl and phenyl rings. The electronic interaction is maximized in the bisected conformer. Only the bisected conformer of phenylcyclopropane (PCP) has been observed using electron diffraction, microwave, NMR, X-ray, and REMPI techniques. Two stable
conformers of PCP were predicted by ab initio calculations: the bisected conformer with $\tau_1 = 0^\circ$ and the perpendicular conformer with $\tau_1 = 90^\circ$. The calculated barrier to torsional motion about the C$_{sp}$-C$_{sp}$ bond is less than 1 kcal/mol at the HF, DFT, and MP2 levels of theory.

The first UV absorption band of tDPCP is red-shifted by 3 nm relative to that of PCP; cDPCP and PCP absorb at the same wavelength. This suggests weak intra-molecular exciton interactions in the excited states of both cDPCP and tDPCP. Therefore, one expects that the two isomers of DPCP can be treated as a weakly coupled dimer of benzene linked by a cyclopropyl bridge. The role of the cyclopropyl bridge is to place the two aromatic rings in a fixed orientation (cis or trans), and alter the electronic properties of the two aromatic rings as a result of electronic interactions between the cyclopropyl and phenyl rings. Exciton coupling in multichromophoric systems is basically mediated by electrostatic Coulombic, exchange, and through-bond mediated interactions. Through-bond interactions in bichromophores incorporating aromatic chromophores linked by aliphatic bridges are primarily determined by the number of $\sigma$ bonds between the aromatic chromophores, and the energy gap between the aromatic ring localized $\pi^*$ states and aliphatic bridge localized $\sigma^*$ states. The presence of the strained cyclopropyl bridge is expected to enhance exciton coupling in DPCP when compared with the closely related 1,2-diphenylethane.

Herein, vibrationally resolved electronic spectroscopy in a supersonic jet has been applied for the first time to investigate the factors governing the conformational stabilities of DPCP and MPCP in the ground and excited singlet states, the nature of their lowest excited singlet states, and the effects of the strained cyclopropyl bridge on exciton coupling in DPCP. The experimental results are analyzed with the support of ab initio electronic structure calculations.
Figure 4.1 Minimum energy conformers of MPCP and DPCP at the B3LYP/6-311G(d,p) level: (a) tMPCP, (b) cMPCP, (c) tDPCP, and (d) cDPCP. The dihedral angles, $\tau_1$ and $\tau_2$, are defined as $C_5$-$C_4$-$C_1$-$H_1$ and $C_{11}$-$C_{10}$-$C_2$-$H_2$, respectively.
4.2 Experimental

A 40:60, cis:trans mixture of MPCP was purchased from Frinton labs.

4.2.1 Synthesis

cMPCP

The procedure of Lorenz et al was used to prepare cMPCP.\textsuperscript{17} Diethylzinc (20 mL, 1 M solution in hexanes) was added to dichloromethane (20 mL) at 0 °C under Ar. A solution of trifluoroacetic acid (1.6 mL) in dichloromethane (10 mL) was then added dropwise into the reaction mixture. After stirring for 20 min, a solution of CH\textsubscript{2}I\textsubscript{2} (1.7 mL) in dichloromethane (10 mL) was added. After stirring for another 20 min, a solution of cis-β-methylstyrene (1.2 mL, 10 mmol) in dichloromethane (10 mL) was added. The reaction mixture was stirred for 30 min at room temperature. Thereafter, the reaction mixture was quenched with saturated NH\textsubscript{4}Cl solution. The aqueous layer was extracted with petroleum ether.

Pure tDPCP-d\textsubscript{0}

Isomerically pure tDPCP-d\textsubscript{0} was also synthesized following the procedure of Lorenz et al.\textsuperscript{17} The procedure is slightly different from the one used to prepare cMPCP. Et\textsubscript{2}Zn (20 mL, 1M solution in hexanes) was added to dichloromethane (20 mL) under Ar at 0 °C. A solution of trifluoroacetic acid (1.6 mL) in dichloromethane (10 mL) was then added dropwise into the reaction mixture. After 20 min of stirring, a solution of CH\textsubscript{2}I\textsubscript{2} (1.7 mL) in dichloromethane (10 mL) was added. After stirring for another 20 min, a solution of trans-stilbene (0.9 g, 5 mmol) in dichloromethane (5 mL) was added. The reaction mixture was further stirred for an hour at room temperature. Thereafter, the reaction mixture was quenched with saturated NH\textsubscript{4}Cl solution, and extracted with petroleum ether.
Pure cDPCP-d₀

Pure cDPCP-d₀ was made starting with cis-stilbene following the same procedure as for the pure tDPCP-d₀.

A mixture of cDPCP-d₁ and tDPCP-d₁

A mixture of cDPCP-d₁ and tDPCP-d₁ was synthesized in four steps. Firstly, a mixture of the cis and trans isomers of l-(p-bromophenyl)-2-phenylcyclopropane was made following the procedure of Applequist et al.¹⁸ A solution of NaOH (1.4 g in 5 mL of water) was added to the stirred mixture of p-bromobenzaldehyde (14 mmol) and acetophenone (14 mmol) in ethanol (20 ml). The reaction mixture was stirred at 35 °C for three hours. After cooling to ca. 0 °C, the product (p-bromochalcone) was filtered. A mixture of p-bromochalcone (10 mmol) and 10 mL of 64% hydrazine hydrate was refluxed under Ar for an hour. The reaction mixture was cooled, and then diluted with water (20mL). The pyrazoline obtained after decanting the aqueous layer, was mixed KOH pellets (1 g) and diethylene glycol (20 ml). The reaction mixture was heated at 220 °C for an hour. The reaction mixture was then cooled, and poured into water (50 ml). The organic layer was extracted with ether. The crude product was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 80:20) to give a mixture of the cis and trans isomers of l-(p-bromophenyl)-2-phenylcyclopropane.

A mixture of cDPCP-d₁ and tDPCP-d₁ was prepared by stirring the synthesized mixture of the cis and trans isomers of l-(p-bromophenyl)-2-phenylcyclopropane (8 mmol) and magnesium (40 mmol) in MeOD (10 ml) under reflux conditions for 20 hours. The reaction mixture was quenched with HCl (10 mL, 3 M), and extracted with petroleum ether.
A mixture of \( \text{cDPCP-d}_2 \) and \( \text{tDPCP-d}_2 \)

A mixture of the cis and trans isomers of 1,2-bis(p-bromophenyl)cyclopropane was prepared starting with p-bromobenzaldehyde and p-bromoacetophenone following the same procedure as for the mixture of the cis and trans isomers of 1-(p-bromophenyl)-2-phenylcyclopropane.

A mixture of \( \text{tDPCP-d}_2 \) and \( \text{cDPCP-d}_2 \) was prepared by refluxing the synthesized mixture of the cis and trans isomers of 1,2-bis(p-bromophenyl)cyclopropane (8 mmol) and magnesium (80 mmol) in MeOD (16 ml) for 20 hours.

**Pure \( \text{tDPCP-d}_1 \)**

Isomerically pure trans isomer of 1-(p-bromophenyl)-2-phenylcyclopropane was made starting with trans-p-bromostilbene following the same procedure as for the pure \( \text{tDPCP-d}_0 \). The procedure used to synthesize trans-p-bromostilbene has been described in chapter 2. Pure \( \text{tDPCP-d}_1 \) was made by reducing the trans isomer of 1-(p-bromophenyl)-2-phenylcyclopropane with magnesium in MeOD.

The synthesized compounds were analyzed by GC/MS.

**4.2.2 Spectroscopy**

The supersonic jet spectrometer used in this work has been described chapter 1. The sample is heated (to 120 °C for cDPCP and tDPCP, 30 °C for tMPCP, and 50 °C for cMPCP); and then seeded in neon or helium carrier gas at a backing pressure of 1-3 atm.
4.3 Results and analysis

4.3.1 Ab initio Calculations

Ground state data were computed at the Hartree-Fock (HF), and the density functional theory (DFT) using B3LYP functional levels of theory with 6-311G(d,p) basis set. Configuration interaction singles (CIS) method with the same 6-311G(d,p) basis set was employed for the excited states. HF optimized S\(_0\) geometries were used for the single point CIS calculations. Adiabatic excitation energy is the difference in the total energies of the CIS optimized S\(_1\) geometry and the corresponding HF optimized S\(_0\) geometry of each conformer. Normal mode analyses on the optimized geometries were performed at the same level of theory as in the optimization step.

The relative S\(_0\) energies and optimized S\(_0\) values of \(\tau_1\) and \(\tau_2\) of all conformers of MPCP and DPCP are listed in Table 4.1. The vertical excitation energies and the corresponding oscillator strengths for the S\(_1\) \(\leftrightarrow\) S\(_0\) transitions of all conformers MPCP, as well as the S\(_1\) \(\leftrightarrow\) S\(_0\) and S\(_2\) \(\leftrightarrow\) S\(_0\) vertical excitation energies and the corresponding oscillator strengths of all conformers of DPCP are reported in Table 4.2. Also listed in Table 4.2 are the adiabatic S\(_1\) \(\leftrightarrow\) S\(_0\) excitation energies, and the optimized values of \(\tau_1\) and \(\tau_2\) in the S\(_1\) states of some conformers of MPCP and DPCP.

4.3.1.1 tMPCP

The bisected conformer of tMPCP is more stable than the perpendicular conformer at the HF and DFT levels. The energy differences between the two are 300 cm\(^{-1}\) and 36 cm\(^{-1}\) at the DFT and HF levels, respectively. The DFT calculated barrier to torsional motion about the C\(_1\)-C\(_4\) bond of tMPCP is only 67 cm\(^{-1}\) above the local minimum of the perpendicular conformer. Hence,
fast relaxation of the perpendicular conformer in the supersonic expansion is anticipated because of the small barrier.\textsuperscript{19}

**Table 4.1** Calculated $S_0$ relative energies ($E_{\text{rel.}}$, cm\textsuperscript{-1}), and the dihedral angles ($\tau_1$ and $\tau_2$, degrees) of all conformers of MPCP and DPCP, at the HF and DFT levels.

<table>
<thead>
<tr>
<th>Conformer</th>
<th>HF/6-311G(d,p)</th>
<th>B3LYP/6-311G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{rel.}}$</td>
<td>$\tau_1$</td>
</tr>
<tr>
<td>tMPCP</td>
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<td></td>
</tr>
<tr>
<td>bisected</td>
<td>0</td>
<td>2.4</td>
</tr>
<tr>
<td>perpendicular</td>
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<td>86.3</td>
</tr>
<tr>
<td>cMPCP</td>
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<td>67.4</td>
</tr>
<tr>
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<tr>
<td>bisected- bisected</td>
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<td>5.3</td>
</tr>
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</tr>
<tr>
<td>cDPCP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bisected-perpendicular</td>
<td>0</td>
<td>15.3</td>
</tr>
<tr>
<td>perpendicular-perpendicular</td>
<td>121</td>
<td>55.8</td>
</tr>
</tbody>
</table>

(TS)$^a$

$^a$Transition state at the HF level.
Table 4.2 Summary of the CIS/6-311G(d,p) computed data.

<table>
<thead>
<tr>
<th></th>
<th>Vertical excitation at the HF S₀ geometryᵃ</th>
<th>Optimized S₁ states</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E₁</td>
<td>f₁</td>
</tr>
<tr>
<td>tMPCP</td>
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<td></td>
</tr>
<tr>
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</tr>
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<td>0.0009</td>
</tr>
<tr>
<td>cMPCP</td>
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<td>0.0023</td>
</tr>
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<td>tDPCP</td>
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<td></td>
</tr>
<tr>
<td>bisected- bisected</td>
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</tr>
<tr>
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</tr>
<tr>
<td>perpendicular-</td>
<td>49733</td>
<td>0.0021</td>
</tr>
<tr>
<td>perpendicular</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(TS)ᶜ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cDPCP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bisected-perpendicular, (S₁b)ᵈ</td>
<td>49324</td>
<td>0.00043</td>
</tr>
<tr>
<td>bisected-perpendicular, (S₁p)ᵈ</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>bisected-perpendicular, (S₁TS)ᵈ</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

ᵃ Vertical S₁ ← S₀ and S₂ ← S₀ excitation energies (E₁ and E₂, cm⁻¹) with their oscillator strengths, f₁ and f₂. ᵇ Adiabatic S₁ ← S₀ excitation energies (E₀, cm⁻¹). ᶜThe optimized S₁ state is a transition state. ᵈSee Section 4.4.2.2 for the details.
4.3.1.2 cMPCP

The calculated barrier to torsional motion about the C1-C4 bond of cMPCP is 1242 cm$^{-1}$ at the DFT level. The higher barrier in cMPCP reflects the steric effects of the methyl group in cMPCP. Electronic excitation of cMPCP to the $S_1$ state is predicted to be accompanied by 19.9° decrease in the value of $\tau_1$ by the HF and CIS methods.

The HF and CIS computed barriers to methyl torsion in cMPCP are 976 cm$^{-1}$ and 815 cm$^{-1}$ in the $S_0$ and $S_1$ states, respectively. These barriers are very similar to the torsional barrier of 2860±50 cal/mol (~1000 cm$^{-1}$) obtained from the analysis of the microwave spectrum of methylcyclopropane,$^{20}$ which perfectly agrees with our HF calculated barrier of 1038 cm$^{-1}$ in methylcyclopropane. Therefore, unlike in the case of methyl groups that are directly attached to aromatic or substituted aromatic rings such as fluorotoluenes and xylenes,$^{21, 22}$ no tunneling splittings are expected in the spectrum of cMPCP owing to the high barrier. The calculated orientations of the methyl rotors are the same in the $S_0$ and $S_1$ states of cMPCP.

4.3.1.3 tDPCP

Three starting structures tDPCP were generated by taking different combinations of $\tau_1$ and $\tau_2$: bisected-bisected with $\tau_1 = \tau_2 \sim 0°$, bisected-perpendicular with $\tau_1 \sim 0°$, $\tau_2 \sim 90°$, and perpendicular-perpendicular with $\tau_1 = \tau_2 \sim 90°$. All the three starting structures are found to be stable at the HF level, their relative energies are within 51 cm$^{-1}$ range. On the other hand, DFT results indicate that the asymmetric bisected-perpendicular conformer essentially relaxes to the $C_2$ symmetric bisected-bisected conformer, because the optimized values of $\tau_1$ and $\tau_2$, as well as the energies of the two conformers are very much the same.
The $S_1$ state of the perpendicular-perpendicular conformer optimized under the constraints of the $C_2$ symmetry is found to be a transition state (one imaginary frequency, 11749 cm$^{-1}$, that is associated with the breathing mode of the phenyl rings). The CIS optimizations of the $S_1$ states of the bisected-bisected and the bisected-perpendicular conformers failed to converge.

4.3.1.4 cDPCP

Two starting structures of cDPCP were generated by taking two combinations of $\tau_1$ and $\tau_2$. The two starting structures were bisected-perpendicular ($\tau_1 \sim 0^\circ$, $\tau_2 \sim 90^\circ$), and perpendicular-perpendicular ($\tau_1 = \tau_2 \sim 90^\circ$). At the HF level, the $C_5$ symmetric perpendicular-perpendicular conformer is predicted to be a transition state along the phenyl ring torsional coordinate, as the single imaginary frequency (13 cm$^{-1}$) involving phenyl torsions implies. The non symmetric bisected-perpendicular conformer is just 121 cm$^{-1}$ below the transition state. In contrast to the HF results, DFT calculations predicted stable bisected-perpendicular and perpendicular-perpendicular conformers, the non symmetric conformer is 145 cm$^{-1}$ more stable than the $C_5$ symmetric perpendicular-perpendicular conformer. The results of the CIS optimizations of cMPCP will be discussed in section 3.4.2.2.

4.3.2 Resonant enhanced two-photon ionization (R2PI) spectra

4.3.2.1 R2PI spectrum of cis:trans mixture of MPCP

The first intense peak in the spectrum of 40:60, cis:trans mixture of MPCP shown in Figure 4.2 occurs at 36751.4 cm$^{-1}$. At very high sensitivity, a second set of bands is seen at ca. 37000 - 37400 cm$^{-1}$. The weak bands are due to cMPCP (See section 4.3.2.2).
The intense band at 36751.4 cm\(^{-1}\) is assigned to the \(0^0\) transition of the bisected conformer of tMPCP. Most of the observed vibronic transitions can be assigned by comparison with the recently reported R2PI spectrum of PCP: \(^9\) 6a\(_0^1\) at 363 cm\(^{-1}\), 6b\(_0^1\) at 525 cm\(^{-1}\), 1\(_0^1\) at 726 cm\(^{-1}\), 9a\(_0^1\) at 906 cm\(^{-1}\), 18a\(_0^1\) at 938 cm\(^{-1}\), and 12\(_0^1\) at 967 cm\(^{-1}\). The peaks at 825 cm\(^{-1}\) and 997 cm\(^{-1}\), which have no counterparts in the spectra of alkylbenzenes\(^{23}\) may be associated with modes that involve substantial motion of both phenyl and methycyclopropyl groups. The weak band 165 cm\(^{-1}\) can be assigned to the fundamental of bending about the C\(_4\)-C\(_1\)-C\(_2\) angle, the CIS computed frequency of this mode in the S\(_1\) state of the bisected conformer of tMPCP is 175 cm\(^{-1}\).

Although cMPCP constitutes 40 % of the commercial sample, vibronic bands due to cMPCP could only be seen at high sensitivity, and still at the baseline level. The weakness of the vibronic bands of cMPCP can be attributed to the spread of the line strength in the origin region of cMPCP over several low frequency vibronic transitions, lower ionization potentials of cMPCP, isomerization of cMPCP, and low oscillator strength for the S\(_1\) \(\leftarrow\) S\(_0\) transition of cMPCP compared to the bisected conformer of tMPCP. The CIS calculated oscillator strength for the S\(_1\) \(\leftarrow\) S\(_0\) transition is ca. six times higher in the bisected conformer of tMPCP (0.0122) than in cMPCP (0.0023), thanks to the favorable electronic interaction of the phenyl and cyclopropyl rings in the bisected conformer of tMPCP.
Figure 4.2 R2PI spectrum of the commercial 40:60, cis:trans mixture of MPCP.

The intense vibronic bands (marked by their energies) are due the trans isomer. The very weak bands at ca. 37000 - 37400 cm\(^{-1}\) are due to the cis isomer.

4.3.2.2 R2PI spectrum of pure cMPCP

The spectrum of pure cMPCP displayed in Figure 4.3 is congested with 23 lines within the first 370 cm\(^{-1}\) of the spectrum. The expanded view of the lower energy portion of the
spectrum taken under cold and warm expansion conditions is displayed in Figure 4.4. Hot bands are clearly seen at 36999 cm\(^{-1}\), 37029 cm\(^{-1}\), 37043 cm\(^{-1}\), and 37073 cm\(^{-1}\). The weak band at 37018.8 cm\(^{-1}\) in the cold spectrum is assigned to the electronic origin transition of cMPCP. Based on this origin, two vibronic progressions are identified having fundamental frequencies of 44.1 cm\(^{-1}\) and 79.3 cm\(^{-1}\). The 44.1 cm\(^{-1}\) progression is harmonic, while the 77.9 cm\(^{-1}\) progression exhibits considerable anharmonicity as revealed by the unequal spacings in the frequencies of the members. Most of the observed vibronic bands can be assigned in terms of the overtones and combinations of these two fundamentals (abbreviated as A and B) as summarized in Table 4.3. The 44.1 cm\(^{-1}\) fundamental is assigned to the torsional motions of the methylcyclopropyl and phenyl groups, the HF and CIS calculated frequencies of this mode are 44 cm\(^{-1}\) and 24 cm\(^{-1}\) in the \(S_0\) and \(S_1\) states, respectively. The second HF/CIS computed lowest frequency mode involves flapping of the methylcyclopropyl and phenyl groups, and has a frequency of 106 cm\(^{-1}\) and 87 cm\(^{-1}\) in the \(S_0\) and \(S_1\) states, respectively. The 79.3 cm\(^{-1}\) fundamental is therefore assigned to the flapping mode of the methylcyclopropyl and phenyl groups.

Harmonic one dimensional Franck-Condon analysis of the origin based 44.1 cm\(^{-1}\) progression was performed following the procedure described by Finley et al.,\(^{24}\) the HF computed \(S_0\) geometry of cDPCP was used to determine the rotational constant, \(B\), a value of 0.299 cm\(^{-1}\) was obtained for \(B\). Only the first five members of the progression were included in the analysis, because the intensities of the other members are obviously distorted, most likely by Fermi resonances and overlap with other bands. Good agreement between the calculated and observed relative intensities was achieved with the dimensionless displacement parameter, \(S = 4.55\), and the ratio of the torsional frequencies in the \(S_0\) and \(S_1\) states, \(R = 1.08\). The results of the Franck-Condon analysis indicate that the torsional angle, \(\tau_1\), decreases by 20.9° upon excitation
to the S<sub>1</sub> state. The \( A'_0 \) transition is predicted to be five times more intense than the \( 0'_0 \) transition, supporting the assignment of the very weak band at 37018.8 cm\(^{-1}\) to the \( 0'_0 \) transition.

**Figure 4.3** R2PI spectrum of cMPCP. The bands marked by the (T) symbol are due to the traces of tMPCP present in the synthesized sample of cMPCP.
Figure 4.4 Expanded view of the low energy portion of the R2PI spectrum of cMPCP in the supersonic expansions of (a) neon, and (b) helium. The $0^0$ transition is found at 37018.8 cm$^{-1}$. 
Table 4.3 Assignment of the observed vibronic transitions of cMPCP.

<table>
<thead>
<tr>
<th>Transition energy, cm$^{-1}$</th>
<th>Vibrational energy, cm$^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>37018.8</td>
<td>0.0</td>
<td>0$^0_0$</td>
</tr>
<tr>
<td>37062.9</td>
<td>44.1</td>
<td>A$^1_0$</td>
</tr>
<tr>
<td>37098.1</td>
<td>79.3</td>
<td>B$^0_0$</td>
</tr>
<tr>
<td>37107.1</td>
<td>88.3</td>
<td>A$^3_0$</td>
</tr>
<tr>
<td>37138.8</td>
<td>120.0</td>
<td>B$^1_0$ A$^1_0$</td>
</tr>
<tr>
<td>37151.1</td>
<td>132.3</td>
<td>A$^3_0$</td>
</tr>
<tr>
<td>37175.0</td>
<td>156.2</td>
<td>B$^2_0$</td>
</tr>
<tr>
<td>37181.9</td>
<td>163.1</td>
<td>B$^1_0$ A$^2_0$</td>
</tr>
<tr>
<td>37195.5</td>
<td>176.7</td>
<td>A$^4_0$</td>
</tr>
<tr>
<td>37213.1</td>
<td>194.3</td>
<td>B$^2_0$ A$^1_0$</td>
</tr>
<tr>
<td>37224.6</td>
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<td>B$^1_0$ A$^3_0$</td>
</tr>
<tr>
<td>37239.4</td>
<td>220.6</td>
<td>A$^5_0$</td>
</tr>
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<td>37249.1</td>
<td>230.3</td>
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</tr>
<tr>
<td>37257.4</td>
<td>238.6</td>
<td>B$^2_0$ A$^2_0$</td>
</tr>
<tr>
<td>37267.7</td>
<td>248.9</td>
<td>B$^1_0$ A$^4_0$</td>
</tr>
<tr>
<td>37284.5</td>
<td>265.7</td>
<td>B$^3_0$ A$^1_0$ + A$^6_0$</td>
</tr>
<tr>
<td>37297.3</td>
<td>278.5</td>
<td>B$^2_0$ A$^3_0$</td>
</tr>
<tr>
<td>37310.6</td>
<td>291.8</td>
<td>B$^1_0$ A$^5_0$</td>
</tr>
<tr>
<td>37320.3</td>
<td>301.5</td>
<td>B$^4_0$</td>
</tr>
<tr>
<td>37331.9</td>
<td>313.1</td>
<td>B$^3_0$ A$^2_0$ + A$^7_0$</td>
</tr>
<tr>
<td>37339.9</td>
<td>321.1</td>
<td>B$^2_0$ A$^4_0$</td>
</tr>
<tr>
<td>37352.9</td>
<td>334.1</td>
<td>B$^1_0$ A$^6_0$</td>
</tr>
<tr>
<td>37368.5</td>
<td>349.7</td>
<td>B$^3_0$ A$^3_0$ + B$^4_0$ A$^1_0$</td>
</tr>
<tr>
<td>37381.4</td>
<td>362.6</td>
<td>B$^2_0$ A$^5_0$</td>
</tr>
</tbody>
</table>
4.3.2.3 R2PI spectra of pure tDPCP-d$_1$ and cis/trans mixture of DPCP-d$_1$

The spectra of the deuterated isotopomers of tDPCP and cDPCP were recorded using the synthesized cis and trans mixtures. This was done because of the difficulty associated with the synthesis and handling of the deuterated isotopomers of isomerically pure cDPCP. The spectrum of pure tDPCP-d$_1$ displayed in Figure 4.5b permits us to separate bands due to the cis and trans isomers of DPCP-d$_1$, respectively. The spectral analysis of tDPCP, cDPCP, and their deuterated isotopomers will be discussed in sections 4.3.2.4 and 4.3.2.5.

![Figure 4.5 R2PI spectra of (a) cis and trans mixture of DPCP-d$_1$, and (b) pure tDPCP-d$_1$.](image-url)
4.3.2.4 R2PI spectra of tDPCP, tDPCP-d1, and tDPCP-d2

Figure 4.6b features the spectrum of tDPCP covering 1300 cm\(^{-1}\) above the intense origin band at 36624.0 cm\(^{-1}\). Scanning to the red of the assigned origin reveals a hot band at 31.0 cm\(^{-1}\) to the red. The intensity of the hot band decreases sharply under cold expansion conditions. Vibronic activity is seen in the origin region, and at 738-1016 cm\(^{-1}\) above the origin. The \(6a^1\) and \(6b^1\) transitions, which occur at ca. 300-600 cm\(^{-1}\) in the spectra of most benzene derivatives,\(^9,23,25-28\) are missing in the spectrum of tDPCP.

![R2PI spectra of (a) cDPCP and (b) tDPCP.](image)

**Figure 4.6** R2PI spectra of (a) cDPCP and (b) tDPCP.
The origin region of the spectra of tDPCP-d₀, tDPCP-d₁, tDPCP-d₂ is displayed in Figure 4.7. The spectra of tDPCP-d₀ and p-tDPCP-d₂ are dominated by a progression in a mode with a fundamental frequency of ca. 30 cm⁻¹. The frequencies and intensities of the vibronic features in the spectrum of tDPCP-d₂ are similar to those in the spectrum of the undeuterated molecule; hence, the 30 cm⁻¹ fundamental can be assigned to the symmetric torsions of the two phenyl rings about the C₁-C₄ and C₂-C₁₀ bonds. The electronic origin of tDPCP-d₂ is blue-shifted by 25.9 cm⁻¹ relative to that of tDPCP-d₀ due to the deuterium induced changes of zero point energies in the ground and excited states.

The frequencies of the torsional progression in the spectrum of tDPCP-d₁ are slightly different from those seen in the spectra of tDPCP-d₀ and tDPCP-d₂, but the relative intensities are similar, implying the same geometrical structures of the symmetric and asymmetric isotopomers in the ground and excited states. A progression with a fundamental frequency of 26.4 cm⁻¹ is built off the band at 36680.3 cm⁻¹ in the spectrum of tDPCP-d₁. The band at 36680.3 cm⁻¹ is therefore, assigned as the \( S₂ \leftrightarrow S₀ \) origin which is forbidden in the spectra of tDPCP-d₀ and tDPCP-d₂.

The observation of forbidden \( S₂ \leftrightarrow S₀ \) vibronic transitions in the spectra of the symmetric isotopomers suggests that the spectrum of tDPCP is due to a symmetric conformer. Experience with PCP has shown the failure of the HF method to predict the relative stabilities of the bisected and perpendicular conformers, predicting the latter to be more stable in disagreement with the experimental results.⁶⁻⁸, ²⁹ The perpendicular-perpendicular conformer is predicted to be 570 cm⁻¹ less stable than the bisected-bisected conformer by the DFT calculations. Hence, only the \( C₂ \) symmetric bisected-bisected conformer is present in the gas phase.
Figure 4.7 R2PI spectra of (a) tDPCP-d$_2$, (b) tDPCP–d$_1$, and (c) tDPCP-d$_0$ in the origin region.
The complexity of the spectrum of tDPCP-d1 arises from the difference in the electronic structures of the symmetric and asymmetric isotopomers. In the asymmetric p-tDPCP-d1, the degeneracy of the zeroth order excited states is lifted by the asymmetric deuteration. The $S_1 \leftarrow S_0$ electronic origins of benzene and some of its derivatives are blue-shifted by an average of 32 cm$^{-1}$ upon replacing a single hydrogen atom with deuterium. Based on these observations, the $0_0^0$ band of tDPCP-d2 will be expected to blue-shift by about 64 cm$^{-1}$ relative to that of tDPCP-d0; however, the observed shift is only 25.9 cm$^{-1}$. The plausible explanation to this observation is that the deuterium effect is equally shared by the two close lying exciton states in such a way that the allowed $S_1 \leftarrow S_0$ origin goes with one half of the deuterium effect, the other half goes to the forbidden $S_2 \leftarrow S_0$ transition.

The smaller blue-shift of the origin of tDPCP-d2 indicates that the electronic excitation energy is spread over both phenyl and cyclopropyl rings; in the language of Buma et al., about (25.9/32) 81% of the excitation is localized on the phenyl chromophores, the remaining 19% on the cyclopropyl bridge. Since the two phenyl rings are not equivalent in tDPCP-d1, the deuterium effect would be different for the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ origins of tDPCP-d1. The $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ origins of tDPCP-d1 are blue-shifted by 6.8 cm$^{-1}$ and 56.3 cm$^{-1}$ with respect to the origin of tDPCP-d0, a total blue-shift of 63.1 cm$^{-1}$. The energy difference between the electronic origins of tDPCP-d0 and tDPCP-d2 (25.9 cm$^{-1}$) is the expected total blue-shift induced by the single deuterium in tDPCP-d1. Since the $S_1 \leftarrow S_0$ origin is shifted by 6.8 cm$^{-1}$, the $S_2 \leftarrow S_0$ origin will then shift by (25.9 - 6.8) 19.1 cm$^{-1}$. The $S_2 \leftarrow S_0$ origin of tDPCP-d0 is then expected to appear at (36680.3 - 19.1) 36661.2 cm$^{-1}$; hence, the exciton splitting in tDPCP-d0 is (36661.2 - 36624.0) 37.2 cm$^{-1}$. The same splitting (37.2 cm$^{-1}$) was obtained following the procedure, described in details by Fung et al. for benzene dimer.
The HF calculated $S_0$ frequencies of the symmetric and asymmetric torsional modes of the two phenyl rings of tDPCP are reported in Table 4.4. The weak bands at 72.9 cm$^{-1}$ and 72.5 cm$^{-1}$ in the spectra of tDPCP-d$_2$ and tDPCP-d$_0$ can be assigned to the first overtones of asymmetric torsions, the fundamental transition of this mode is forbidden for symmetry reasons. The weak band at 37.9 cm$^{-1}$ above the $S_1 \leftarrow S_0$ origin in the spectrum of the less symmetric tDPCP-d$_1$ can be assigned to the fundamental transition of the asymmetric phenyl torsions, the combination of this fundamental and that of the symmetric torsions appears at 66.2 cm$^{-1}$ above the $S_1 \leftarrow S_0$ origin of DPCP-d$_1$. The peak at 98.6 cm$^{-1}$ in the spectrum of DPCP-d$_1$ can be assigned to the combination of the first overtone of the symmetric torsions and the fundamental of the asymmetric phenyl torsions. The second overtone of the asymmetric torsions occurs at 76.1 cm$^{-1}$ above the $S_1 \leftarrow S_0$ origin, overlapping the first overtone of the fundamental of the symmetric torsions in the $S_2$ state. Similarly, the band at 84.1 cm$^{-1}$ (34.9 cm$^{-1}$ above the $S_2 \leftarrow S_0$ origin) can be assigned to the asymmetric phenyl torsions in the $S_2$ state.

4.3.2.5 R2PI spectra of cDPCP, cDPCP-d$_1$, and cDPCP-d$_2$

The spectrum of cDPCP displayed in Figure 4.6a features a strong origin band at 36782.5 cm$^{-1}$, and some weaker bands to the blue of the origin. At higher sensitivity, the $a_0^1$, $b_0^1$, and $l_0^1$ fundamental transitions can be seen at 347 cm$^{-1}$, 527 cm$^{-1}$, and 712 cm$^{-1}$, respectively.

The relative energy of the two conformers of cDPCP is below 150 cm$^{-1}$ at the HF and DFT levels; therefore, the spectrum of cDPCP cannot be reliably assigned based on the calculated relative stabilities alone. The single electronic origin may imply a symmetric ground state structure, for which one of the exciton origins is forbidden or weakly allowed, in the latter case one of the weak bands to the blue of the intense origin could be the origin of the $S_2 \leftarrow S_0$
transition. Another possibility is that the two rings are not symmetric, in which case the zeroth order excited states of the two phenyl chromophores are not degenerate, and if the energy gap between the non degenerate excited states is large enough, exciton interactions may not occur.

A definite solution to this problem can be found by examining the spectra of cDPCP-d$_1$ and cDPCP-d$_2$, shown in Figure 4.8a and 4.8b. Two intense origins appear in the spectrum of cDPCP-d$_1$ at essentially the same energies (36781.5 cm$^{-1}$ and 36808.4 cm$^{-1}$) as the electronic origins of cDPCP-d$_0$ (36782.5 cm$^{-1}$) and cDPCP-d$_2$ (36809.8 cm$^{-1}$), so also the weak vibronic bands. The spectrum of cDPCP-d$_1$ is essentially the sum of the spectra of cDPCP-d$_0$ and cDPCP-d$_2$. These observations provide unambiguous evidence for the lack of exciton interactions in cDPCP; if exciton interactions occurred, the two electronic origins of cDPCP-d$_1$ will not coincide with those of cDPCP-d$_0$ and cDPCP-d$_2$. Therefore, the phenyl rings are not equivalent in cDPCP. Thus, the spectrum of cDPCP is due to the non symmetric bisected-perpendicular conformer, in which one phenyl ring is in a nearly bisected conformation ($\tau_1 = 10-15^\circ$) and the other in a nearly perpendicular ($\tau_2 = 72-76^\circ$) conformation relative to the cyclopropyl ring; henceforth, we will refer to the two rings as bisected and perpendicular rings, respectively.

Asymmetric deuteration of cDPCP will result in two distinct ground state conformers, in one of which the deuterium is on the bisected phenyl ring, the deuterium is on the perpendicular ring in the other conformer. Two overlapping electronic spectra are thus anticipated. By comparison with the location of the electronic origins of tMPCP and PCP,$^9$ the first origin in the spectrum of cDPCP-d$_1$ is assigned to the conformer in which the deuterium is on the perpendicular ring, so the electronic origin is that of the localized excitation of the undeuterated bisected ring. The reverse is the case for the second origin; here the observed origin is that of the deuterated bisected ring. The major low frequency vibronic bands in the spectrum of cDPCP
have been assigned by comparison with the calculated vibrational modes of the bisected-perpendicular conformer of cDPCP. The proposed assignments are summarized in Table 4.4.

Table 4.4 Assignment of the lowest frequency vibronic transitions of cDPCP and tDPCP.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$S_0$ (HF), cm$^{-1}$</th>
<th>$S_{1b}$ (CIS), cm$^{-1}$</th>
<th>Approximate description</th>
<th>Expt. $S_1$, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>29.9</td>
<td>22.9</td>
<td>Torsion of the perpendicular phenyl ring + flapping of the bisected ring</td>
<td>27.6</td>
</tr>
<tr>
<td>$v_2$</td>
<td>40.1</td>
<td>37.3</td>
<td>Torsions of the two phenyl rings</td>
<td>38.5</td>
</tr>
<tr>
<td>$v_3$</td>
<td>56.0</td>
<td>59.2</td>
<td>Torsion of the bisected phenyl ring + flapping of the perpendicular ring</td>
<td>57.3</td>
</tr>
<tr>
<td>$v_4$</td>
<td>145.4</td>
<td>114.0</td>
<td>Bending out of the plane of the cyclopropyl ring</td>
<td>91.9</td>
</tr>
</tbody>
</table>

**Calculated for tDPCP**

| $v_1$ | 29.5 | Symmetric torsions of the two phenyl rings | 30.1 |
| $v_2$ | 44.5 | Asymmetric torsions of the two phenyl rings | $36.5 \times 2$ |
Figure 4.8 R2PI spectra of (a) cDPCP-d$_2$, (b) cDPCP–d$_1$, and (c) cDPCP-d$_0$ in the origin region.
4.4 Discussion

4.4.1 Conformational stability of the cis and trans isomers of MPCP and DPCP

The electronic origin of tMPCP is red-shifted by 109 cm\(^{-1}\) relative to that of PCP,\(^{29}\) similar red-shifts are observed when methyl group is attached to a conjugating substituent of aromatic chromophores. For instance, the electronic origins of phenylpropyne and trans-\(\beta\)-methylstyrene are red-shifted by 129 cm\(^{-1}\) and 193.7 cm\(^{-1}\), respectively, relative to those of phenylacetylene and styrene.\(^{26, 34}\) Perhaps the most important experimental evidence for the conjugated nature of cyclopropyl ring is the substantial geometry change of cMPCP upon \(S_1 \leftrightarrow S_0\) excitation. The structure of molecules with neighboring \(\pi\) systems is generally governed by steric and electronic (conjugative) effects;\(^{24, 34}\) the electronic effects dominate in the excited singlet states because of the higher polarizability of aromatic rings in the \(\pi\pi^*\) excited states. In most of the studied molecules with neighboring \(\pi\) systems, conjugation is maximized in the planar conformation,\(^{24, 34}\) whereas in phenylcyclopropanes, the conjugation is maximized in the bisected conformation. The ideal bisected conformation (with \(\tau_1 \sim 0\)) is not achieved in the excited state of cMPCP owing to the large steric effects of the methyl group. It is quite remarkable to note the good agreement between the value of \(\Delta\tau_1\) obtained from the Franck-Condon analysis (20.9°) of the observed torsional progression, and the HF/CIS predictions (19.9°).

The bisected phenyl ring in cDPCP maximizes electronic interactions with the cyclopropyl ring. Apparently, the steric effects of the bulky phenyl rings in cDPCP prevent any noticeable structural rearrangements along the torsional coordinates upon electronic excitation. Both HF and DFT methods predicted the same values of \(\tau_1\) and \(\tau_2\) (5.3 °) for tDPCP, there is no any steric effect that can prevent the two dihedrals from being equal to 0-2° as predicted for
tMPCP. The structure of tDPCP can also be influenced by additional electronic interactions between the two phenyl rings, these interactions must be mediated by the weakly conjugated cyclopropyl bridge, as direct through space interactions between two phenyl rings with edge to edge (C4-C10) distance of 3.8 Å is negligible.35

### 4.4.2 The nature of the excited electronic (vibronic) states of MPCP and DPCP

In accordance with Platt’s notation, the lowest excited electronic states of benzene and its derivatives are usually called L_b and L_a states.36 The L_b state is usually lower in energy and has substantially lower oscillator strength than the L_a state.37 The transition dipole moments (TDMs) for the S1←S0 and S2←S0 transitions of benzene derivatives that have an axis or plane of symmetry about the point of substitution are polarized along the long and short molecular axes, respectively. It is well established that the TDM orientation is conformation-dependent; this property of TDM has been exploited to study conformationally flexible molecules.38 Nevertheless, there is still a debate on whether the Platt’s notation is applicable to non symmetric benzene derivatives.39-41 Styrene is a typical asymmetric benzene derivative that has neither axis nor plane of symmetry about the point of substitution. High resolution rotationally resolved electronic spectroscopy of styrene shows that the TDM for the S1←S0 of styrene lies along the long molecular axis; hence, the authors concluded that the S1 state is L_a.40 However, the calculated orientations of the TDM for the S1←S0 and S2←S0 transitions in styrene are both essentially long axis polarized;41 hence, the two transitions cannot be distinguished based on the polarizations of their TDMs alone. The calculated oscillator strength of the S1←S0 transition is substantially lower than that for the S2←S0 transition, in agreement with the experimental results.41
In the original description of the L_b and L_a states, Platt put more emphasis on the nodal pattern of the transition charge density surfaces in defining the states: the two states can be distinguished by looking at the transition charge densities. The transition densities are localized on bonds (with nodes on atoms) in the L_b states, and on atoms in the L_a states. The surfaces of the CIS/6-311G(d,p)//HF/6-311G(d,p) computed transition densities for the vertical $S_1 \leftarrow S_0$ transitions of tMPCP and cMPCP, as well as the vertical $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of cDPCP and tDPCP are depicted in Figure 4.9.

4.4.2.1 cMPCP and tMPCP

The TDM vectors for the vertical $S_1 \leftarrow S_0$ transitions of the bisected conformer of tMPCP and cMPCP are rotated by 16° and 82°, respectively, relative to the long axes (axes passing through C_4-C_7 in Figures 4.1a and 4.1b) of the phenyl rings. The surfaces of the transition densities clearly reveal the L_b nature (nodes on atoms) of the $S_1 \leftarrow S_0$ transitions of tMPCP and cMPCP, despite the substantial rotation of the TDM of tMPCP from the short axes of the aromatic chromophores.
Figure 4.9 Transition density surfaces for the vertical (a) $S_1 \leftarrow S_0$ transition of tMPCP, (b) $S_1 \leftarrow S_0$ transition of cMPCP, (c) $S_1 \leftarrow S_0$ transition of cDPCP, (d) $S_2 \leftarrow S_0$ transition of cDPCP, (e) $S_1 \leftarrow S_0$ transition of tDPCP, and (f) $S_2 \leftarrow S_0$ transition of tDPCP.
4.4.2.2 cDPCP

The surfaces of the transition densities displayed in Figures 4.9c and 4.9d reveal the $L_b$ nature of the vertical $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions in the bisected-perpendicular conformer of cDPCP that are mostly localized on the bisected and perpendicular phenyl rings, respectively. Since the two localized transitions have the same $L_b$ character, we chose to refer to them as $S_{1b}$ and $S_{1p}$ in order to emphasize their localized nature. No imaginary frequency was found in the subsequent normal mode analysis of the optimized $S_{1b}$ and $S_{1p}$ states. The energy gap between the optimized $S_{1b}$ and $S_{1p}$ is 448 cm$^{-1}$, which is very similar to the energy gap of 435 cm$^{-1}$ between the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ vertical energies (Table 4.2). At the optimized geometry of the $S_{1p}$ state, the $S_1 \leftarrow S_0$ transition is localized on the perpendicular phenyl ring. The $S_1 \leftarrow S_0$ transition is localized on the bisected ring in the optimized geometry of the $S_{1b}$ state. These results indicate a surface crossing between the localized $S_{1b}$ and $S_{1p}$ states.

Inter-conversion of the bisected and the perpendicular phenyl rings of cDPCP requires coupled torsions about the $C_1$-$C_4$ and $C_2$-$C_{10}$ bonds, the HF computed barrier to these torsions is 121 cm$^{-1}$ in the $S_0$ state (Table 4.1). CIS computations also found a transition state abbreviated as $S_{1TS}$ in Table 4.2; the $S_{1TS}$ state is characterized by a single imaginary frequency (23 cm$^{-1}$) that involves phenyl torsions, and localized excitation on the perpendicular phenyl ring. The optimized $S_{1TS}$ state is just 60 cm$^{-1}$ above the $S_{1p}$ minimum; thus, essentially there is no minimum on the $S_{1p}$ surface, and this could be the reason for the absence of any vibronic bands in the spectrum of cDPCP that can be assigned to the localized excitation of the perpendicular phenyl ring. The results of the CIS optimizations of the $S_{1b}$, $S_{1p}$, and $S_{1TS}$ states show that the decrease in the values of $\tau_1$ or $\tau_2$ in the localized $S_1$ states is associated with the excited phenyl rings (Table 4.2).
An interesting conclusion regarding the accuracy of the CIS computed relative energies of the $S_{1b}$ and $S_{1p}$ states can be made by comparing the differences in the HF optimized values of $\tau_1$ in the bisected conformer of tMPCP and cMPCP, with their observed vertical excitation energies. The observed vertical excitation energies of tMPCP (36751 cm$^{-1}$) and cMPCP (37249 cm$^{-1}$) differ by 498 cm$^{-1}$, the values of their $\tau_1$ differ by 65°. Similarly, the difference between $\tau_1$ and $\tau_2$ in the HF optimized cDPCP is 61°; therefore, the CIS predicted energy gap of 448 cm$^{-1}$ between $S_{1b}$ and $S_{1p}$ states of cDPCP is quite reasonable. As apparent in Table 4.2, the computed vertical $S_1 \rightarrow S_0$ excitation energy of cMPCP is 550 cm$^{-1}$ higher than that of tMPCP, in good agreement with the experimental energy gap of 498 cm$^{-1}$.

An unusual feature of the R2PI spectrum of cDPCP shown in Figure 4.6a is the weakness of vibronic bands at about 230 cm$^{-1}$ above the electronic origin, no vibronic bands could be seen at all above 712 cm$^{-1}$. This observation suggests very fast radiationless transitions in cDPCP that lead to the reduction of the excited state lifetimes, and consequently the ionization efficiencies of the excited cDPCP. Recently, Sivaguru et al. proposed a mechanism for the photoisomerization of cDPCP, which suggest that the lowest locally excited $\pi\pi^*$ singlet states are unbound, and a nearly barrierless transition from the excited $\pi\pi^*$ singlet states to the excited diradical state. If this mechanism were correct, then, it wouldn’t be possible to record the R2PI spectrum of cDPCP, because the lifetime of the excited states will not be long enough for the subsequent ionization of the exited molecules to occur. Present results however, do suggest the existence of a low barrier to some nonradiative process, most likely photochemistry, which is the dominant decay channel of the excited cDPCP.$^3,^4$
4.4.2.3 tDPCP

The absence of $6a^1_0$ and $6b^1_0$ like transitions in the one photon spectrum of tDPCP implies that lowest excited singlet states of tDPCP are different from the excited electronic states of cMPCP and most benzene derivatives, and/or tDPCP undergoes different geometry change in the excited states. The $S_1 \leftarrow S_0$ transition density of tDPCP shown in Figure 4.9e does not exhibit pure $L_b$ or $L_a$ character because the transition densities are spread all over the molecule, but the transition is clearly $\pi\pi^*$ in nature. The computed oscillator strength of this transition, 0.1100, also seems to be too high for $L_b$ state. The $L_b/L_a$ hybrid nature of the $S_1 \leftarrow S_0$ transition might be the reason behind the distinct vibronic structure of the tDPCP spectrum, and the failure of the CIS method to optimize the $S_1$ state of tDPCP.

The relative intensities of vibronically induced bands and origin (and totally symmetric) bands of the absorption spectra of substituted benzenes can be taken as a measure of electronic interactions between the substituents and the aromatic chromophore. The extreme case of such interactions is found in the spectrum of benzene, in which the electronic origin is forbidden for symmetry reasons, the vibronically induced $6^1_0$ fundamental transition serves as the false origin. The absence of $6^1_0$ like transitions in the spectrum of tDPCP may also be attributed to the substantial through-bond electronic interactions of the two phenyl rings in tDPCP.

The estimated exciton splitting in the spectrum of tDPCP is 37.2 cm$^{-1}$; this value is substantially larger than those found for the closely related 1,2-diphenylethane (See chapter 2). The estimated exciton splittings are 4.3 cm$^{-1}$ and 12.0 cm$^{-1}$ for the anti and gauche conformers of 1,2-diphenylethane, respectively. The distance between the centers of the two phenyl rings of the gauche conformer of 1,2-diphenylethane is 4.96 Å, compared to the 6.5 Å in tDPCP. Therefore,
the higher exciton splitting in tDPCP is attributed to through-bond mediated (via the conjugated cyclopropyl bridge) exciton interactions.

4.5 Conclusions

Some the experimental evidence in support of the conjugated nature of cyclopropyl ring include: the 109 cm\(^{-1}\) red-shift of the electronic origin of tMPCP relative to that of PCP, and the 20 ° decrease of \(\tau_1\) upon \(S_i \leftarrow S_0\) excitation of cMPCP. The \(S_i \leftarrow S_0\) transitions in both isomers of MPCP exhibit \(L_b\) character, despite substantial rotation of their transition dipole moments from the short axes of the phenyl chromophores.

The trans isomer of DPCP has \(C_2\) symmetry, and is additionally stabilized by through-bond electronic interactions of the two phenyl rings. An exciton splitting of 37.2 cm\(^{-1}\) was estimated by analyzing the spectra of ring deuterated isotopomers of tDPCP. The absence of \(6a_0^1\) and \(6b_0^1\) like transitions in the spectrum of tDPCP is most likely caused by the \(L_b/L_a\) hybrid nature of the \(S_i \leftarrow S_0\) transition, and through-bond electronic interactions of the two aromatic rings.

The cis isomer of DPCP is asymmetric. The two phenyl rings are in the bisected and perpendicular conformations, respectively, relative to the cyclopropyl bridge. The \(S_i \leftarrow S_0\) and \(S_2 \leftarrow S_0\) transitions of cDPCP exhibit \(L_b\) character, and are mostly localized on the bisected and perpendicular rings, respectively. The \(S_2 \leftarrow S_0\) minimum is only 60 cm\(^{-1}\) below the transition state, along the phenyl torsional coordinates of the excited \(L_b\) state potential energy surface; hence, transitions to the localized \(S_2 \leftarrow S_0\) vibronic states have not been observed in the spectrum of cDPCP. The vibronic bands at ca 230 cm\(^{-1}\) above the electronic origin of cDPCP are
very weak, indicative of very short lifetimes of the excited Lₐ states due to nonradiative transitions.

4.6 References


5.3 Introduction

The weak non-bonded interactions of the $\pi$ electron cloud of aromatic molecules with hydrogen atoms of C-H, N-H, and O-H bonds have been the subject of several investigations. $^{1-7}$ These interactions play an important role in determining the conformational preferences of molecules and clusters. $^{1-7}$ The interactions are generally governed by dispersion and electrostatic forces; the latter are more important in the case of polar N-H and O-H bonds. $^{4}$ The C-H/$\pi$ interactions are dominated by dispersion interactions. The $\pi$ interactions involving N-H and O-H bonds are stronger than the C-H/$\pi$ interactions. For example, the binding energies of benzene-water and benzene-methane clusters are 3.02 kcal/mole and 1.45 kcal/mol, respectively. $^{4}$

C-H/$\pi$ interactions are usually produce a red-shift of vibronic transitions. The $6_0^1$ bands of benzene-ethylene and benzene-methane clusters are red-shifted by 64 cm$^{-1}$ and 39 cm$^{-1}$, respectively, relative to the $6_0^1$ band of benzene. $^{1,8}$ Allylbenzene exists predominantly in the eclipsed conformation, which is stabilized by the C-H/$\pi$ interactions. The electronic origin of the eclipsed conformer is red-shifted by 121 cm$^{-1}$ relative to that of the extended conformer. $^{9}$ The gauche conformer of n-propylbenzene is also stabilized by the C-H/$\pi$ interactions; hence, the $0_0^0$ band of the gauche conformer is red-shifted by 48.8 cm$^{-1}$ relative to the $0_0^0$ band of the trans conformer. $^{10}$ On the other hand, the $\pi$ interactions associated with N-H and O-H bonds are usually associated with the blue shift of the electronic origins of the molecules and clusters capable of forming the weak hydrogen bonds. $^{5}$ The electronic origin of benzene-water cluster
is blue-shifted with respect to that of bare benzene by 49 cm\(^{-1}\).\(^5\) The origin of benzylalcohol is blue-shifted relative to that of toluene by 50 cm\(^{-1}\).\(^{10,11}\)

Recently, indane and its derivatives have been investigated in a supersonic jet with various goals.\(^2\)-\(^4\), \(^6\), \(^7\), \(^12\)-\(^14\) Some researchers focused on mapping out the potential energy surfaces along the puckering and flapping coordinates of indane and its derivatives.\(^6\), \(^12\) These studies provide information about the equilibrium geometries of the investigated molecules and barriers to the strongly coupled puckering and flapping motions. Several conformationally flexible derivatives of indane have been investigated with the primary goal of determining the factors governing the conformational preferences of aromatic molecules.\(^2\), \(^3\), \(^6\), \(^7\), \(^13\), \(^14\) Only two of the six stable conformers of 1-aminoindean have been detected in jet experiments. The observed conformers are stabilized by intramolecular N-H/\(\pi\) hydrogen bonding.\(^3\) The most abundant conformers of 2-aminoindean and 2-indanol are also found to be stabilized by intramolecular N-H/\(\pi\) and O-H/\(\pi\) hydrogen bonding, respectively.\(^2\), \(^6\) The electronic origins of the hydrogen bonded conformers are always blue-shifted relative to the origins of the minor conformers, devoid of intramolecular hydrogen bonding.\(^2\), \(^3\), \(^6\), \(^7\), \(^13\)

The major aims of this work were to study the role of the C-H/\(\pi\) interactions on the conformational stability of aromatic molecules, and interchromophore interactions in molecules with two different chromophores that have similar excitation energies. In order to accomplish these tasks, the following compounds were synthesized: 2-methylindane (2MI), 2-phenylindane (2PI), 2-phenylindane-\(d_5\) (2PI-\(d_5\)), and 2-(4-fluorophenyl)indane (2FPI). The structures of these compounds are shown in Figure 5.1. Mass selective vibrationally resolved electronic spectra of these compounds have been recorded and analyzed.
Figure 5.1 Structures of the investigated compounds: (a) 2-phenylindane (2PI), (b) 2-methylindane (2MI), (c) 2-phenylindane-d$_5$ (2PI-d$_5$), and (d) 2-(4-fluorophenyl)indane (2FPI).

The puckering angle, $p$, is defined as $C_1$-$C_2$-$C_3$-$C_4$. The dihedral angle, $\tau$, is defined as $C_{11}$-$C_{10}$-$C_2$-$H_2$.

5.4 Experimental

5.4.1 Synthesis

2PI-d$_0$

2PI-d$_0$ was synthesized in three steps. An ethereal solution of phenylmagnesiumbromide (16 ml, 1 M) was slowly added to a solution of 2-indanone (12 mmol in 12 ml of diethylether) at 0 °C. The mixture was stirred for two hours to yield 11 mmol of 2-hydroxyl-2-phenylindan. Bromination of 2-hydroxyl-2-phenylindan (11 mmol) with 7 mmol of PBr$_3$ in 25 ml of
dichloromethane at 20 °C for two hours yielded 2-bromo-2-phenylindan. A mixture of 2-bromo-2-phenylindan (10 mmol) and magnesium (50 mmol) in methanol (30 ml) was refluxed for 20 hours. The reaction mixture was quenched with HCl (12 mL, 3 M), and extracted with petroleum ether.

2FPI and 2PI-d₅.

2FPI and 2PI-d₅ were synthesized following the same procedure as for 2PI-d₀. 4-fluorophenyl magnesium bromide and phenyl magnesium bromide-d₅ were made from 1-bromo-4-fluorobenzene and bromobenzene-d₅, respectively, by Grignard reaction following the procedure described in chapter 2.

2MI

Ethereal solution of methyl magnesium bromide (15 mmol, 1 M) was added slowly to a solution of 2-indanone (10 mmol in 15 ml of ether) at 0 °C. The mixture was stirred for two hours at room temperature to yield 2-hydroxyl-2-methylindan. The latter was brominated with PBr₃ in 20 ml of dichloromethane at 20 °C for two hours to yield 2-bromo-2methylindan. 2MI was synthesized by refluxing 2-bromo-2methylindan with magnesium in methanol.

The synthesized compounds were analyzed by GC/MS.

5.2.2 Spectroscopy

The supersonic jet spectrometer used in this work has been described in chapter 1. The carrier gas (He or Ar) at 1-3 atm is passed through a heated sample reservoir containing the sample (at 25 °C for 2MI; 110 °C for 2PI and 2FPI).
5.3 Results and analysis

5.3.1 Ab initio Calculations

Ground state optimizations of the investigated molecules were performed at the second-order Møller–Plesset perturbation (MP2) level of theory with 6-311G(d,p) basis set. Configuration interaction singles (CIS) method with the same 6-311G(d,p) basis set was employed for the excited states. The cyclopentenyl ring of indane is not planar; therefore, monosubstitution at 2-position will lead to two conformers, axial (ax) and equatorial (eq). The results of MP2/6-311G(d,p) optimizations of 2MI, 2PI, and 2FPI are summarized in Table 5.1. All stable conformers of 2MI, 2PI and 2FPI have C₄ symmetry. The calculated vertical $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ excitation energies of 2PI and 2FPI are compiled in Table 5.2.

The optimized structures of the minimum energy conformers of 2MI, and the transition state between the minima are displayed in Figure 5.2. The axial conformer (2MI₀) is 85 cm⁻¹ more stable than the equatorial conformer (2MIₑ) at the MP2/6-311G(d,p) level.

![Figure 5.2 Conformational landscape of 2MI.](image)

The optimized structures of the minimum energy conformers of 2PI and the transition states between the minima are displayed in Figure 5.3. Two different minima along the phenyl torsional coordinate of the potential energy surface of the equatorial isomer of 2PI have been
found at torsional angles of 0 ° (2PIeq0) and 90 ° (2PIeq90). The relative energy of the two
conformers is 449 cm⁻¹ in favor of 2PIeq0. The 2PIeq90 minimum lies at 22 cm⁻¹ below the
transition state (TSeq in Figure 5.3). Only one minimum was found along the phenyl torsional
coordinate of the axial isomer of 2PI, at τ=0 °. The barrier to torsional motion is 1343 cm⁻¹ (TSax
in Figure 5.3). The high barrier in the axial conformer is due to the repulsive non bonded
interactions between the two ortho hydrogens of the phenyl ring and the two α hydrogens of the
indan ring. The distance between the ortho hydrogens of the phenyl ring and the α hydrogens of
the indan ring is 1.95 Å. It has been reported that the H…H repulsion energy is negligible
beyond 2.4 Å but increases to 1 kcal/mol at H…H distance of about 2.0 Å.¹⁵

Figure 5.3 Conformational landscape of 2PI.
Table 5.1 MP2/6-311G(d,p) calculated $S_0$ relative energies ($E_{\text{rel}}$), superscript a puckering angles (p), superscript b and dihedral angles ($\tau$) superscript b of the stable conformers of 2MI, 2PI, and 2FPI.

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<th>2MI</th>
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<th>2FPI</th>
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<td>279</td>
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<sup>a</sup>Relative to the axial conformers. <sup>b</sup>The puckering angle, p, and the torsional angle, $\tau$, are defined in Figures 5.1a and 5.1b.
5.3.2 R2PI spectrum of 2MI

The spectrum of 2MI is displayed in Figure 5.4. Two electronic origins are identified at 36903.3 cm\(^{-1}\) and 36924.0 cm\(^{-1}\). The fundamental transitions of puckering mode appear at 73.6 cm\(^{-1}\) and 75.7 cm\(^{-1}\) from the first and second origins, respectively. The peaks at 36903.3 cm\(^{-1}\) and 36924.0 cm\(^{-1}\) are assigned to the electronic origins of 2MI\(_{ax}\) and 2MI\(_{eq}\), respectively. This assignment is made by comparison with closely related n-propylbenzene and allylbenzene.\(^9\),\(^{10}\) The electronic origins of the gauche conformers (in which the substituent group points toward the aromatic chromophores) of n-propylbenzene and allylbenzene are red-shifted relative to those of the extended trans conformers. The calculated vertical \(S_1 \leftarrow S_0\) excitation energy of 2MI\(_{ax}\) (48110 cm\(^{-1}\)) is less than that of 2MI\(_{eq}\) (48150 cm\(^{-1}\)). The computed puckering frequency in the \(S_1\) state of 2MI\(_{ax}\) (78 cm\(^{-1}\)) is also less than that of 2MI\(_{eq}\) (84 cm\(^{-1}\)). Thus, the computed relative \(S_1 \leftarrow S_0\) excitation energies and the puckering frequencies are consistent with the assignment of the two electronic origins.

A MI\(_{eq}/MI_{ax}\) conformer ratio of 2.3 was estimated by integrating the areas under the origin band of each conformer. The Boltzmann distribution law was then used to estimate the relative energy, \(\Delta E = E_{2MI_{ax}} - E_{2MI_{eq}}\), of 172 cm\(^{-1}\). Thus, the MP2 calculation reverses the relative energies of the two conformers.

5.3.3 R2PI spectra of 2PI and 2PI-\(d_5\)

The expanded view of the low energy portion of the spectrum of 2PI in the supersonic expansions of helium and argon is displayed in Figure 5.5. The weak bands at 36670 – 36720 cm\(^{-1}\) disappear when argon was used as the carrier gas; consequently, the weak features may be associated with hot bands or clusters of 2PI with some impurities contained in the helium tank.
Shown in Figure 5.6 are the R2PI spectra of 2PI obtained at two different laser powers; as the laser power is increased the intensities of all vibronic bands increase relative to the intensity of the first intense peak at 36884.4 cm\(^{-1}\). Thus, laser power saturation experiments suggest a single ground state conformer of 2PI. The peak at 36884.4 cm\(^{-1}\) is assigned as the electronic origin of 2PI.

**Figure 5.4** R2PI spectrum of 2MI.
Figure 5.5 Expanded view of the low energy portion of the spectrum of 2PI in the supersonic expansions of (a) argon, and (b) helium.

The spectra of 2PI, 2FPI, and 2PI-d₅ are displayed in Figure 5.7. The frequencies of the electronic origins, and relative frequencies of the major vibronic bands are also shown in the Figure. Full deuteration of the phenyl ring of 2PI causes the electronic origin of 2PI to blue-shift by only 0.4 cm⁻¹, suggesting that the $S_1 \leftarrow S_0$ transition is localized on the ortho-xylyl
chromophore. The biggest difference between the spectra of 2PI and 2PI-d₅ is associated with the peaks at 605.4 cm⁻¹ and 773.1 cm⁻¹ above the origins of 2PI and 2PI-d₅, respectively. The two peaks are assigned to the electronic origins of the $S_2 \leftarrow S_0$ transitions that are localized on the phenyl and phenyl-d₅ chromophores, respectively.

Figure 5.6 R2PI spectra of 2PI at (a) high, and (b) low laser powers.
The first intense band at 36894.8 cm\(^{-1}\) in the spectrum of 2PFI is assigned as the \(S_1 \leftarrow S_0\) electronic origin. The major difference between the R2PI spectra of 2PI and 2PFI is the appearance of a peak at 33.1 cm\(^{-1}\) above the \(S_1 \leftarrow S_0\) origin of 2PFI (Figure 5.7). The latter peak is assigned as the origin of the \(S_2 \leftarrow S_0\) transition. The low energy portion of the spectrum of
2FPI shown in Figure 5.8 reveals the presence of weak vibronic bands at 36667 - 36734 cm$^{-1}$ in the supersonic expansion of helium. However, the weak bands disappear when argon was used as the carrier gas as found in the case of 2PI. The spectra of 2FPI obtained at two different laser powers are displayed in Figure 5.9. As the laser power is increased, the relative intensities of all vibronic bands increase. The only exception is the weak band marked by the (X) symbol. This band disappears when He is used as the carrier gas; hence, the band is due to argon cluster(s). Thus, laser power saturation experiments suggest a single ground state conformer of 2FPI.

**Figure 5.8** Expanded view of low energy portion of the spectrum of 2FPI in the supersonic expansions of (a) argon, and (b) helium.
Figure 5.9 R2PI spectra of 2FPI at (a) high, and (b) low laser powers.
5.5 Discussion

5.4.1. Assignment of the observed vibronic transitions of 2PI, 2PI-d_5, and 2FPI

The calculated S_1 ← S_0 vertical excitation energies of the axial conformers of 2PI and 2FPI are lower than those of the equatorial conformers by 312 – 382 cm\(^{-1}\) (Table 5.2). The lower excitation energies of the axial conformers can be attributed to the lower puckering angles, p, of the axial conformers (Table 5.1). The greater planarity of the axial conformers is most likely caused by the intramolecular C-H/\(\pi\) interactions, because the values of p in the two conformers of 2MI and the equatorial conformers of 2PI and 2FPI are similar. Thus, the calculations suggest that intramolecular C-H/\(\pi\) interactions occur only in the axial conformers of 2PI and 2FPI.

The most likely candidate for the origin of another conformer of 2PI is the band at 141.6 cm\(^{-1}\) from the assigned origin. However, the corresponding band in the spectrum of 2PI-d_5 has a frequency of 139.9 cm\(^{-1}\). Hence the band at 141.6 cm\(^{-1}\) is not an electronic origin because of the associated isotope effect.\(^{11}\) The red-shift of the 2PI origin with respect to the origins of 2MI conformers is attributed to the intramolecular C-H/\(\pi\) interactions.\(^{1,8}\) These interactions occur only in 2PI\(_{ax}\); therefore, the whole spectrum of 2PI is that of the 2PI\(_{ax}\) conformer. Similarly, the whole spectrum of 2FPI is due to the 2FPI\(_{ax}\) conformer. The CIS/6-311G(d,p) calculated lowest frequency symmetric modes of 2PI\(_{ax}\) in its optimized S_1 state are associated with the puckering and flapping modes. The calculated frequencies (38 cm\(^{-1}\) and 163 cm\(^{-1}\) of these modes are very close to the observed frequencies of 41.1 cm\(^{-1}\) and 141.6 cm\(^{-1}\) for the lowest frequency vibronic transitions. Therefore, the 41.1 cm\(^{-1}\) and 141.6 cm\(^{-1}\) fundamentals are assigned to the puckering and flapping modes, respectively.

A progression in the puckering mode with a fundamental frequency of about 40 cm\(^{-1}\) dominates the origin region of the spectra of 2PI, 2FPI, and 2PI-d_5. The drop in the frequencies
of the puckering and flapping modes of 2FPI to 40.1 cm\(^{-1}\) and 138.4 cm\(^{-1}\), respectively, is caused by the higher reduced mass of the modes in 2FPI than in 2PI. The frequencies of the puckering and flapping modes of 2PI-d\(_5\) are 40.2 cm\(^{-1}\) and 139.9 cm\(^{-1}\), respectively, for the same reason. The relatively intense vibronic transition at \(\sim 700\) cm\(^{-1}\) in the spectra of indane derivatives is associated with the in-plane bending of indan.\(^2,3\) Similar transitions also appear in the spectra of 2PI, 2PI-d\(_5\), and 2FPI at 730.0, 723.0, and 721.8 cm\(^{-1}\), respectively. The combination of these fundamentals with the fundamentals of puckering mode appear at 771.2, 762.8, and 760.2 cm\(^{-1}\), respectively.

**Table 5.2** CIS/6-311G(d,p) calculated vertical S\(_1\) \(\leftarrow\) S\(_0\) and S\(_2\) \(\leftarrow\) S\(_0\) excitation energies (E\(_1\) and E\(_2\), cm\(^{-1}\)) and oscillator strengths (f\(_1\) and f\(_2\)) for 2PI and 2FPI.

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<th>f(_1)</th>
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5.4.2 Conformer relaxation

Very fast relaxation of $2\text{PI}_{eq0}$ ($2\text{FPI}_{eq0}$) to the more stable $2\text{PI}_{eq0}$ ($2\text{FPI}_{eq0}$) is expected due to the low barrier of 22 cm$^{-1}$ ($T_{\text{Seq}}$ in Figure 5.3) to such transition. Therefore, only two conformers of 2PI and 2FPI are expected to be observed in the jet experiments. However, the most intriguing aspect of this work appears to be the absence of the equatorial isomers of 2PI and 2FPI in the supersonic expansions of helium and argon. Barriers to conformer interconversions in supersonic expansions can be surmounted if the barriers are less than $2kT$.\textsuperscript{14} Where $k$ is the Boltzmann constant; $T$ is the pre-expansion temperature (383 K for 2PI and 2FPI, and 298 K for 2MI). The computed barrier to axial-equatorial interconversion in 2PI ($T_{\text{ax-eq}}$ in Figure 5.3) is 589 cm$^{-1}$ above the $2\text{PI}_{eq0}$ local minimum. This barrier is about the same as $2kT$ (530 cm$^{-1}$) of 2PI. Meanwhile, the barrier to axial-equatorial interconversion in 2MI ($T_{\text{ax-eq}}$ in Figure 5.2) is 815 cm$^{-1}$ above the $2\text{MI}_{eq}$ minimum. Thus, the barrier in 2MI is substantially larger than $2kT$ (405 cm$^{-1}$) of 2MI. The lower barrier in 2PI is attributed to the higher stabilizing effect of the C-H/π interactions in the transition state of 2PI than in the transition state of 2MI. Therefore, conformational relaxation of the equatorial isomers of 2PI and 2FPI occurs because of the high pre-expansion temperatures and relatively low barrier to axial-equatorial interconversion.

5.4.3 Inter-chromophore interactions in 2PI and 2FPI

The observed energy gap between the $S_2 \leftarrow S_0$ origins of 2PI and 2PI-d$_5$ is 168.5 cm$^{-1}$, which is very close to the energy gap of 165.9 cm$^{-1}$ between the electronic origins of toluene and toluene-d$_5$.\textsuperscript{16} This observation suggests that the $S_2 \leftarrow S_0$ transition of 2PI is completely localized on phenyl chromophore despite the close proximity of the two chromophores. Similarly, the
energy gap between the localized $S_2 \leftarrow S_0$ origins of 2PFI and 2PI is 561.5 cm$^{-1}$; this energy gap is comparable to the energy gap of 558 cm$^{-1}$ between the $S_1 \leftarrow S_0$ origins of toluene and p-fluorotoluene,$^{17}$ indicating that the $S_2 \leftarrow S_0$ transition is localized on 4-fluorophenyl chromophore.

The computed transition density surfaces for the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of the axial conformers of 2PI and 2FPI are displayed in Figure 5.10. The surfaces indicate that the first and second excited singlet states of 2PI$_{ax}$ and 2FPI$_{ax}$ are $\pi\pi^*$ $L_b$ states,$^{18}$ that are completely localized on the ortho-xyl saw and phenyl (4-fluorophenyl) chromophores, respectively. As seen in Table 5.2, the $S_1 \leftarrow S_0$ transitions of both 2PI and 2FPI are more intense than the $S_2 \leftarrow S_0$ transitions. The vertical energy gap between the computed $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions is higher in 2PI$_{ax}$ than in 2FPI$_{ax}$. However, the energy gap between the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of each molecule is substantially higher than the experimental energy gaps most likely because the relaxation energies of the two chromophores are different. Rigorous comparison of the observed and calculated energy gaps between the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions requires geometry optimizations of the two excited states.
Figure 5.10 Transition density surfaces for the (a) $S_1 \leftarrow S_0$ transition of 2PI, (b) $S_2 \leftarrow S_0$ transition of 2PI, (c) $S_1 \leftarrow S_0$ transition of 2FPI (d) and $S_2 \leftarrow S_0$ transition of 2FPI.

5.5 Conclusions

The two stable conformers of 2MI have been observed. A $2\text{MI}_{\text{eq}}/2\text{MI}_{\text{ax}}$ conformer ratio of 2.3 was estimated at 298 K, leading to the energy difference, $\Delta E = E_{2\text{MI}_{\text{ax}}} - E_{2\text{MI}_{\text{eq}}}$, of 172 cm$^{-1}$. Theory predicts three stable conformers of 2PI and 2FPI, two equatorial conformers and one
axial conformer. The axial conformers of 2PI and 2FPI are slightly more planar due to the intramolecular C-H/π interactions. Only the axial conformers of 2PI and 2FPI were observed. The equatorial conformers relax to the more stable axial conformers because of the high pre-expansion temperatures and relatively low barrier to axial-equatorial interconversion. The barrier to axial-equatorial interconversion in 2MI is high enough to prevent conformer relaxation at the pre-expansion temperature of 298 K. The $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ of 2PI are found to be completely localized on the ortho-xylyl and phenyl chromophores, respectively, by analyzing the spectra 2PI-d$_0$ and 2PI-d$_5$. The $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of 2FPI are also found to be localized. The transition density surfaces for the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions the axial conformers of 2PI and 2FPI show that the first and second excited singlet states of 2PI$_{ax}$ and 2FPI$_{ax}$ are ππ$^*$ L$_b$ states that are completely localized on the ortho-xylyl and phenyl (4-fluorophenyl) chromophores, respectively.

5.6 References


Figure A1. GC/MS spectrum of α,α'-DPE-d₂
Figure A2. GC/MS spectrum of p-DPE-d$_1$
Figure A3. GC/MS spectrum of a mixed sample of DPE-d₀, DPE-d₅, and DPE-d₁₀
Figure A4. GC/MS spectrum of THDC-d₀
Figure A5. GC/MS spectrum of tDPCP-d$_0$
Figure A6. GC/MS spectrum of a mixed sample of tDPCP-d$_1$, and cDPCP-d$_1$
Figure A7. GC/MS spectrum of a mixed sample of tDPCP-d$_2$, and cDPCP-d$_2$
Figure A8. GC/MS spectrum of 2-methylindane