

Conformational energy and dynamics of 9-ethylfluorene

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The S_1 excited state and cation ground state of jet cooled 9-ethylfluorene have been studied experimentally using resonant enhanced multiphoton ionization and zero electron kinetic energy (ZEKE) photoelectron spectroscopy. The spectroscopy has identified two conformations of the ethyl chain which are labeled symmetric and unsymmetric both of which exist in the supersonic expansion. Density functional quantum chemical calculations are used to calculate the ground state and cation energies of each conformer as well as the barrier to conformer interconversion via a bond rotation. Dynamics on the S_1 surface are measured using picosecond and nanosecond ZEKE photoelectron spectroscopy. Fast irreversible vibrational redistribution is measured at energies ≥ 990 cm^{-1} and the ZEKE spectra are shown to have a unique signature for each of the two isomers. Picosecond and nanosecond ZEKE spectroscopy are used to search for conformer interconversion but even at the highest energy probed (2648 cm^{-1}) no evidence is seen for a dynamic barrier crossing. Statistical density of states calculations are used to predict the relative populations of each conformer expected as a function of excess energy as well as related Rice–Ramsperger–Kassel–Marcus calculations to predict the expected isomerization rates. © 1999 American Institute of Physics. [S0021-9606(99)01305-7]

I. INTRODUCTION

In recent years electronic spectroscopy in supersonic jets has been successfully used to identify and characterize multiple conformational minima in gas phase molecules. The spectral simplification of jet cooling often allows small features to be associated with minor conformations. Examples of molecules with separate conformers identified are alkylbenzenes,^{1–4} alkylnilines,^{5–7} alkylphenols,^{8,9} naphthols,^{10–13} tryptaphan,^{14,15} tryptamine,^{15,16} alkylcyclohexanone,¹⁷ and many others.^{18–20} The identification of separate transition origins of conformers, as opposed to vibronic structure and hot bands, has been accomplished with many different techniques such as dispersed fluorescence,^{1–5,14,15,18} saturation spectroscopy,^{14,15} hole burning,^{13,18} rotational structural analysis,^{11,16} and photoelectron spectroscopy,^{7,12,19} among others.^{20,21}

The most severe limitation of using jet spectroscopy to identify conformers is the difficulty in assigning the relative energetics of the observed conformers. In most spectroscopies a Boltzmann population analysis can lead to an accurate estimate of the relative stability of the observed conformers. However, the potential nonequilibrium nature of the population distribution in the jet has limited the usefulness of such an approach. Recently, Baer *et al.*¹⁷ have studied this question quite thoroughly and have concluded that with careful measurement it is possible, in at least some cases, to do a thermal analysis of the ground state energetics based on the observed intensities of electronic transitions. In particular if the barrier to the conformer interconversion is high enough then the populations in the jet reflect the temperature of the nozzle prior to expansion. This point has been demonstrated

in other work as well²² where it was determined that even a barrier height of 350 cm^{-1} was sufficient to prevent complete cooling in the molecular beam. In addition to the barrier height other factors influence the cooling of conformations such as carrier gas components and backing pressure.

The determination of the relative energetics of ground state conformations can perhaps best be done today using *ab initio* theoretical calculations. Particularly since one is interested in the difference in energy between two structures it is reasonable, on even large molecules, to have a theoretical accuracy of less than 1 kcal/mol.²³

While electronic spectroscopy in jets has difficulty in determining the energetic differences in the ground state it is a very accurate technique for determining the change in conformer stability with electronic excitation. This information is contained directly in the spectral shifts of the electronic origins of the various isomers and can easily have subwave number accuracy. A very powerful combination of approaches, then, has been to use theoretical calculations of ground state energies and then extend them to the excited state by utilizing spectroscopic information. Excited states are still quite difficult for theoretical calculations and thus greatly improved *relative* excited state energies can be obtained.

In this article we report on studies of the conformations of 9-ethylfluorene (EF) in the ground state, the S_1 excited electronic state, and the cation ground state. Two conformations of EF are identified which involve rotation of the ethyl group about the C_9-C_α bond and are labeled symmetric (sym) and unsymmetric (unsym). The structures of these two conformations are depicted in Fig. 1. The sym and unsym

Ethylfluorene Conformations

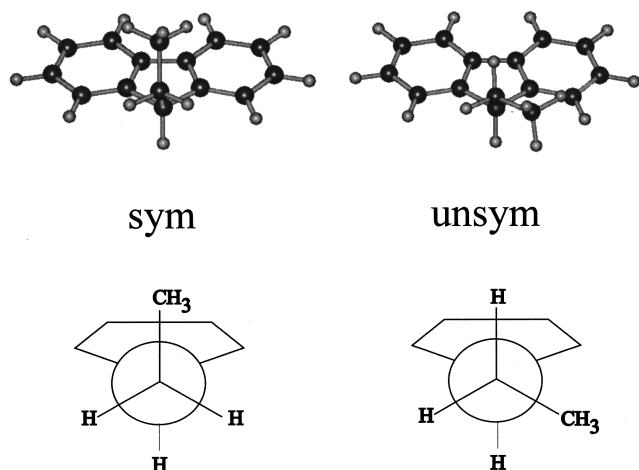


FIG. 1. Representations of the two configurations of ethylfluorene. The symmetric configuration (sym) is characterized by a symmetry plane perpendicular to the fluorene plane and bisecting the five membered ring and the ethyl substituent. The unsymmetric conformation (unsym) has the ethyl chain rotated by 120° breaking the symmetry and allowing two equivalent conformations.

labels are a simple way to uniquely distinguish the conformations since gauche and anti designations are not appropriate in this case. As noted above we use a combination of *ab initio* calculations combined with electronic spectroscopy to determine the relative energies of these structures in all three electronic states. There is an additional interesting check between theory and experiment since the cation can be measured experimentally (relative to the ground state) and also calculated accurately. Thus the change in stability of the conformations upon ionization can be measured experimentally and also calculated with some accuracy. It will be shown that the agreement between theory and experiment is excellent.

In addition to the characterization of the static potential energy minima we have applied time resolved ZEKE photoelectron spectroscopy to the excited state dynamics. Each conformation has a unique ZEKE spectral signature which is used to monitor the excited state vibrational dynamics. Irreversible vibrational redistribution is measured for each conformation and attempts are made to measure the subsequent conformer isomerization using ZEKE probing techniques.

II. EXPERIMENT

A detailed description of the experimental apparatus has been given elsewhere,^{24,25} so only a brief synopsis is given here. Two color 1 + 1 resonance enhanced multiphoton ionization (REMPI) spectroscopy with mass resolved detection is used to study the spectroscopy of the S_1 electronic state of the jet cooled molecules. Mass analyzed threshold ionization (MATI) spectroscopy,²⁶ the mass resolved equivalent of zero electron kinetic energy (ZEKE) spectroscopy, and ZEKE spectroscopy itself are used to measure the photoelectron spectroscopy of the ion ground state. In this study ZEKE and MATI spectroscopy are used interchangeably and at the reso-

lution of interest they can be considered to give exactly the same spectral information. The choice of ZEKE versus MATI is often one of experimental convenience, with ZEKE spectroscopy usually being used for the weakest signals.

Nanosecond and picosecond laser systems were separately used in this study. The nanosecond laser system employed in these experiments consists of two dye lasers (Lumonics HD-500) pumped by the second harmonics of a pulsed Nd:yttrium-aluminum-garnet (YAG) (Continuum NY-61) operating at 20 Hz. The visible output of each dye laser has a pulse width of 6 ns and a band width of 0.04 cm^{-1} . Both dye lasers are frequency doubled and one functions as the pump and the other as the probe. The pump and probe lasers were temporally overlapped by an appropriate optical delay and spatially overlapped in the vacuum chamber under slightly focused conditions. Care was taken to minimize any signal from either laser alone. The second laser system is a pulse amplified picosecond system used for time resolved studies. This consists of a continuous wave mode-locked Nd:YAG (Coherent Antares) synchronously pumping two dye lasers. Each dye laser is amplified in separate three stage dye amplifiers, pumped by the second harmonic of a Nd:YAG regenerative amplifier (Continuum RGA-67) operating at 20 Hz. The amplified output pulse width is $\sim 15 \text{ ps}$ with a bandwidth of 5 cm^{-1} and an energy of $0.2\text{--}1 \text{ mJ/pulse}$ in the visible. The overall cross correlation is $>20 \text{ ps}$ due to jitter between the two dye lasers. Laser wavelengths were calibrated with a Na/K/Ne hollow cathode lamp.

A pulsed supersonic beam originates in the first of two differentially pumped chambers. The nozzle has a sample container which holds the EF sample (Aldrich) and is heated to $130\text{--}150^\circ \text{C}$. The exact vapor pressure is unknown but we estimate it as significantly below 1 Torr. The pulsed beam is skimmed and enters the second chamber where the spectroscopy takes place.

The REMPI spectra were obtained by fixing the probe slightly higher than the ionization potential of the complex and scanning the pump. For a number of scans it was advantageous to measure a "probe selective" REMPI spectrum in which the probe was tuned to exceed the IP of one conformer and not the other. This helped separate out the contributions of the individual conformers to the overall spectrum.

The MATI/ZEKE spectra were obtained by fixing the pump to the S_1 vibronic band of interest and scanning the probe through the IP. To achieve clean separation of the prompt and MATI signals we implemented a pulsed Wiley-McClaren²⁷ extraction scheme in which the upper grid pulse width was varied to act as a mass filter. In this way the contribution from the cluster and fragments, other than the one of interest, could be eliminated. The MATI scheme used a delayed discrimination field of -2 V/cm and an extraction pulse of 560 V/cm which was delayed $\geq 15 \mu\text{s}$. The ions then traverse the time-of-flight (TOF) mass spectrometer and are detected on dual stack microchannel plates (Galileo Electro-Optic Corp). ZEKE spectra were obtained by collecting electrons in a second microchannel plate detector. The interaction region was held field free while pump and probe laser excitation occurred and then a -50 V pulse was

TABLE I. Summary of *ab initio* quantum chemical calculations.

Molecular conformation		Energy (cm ⁻¹)	Energy (cm ⁻¹) ^b	$C_{10}-C_9-C_\alpha-C_\beta$ ^c Torsion angle
		B3LYP 6-31G*	B3LYP 6-311G**	
Neutral ground state	sym ^d	0	0	59
	TS	1910	...	-5
	unsym	220	183	-70
Cation ground state	sym ⁺	58 800	60 285	59
	unsym ⁺	58 940	60 410	-70
	TS ⁺	60 510	...	-4.5
	unsym ⁺ -sym ⁺	140	125	...
	TS ⁺ -sym ⁺	1710

^aThis is the method and basis set used for the geometry optimization.

^bEnergy calculated at the geometry optimized for the smaller 6-31G* basis set.

^cDetermined using the 6-31G* basis set.

^dAll energies are referenced to the ground state sym energy.

applied after a 1 μ s delay to field ionize the remaining high Rydberg states and accelerate the resulting electrons to the detector.

MATI/ZEKE spectra have been recorded by pumping a number of S_1 resonance bands. In general these spectra have not been scanned over a wide spectral range but rather in a narrow region centered on the $\Delta v = 0$ transition to the cation. Scans of this region have been found to give important spectral information (in particular the frequency of the pumped band in the cation) as well as a view of vibrational dynamics which may occur. For studies of vibrational dynamics the ZEKE/MATI spectra are monitored at different probe time delays which can be on the picosecond or nanosecond time scale. For picosecond time delays a computer controlled optical delay line is used to collect data with a carefully calibrated probe delay which can extend up to 8 ns if necessary. Delayed probe scans with nanosecond lasers involve simply using a fixed optical delay line which was varied to as late as 15 ns. Given the 6 ns inherent width of the nanosecond dye laser pulses the nanosecond delayed spectra necessarily take a convolution of the delay with the broad laser pulses and is meant to give a course view of the dynamics.

III. RESULTS

A. *Ab initio* calculations

A number of quantum chemical calculations were performed on the ground state of EF in order to calculate the relative stability of the sym and unsym configurations, to determine the barrier height for interconversion of these species and to calculate the vibrational frequencies. In addition similar properties were calculated for the cation species to compare directly with the measured results of the photoelectron spectroscopy.

The GAUSSIAN 94 program²⁸ was used in all calculations. To determine the energies of the unsym and sym configurations the initial guesses were chosen to approximate each respective conformation. A structural optimization was performed using the B3LYP hybrid density functional method with a 6-31G* basis set. The B3LYP²⁹ method has been shown to be an accurate, cost effective method which has

accuracy similar to MP2 calculations at considerably reduced computational time. A discussion of these methods with respect to fluorene is given in Ref. 30. The cation was calculated with the same methods except that the charge was set to +1, the multiplicity was set to 2, and a spin unrestricted calculation was performed. Several single point calculations with an expanded 6-311G** basis set were done at the optimized structures of the smaller basis set. For the ground state the most accurate calculations indicate that the sym configuration is more stable by 183 cm⁻¹. The computational results for the ground state and the cation are summarized in Table I.

An important goal of this work was to determine the role of conformer interconversion on the observed dynamics so it was critical to determine the barrier for rotation between the unsym and sym forms. This was accomplished using the QST3 method within GAUSSIAN 94, which allows input of the reactant structure (optimized unsym), product structure (optimized sym), and an initial guess of the transition state structure. This search was performed with the B3LYP method and a 6-31G* basis set. A stable transition state was found which was 1910 cm⁻¹ above the sym structure and 1690 cm⁻¹ above the unsym structure. The transition state structure was found, as expected, at a torsional angle, $C_{10}-C_9-C_\alpha-C_\beta$, directly between the unsym and sym conformation at a nearly eclipsed geometry. The only other structural change of note in the transition state was a slight increase in the $C_9-C_\alpha-C_\beta$ bond angle due to interaction of C_β with the hydrogen at C_1 . For comparison the transition state was also determined in the cation using the same method. A similar transition state geometry was found but with a somewhat reduced barrier. The barrier from the sym configuration was 1710 cm⁻¹ while it was only 1570 cm⁻¹ from the unsym form.

In addition to the conformer energetics the calculations were used to determine the vibrational frequencies in the neutral and cation stable conformations and transition state. The frequencies were determined at the HF level of theory and scaled by 0.893. The theoretical results will be elaborated and compared to the experimental results in the discussion section below.

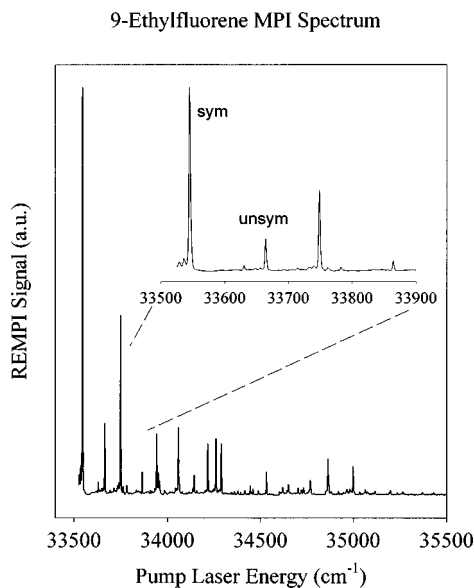


FIG. 2. REMPI spectrum of the S_1 state of ethylfluorene. The insert is a blow-up of the origin region showing the major, sym, conformer origin and the substantially weaker unsym conformer.

B. S_1 spectroscopy

The jet-cooled S_1 spectrum of EF has been reported several times in the literature.^{31–33} Auty *et al.*³¹ measured the fluorescence excitation and dispersed fluorescence spectra as part of a study on carbazole and carbazole analogs. Our measured spectra agree well with this report but differs significantly in interpretation of the vibronic structure since the entire spectrum was ascribed to a single conformation. The other articles^{32,33} focus on excimer properties of EF containing clusters but again the reported spectra agree with our results.

The jet cooled REMPI spectrum of EF is shown in Fig. 2 from the electronic origin to greater than 1900 cm^{-1} excess energy. A detailed view of the origin region is shown in the figure. The bands at $33\,543$ and $33\,663\text{ cm}^{-1}$ have been identified as origin bands of the sym and unsym conformations, respectively (the assignment will be justified below). This measured energy difference immediately indicates that the sym conformation is stabilized by an additional 120 cm^{-1} in the S_1 state relative to the ground state. Coupled with the *ab initio* calculation this yields an energy difference of 300 cm^{-1} in S_1 .

In viewing the higher energy region it becomes difficult to confidently identify which conformer each band is assigned to due to spectral congestion. To sort out these bands probe selective two color REMPI spectra were taken. In measuring the photoelectron spectra (below) it was observed that the sym conformer required a higher energy probe ($>29\,688\text{ cm}^{-1}$) than the unsym ($>29\,490\text{ cm}^{-1}$). Two sets of REMPI spectra were obtained with the probe at $29\,550$ and $30\,200\text{ cm}^{-1}$. The results are shown in Fig. 3. The spectrum with the redder probe, Fig. 3(b), shows a dramatic increase in the intensity of the unsym bands, which is the minor species. The selectivity is not perfect because there was some pump alone signal, and more importantly, as higher

Ethylfluorene Probe Dependent REMPI Spectra

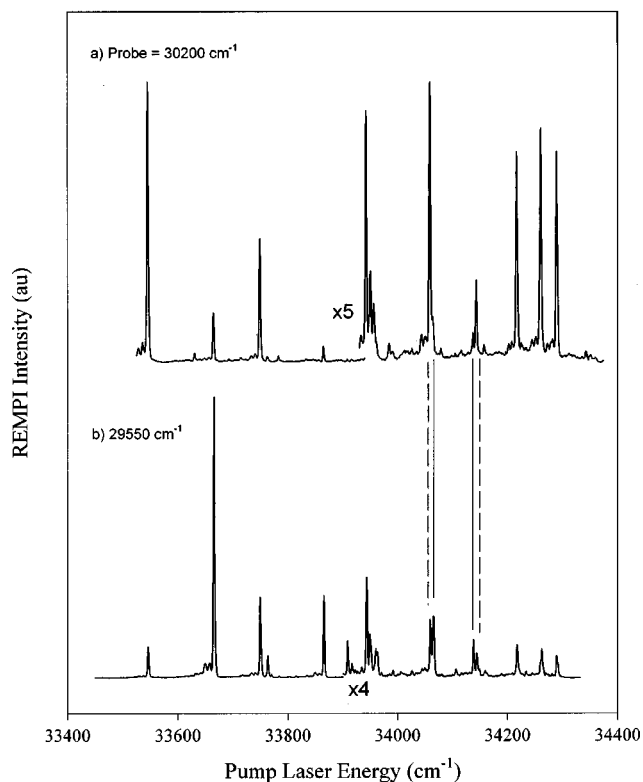


FIG. 3. Two-color REMPI spectra of ethylfluorene at higher energy in S_1 . (a) and (b) differ in the probe laser energy as indicated. As discussed in the text the lower trace is selective toward the weaker, unsym, conformer due to its lower IP.

energy bands are scanned the probe effectively becomes more energetic with respect to the ionization threshold. The spectra obtained with the higher energy probe should be equally sensitive to the two conformations. By comparing the two spectra a greater number of weaker bands could be confidently assigned to their respective origins.

The vibrational spectroscopy has not been analyzed in any systematic way other than noting some of the stronger bands for further MATI experiments and dynamics measurements. Several observations on the vibronic bands can be made. The low frequency region was scrutinized closely to identify bands which may be due to torsional motion of the ethyl group. Only one small band of the sym conformer was identified at 87 cm^{-1} . This can be compared to several low frequency bands in the ground state calculations. A calculated band at a scaled frequency of 80 cm^{-1} is primarily an ethyl torsion about the C_1-C_α bond and is a likely assignment for the observed 87 cm^{-1} S_1 band. Most of the other major observed bands can be related to strong vibrations in the electronic spectroscopy of fluorene with the exception of the 515.5 cm^{-1} band. This band is strong in the electronic spectrum of sym EF but is weak or absent in unsym EF and has no direct counterpart in the fluorene³⁴ or phenylfluorene³⁵ electronic spectrum. A ground state mode calculated to have a frequency of 524 cm^{-1} does have a significant component of ethyl chain motion in the sym conformation so this may be the mode but it also involves out of

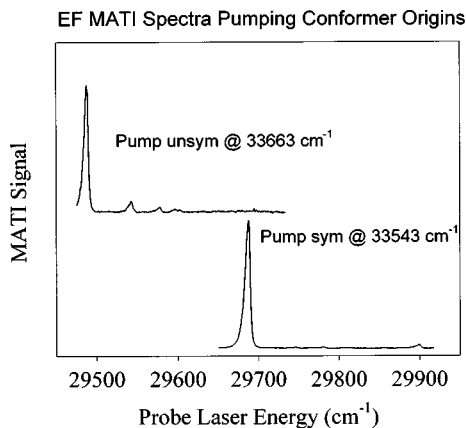


FIG. 4. MATI spectra obtained by pumping the origins of the sym and unsym conformers as indicated. The peaks are the origins of the cation spectra and together with the pump wavelength give directly the IP of each conformer.

plane deformation of the ring system which would not be favored when considering the local symmetry of the fluorene system. A calculated in plane mode of 494 cm^{-1} perhaps is more reasonable but this looks very similar in the unsym compound so it is puzzling why it would not be observed there as well.

C. MATI spectroscopy

Mass analyzed threshold ionization spectra were obtained for a large number of S_1 bands of both conformations of EF. Due to the predominance of the sym conformation more bands were studied of this conformation, particularly at high energy where selective excitation of the minor, unsym, conformation became impossible. In the spectra that follow an intermediate S_1 band was selectively pumped and the probe laser was scanned to obtain the photoelectron spectrum. EF, like similar molecules, exhibits a very strong $\Delta v = 0$ propensity in the S_1 to cation transition so in general only a small number of vibronic bands have any intensity in the photoelectron spectrum. As such most of the scans recorded were concentrated in a narrow region around the $\Delta v = 0$ transition. Thus if a 1000 cm^{-1} S_1 band was pumped the probe would be scanned in the region approximately 1000 cm^{-1} above the adiabatic IP. Although the spectral information is thus limited it generally yields the shift in the vibration of interest upon ionization and exhibits dynamic information in the time resolved experiments as shown below.

Figure 4 is the MATI spectrum obtained when pumping the S_1 origin of the sym and unsym conformations. Note that while the sym conformation has the redder S_1 transition energy it exhibits a bluer probe to the ionization threshold. In fact the overall ionization threshold of the sym ($63\,231 \pm 3\text{ cm}^{-1}$) is greater than the unsym conformation ($63\,151 \pm 3\text{ cm}^{-1}$) by 80 cm^{-1} . The well separated, clearly distinguished MATI spectra of the two conformations suggests that the conformational identity of the molecule can be probed even when the total internal energy is above the barrier for interconversion. In Sec. IIID experiments are presented which probe this interconversion.

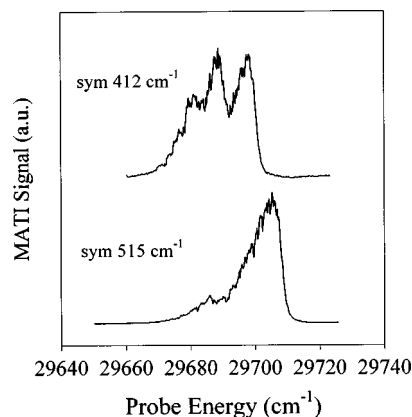


FIG. 5. Representative MATI spectra of two intermediate energy S_1 bands at 412 and 515 cm^{-1} of the major, sym, conformer. The spectra did not change as a function of probe delay.

As higher bands in S_1 are pumped some of the MATI spectra become more complicated with several distinct transitions appearing in the $\Delta v = 0$ region. For instance the 412 cm^{-1} band of the sym shows three peaks in the MATI spectrum, whereas the 515 cm^{-1} band exhibits a single peak, as shown in Fig. 5. The question as one goes to higher energy is when do the bands begin to exhibit structure which is indicative of restricted or dissipative IVR³⁶ as opposed to spectral complication?

D. S_1 dynamics

Vibrational dynamics were measured by recording photoelectron spectra as a function of probe laser delay. This was accomplished with both picosecond and nanosecond lasers. In certain cases the appearance of the photoelectron spectrum changed and the dynamics could then be measured, however at higher energy the vibrational redistribution dynamics were too fast and could not be resolved, yielding broad spectra at all time delays. None of the bands measured exhibited restricted IVR as evidenced by quantum beats in the photoelectron spectrum, however this region was not searched extensively since the focus was on measuring conformer interconversion at higher energy.

In probing the dynamics at higher energy the question arose as to the overall excited state lifetime. The lifetime for EF has been reported twice in the literature. Auty *et al.*³¹ reported a value of 121 ns using picosecond time correlated single photon counting. Itoh and Morita³² report a value of 14.7 ns which is much closer to the published value of 18.3 ns for fluorene.³⁴ Our picosecond pump-probe experiments are not designed to measure such long lifetimes but the late time nanosecond photoelectron spectra seemed to indicate a decay significantly faster than 121 ns. To answer this question the excited state fluorescence lifetime was measured³⁷ and found to be 23 ns, which is more consistent with the value of Itoh and Morita³² and the value of fluorene itself.

In the following sections the results for some of the more prominent bands will be presented.

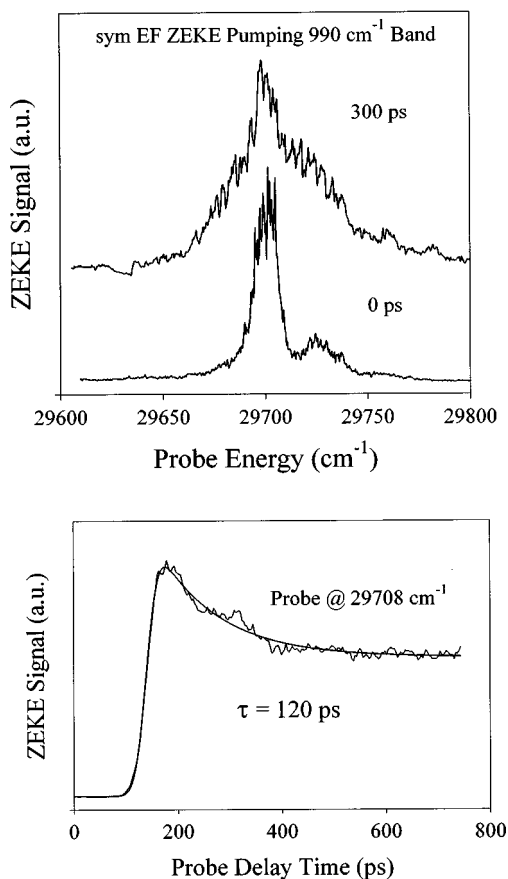


FIG. 6. Picosecond time resolved ZEKE spectra obtained by pumping the 990 cm^{-1} band of the sym conformer. The upper trace shows the change in the spectrum with time which is quantified in the transient decay shown in the lower figure.

1. 990 cm^{-1} band

Figure 6 shows the photoelectron spectra and transient decay obtained by pumping the sym 990 cm^{-1} band. This is a picosecond time resolved experiment which clearly shows sharp structure at early time which then broadens to a peak centered at 29708 cm^{-1} . The position of this late time broadened peak is consistent with the $\Delta v = 0$ transition of the sym conformer. This band is then interpreted as a signature of extensive IVR in the sym conformer with most of the vibrational energy centered in the alkyl chain. As will be shown below, this peak is observed for all of the higher bands of the sym conformer at late time. The redistribution time is measured by probing the early time sharp structure and measuring the loss of signal as a function of probe delay. The decay is fit to 120 ps using a nonlinear least squares algorithm which deconvolutes the laser response function.

It is clear from the spectrum that redistribution has occurred but has isomerization between the sym and unsym configuration occurred? The calculations suggest the barrier is much higher ($\sim 1900\text{ cm}^{-1}$). This can be probed experimentally by looking for the redistributed unsym photoelectron signature when pumping the 990 cm^{-1} sym band. To identify the signature of redistribution to the unsym conformation a late time photoelectron spectrum was obtained by directly pumping the unsym 990 cm^{-1} . Figure 7 shows a comparison of the late time (+6 ns) photoelectron spectro-

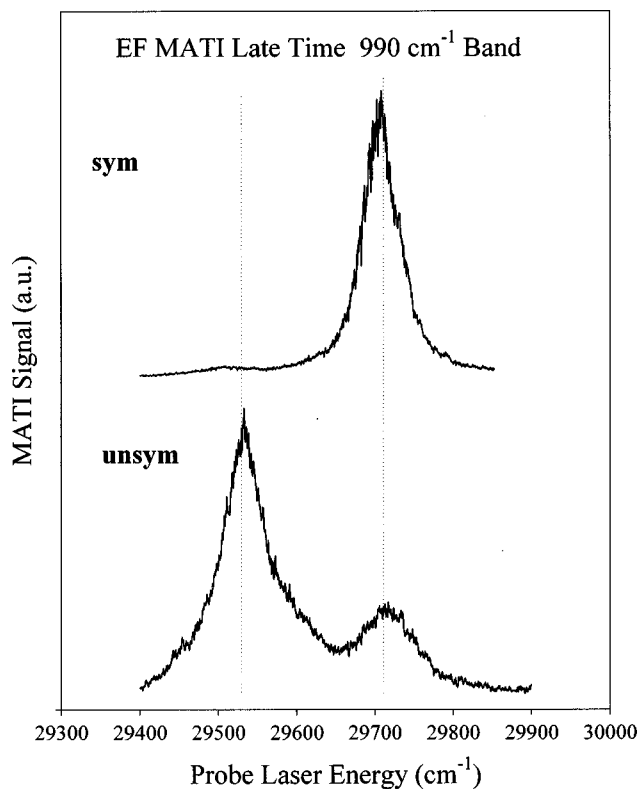


FIG. 7. Comparison of the MATI spectrum of the sym and unsym conformer excited to 990 cm^{-1} excess energy and probed at late time (+6 ns).

copy (PES) of the two conformers. The unsym compound shows an intense peak at 29530 cm^{-1} which is where redistribution of this conformer is expected. There is also a peak at the position where the sym conformation occurs. On the other hand the sym conformer shows very little signal in the position of the unsym conformation. Thus it is concluded that sym does not convert to unsym at this excess energy. The spectrum obtained by pumping the unsym conformation does however suggest that the unsym does convert to the sym. However, based on several different pieces of evidence, it appears that the structure in the spectrum due to the sym conformer can be ascribed to background excitation of small bands of the much more dominant sym population. In fact at this excess energy, and higher, selective excitation of the unsym conformer is almost impossible.

2. Sym 1225 cm^{-1} band

Figure 8 shows the picosecond ZEKE spectra and time profile of the 1225 cm^{-1} band of the sym conformer. The spectral change from 0 to 300 ps clearly shows the influence of redistribution which is measured to have a lifetime of 23 ps. Nanosecond late time spectra show no evidence of signal at 29550 cm^{-1} where the unsym conformer is expected to be, indicating that significant barrier crossing is not occurring at this excess energy.

3. Sym 1323 cm^{-1} band

This band shows one of the clearest examples of the change in the MATI spectrum as redistribution occurs. Fig-

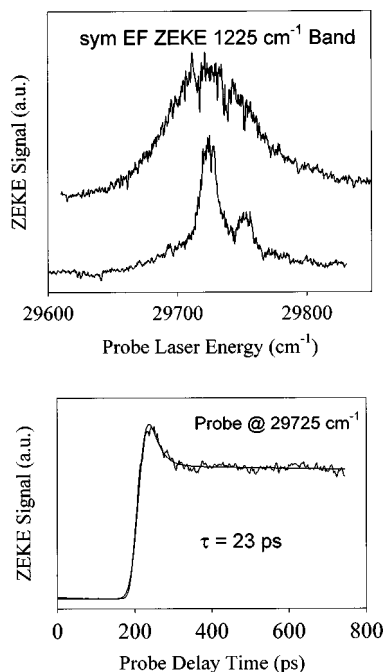


FIG. 8. Picosecond time resolved ZEKE spectra obtained by pumping the 1225 cm^{-1} band of the sym conformer. The upper trace shows the change in the spectrum with time which is quantified in the transient decay shown in the lower figure.

Figure 9 shows a comparison of the picosecond ZEKE spectra obtained at 0 and 300 ps probe delay time. At early time the $\Delta v = 0$ regions shows a number of bands but they all appear sharp. At late time a single broad peak appears, with essentially zero signal in the region of the unsym $\Delta v = 0$ transition at 29550 cm^{-1} . Thus there appears to be no detectable barrier crossing even when measuring the nanosecond resolved spectra at a delay of 6 ns. The vibrational redistribution rate is determined by measuring the decay of the sharp structure as shown in Fig. 9 and is fit to a lifetime of 40 ps.

4. Higher energy bands of sym conformer

A combination of nanosecond and picosecond spectroscopy was applied to a number of higher energy bands of the sym conformer. Figure 10 shows the late time spectra of all the bands. None of the band structure showed any dynamical change on the nanosecond time scale from early probing at 0 ns to probing as late as 15 ns. The overall fluorescence decay limited how late the ZEKE spectra could be measured. The full-width at half-maximum (FWHM) of the broad components are plotted in Fig. 11 as a function of excess energy. There is a steady increase with excess energy and perhaps a change in slope between 2000 and 2500 cm^{-1} . More importantly, there is little spectral evidence of the unsym conformation being formed even at the highest excess energy of 2648 cm^{-1} . In several spectra, most notably the 2450 band, there is a significant component at the probe energy of the unsym conformer. This band was scanned carefully at a number of delay times and no dynamic change in the ratio was found. It appears that this component is most likely due to contamination by overlapping excitation of the unsym species, but this will be discussed further below.

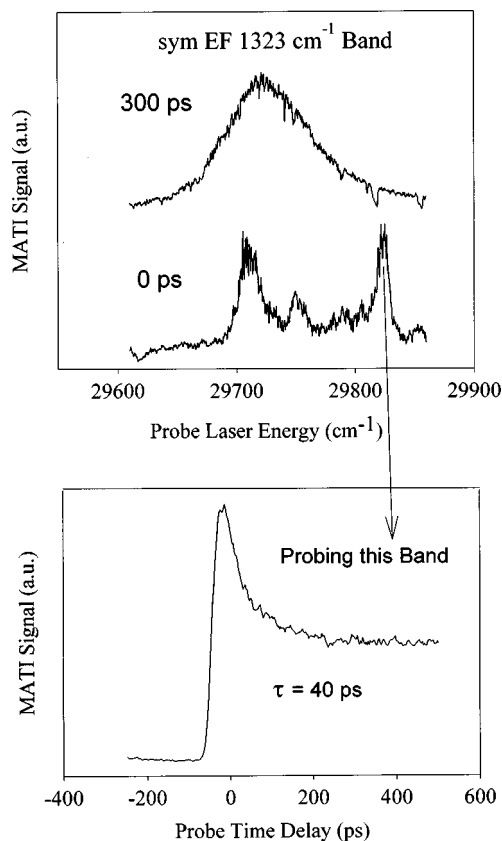


FIG. 9. Picosecond time resolved ZEKE spectra obtained by pumping the 1323 cm^{-1} band of the sym conformer. The upper trace shows the change in the spectrum with time which is quantified in the transient decay shown in the lower figure.

E. Statistical rate calculations

For comparison to the experimental data some of the microcanonical statistical properties of EF were calculated. The two parameters that are of particular interest are the statistical ratio of the sym and unsym forms of EF as a function of excess energy and the rate for interconversion as a function of excess energy above the barrier. The population ratios are given by the energy dependent microcanonical equilibrium constant which is:³⁸

$$\frac{[\text{sym}]}{[\text{unsym}]} = \frac{\rho_s(E_{\text{sym}})}{2\rho_u(E_{\text{unsym}})}, \quad (1)$$

where $\rho_s(E_{\text{sym}})$ is the density of states of the sym conformer and $\rho_u(E_{\text{unsym}})$ is the density of states of the unsym conformer. The energy values are related to the difference in energy between the conformers which is 180 cm^{-1} in the ground state as given by density functional theory (DFT) calculations reported above and then adjusted to a 300 cm^{-1} difference in the excited state based on the spectral shift. The density of states of the unsym conformation is multiplied by 2 to account for the fact that there are two equivalent unsym conformations relative to the 1 unique sym conformation. The density of states are calculated using a direct state counting method^{38,39} including all the normal mode frequencies of the sym and unsym conformations. Only the $j=0$ rotational states were considered. The frequencies were obtained from the *ab initio* calculations at the HF level. Both harmonic and

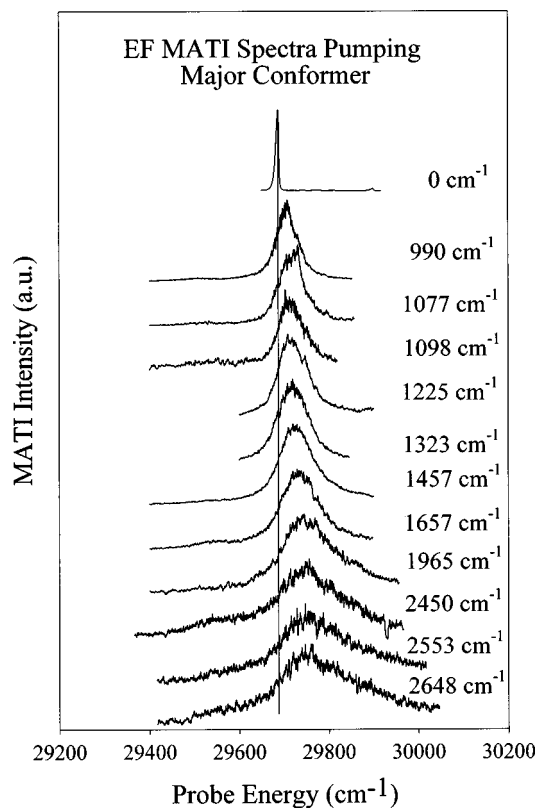


FIG. 10. MATI spectra of a number of S_1 bands of the sym conformer obtained at late time probing (+6 ns). The spectral region covered is the $\Delta v=0$ transition in each case. The broadening at high energy is a result of vibrational redistribution.

anharmonic state counting algorithms were used with a generic anharmonic factor of 0.15 used for all modes. This microcanonical equilibrium constant is plotted in Fig. 12 as a function of excess energy. The particular plot shown is for the anharmonic state counting method but the harmonic results are qualitatively similar. The data is smoothed for pre-

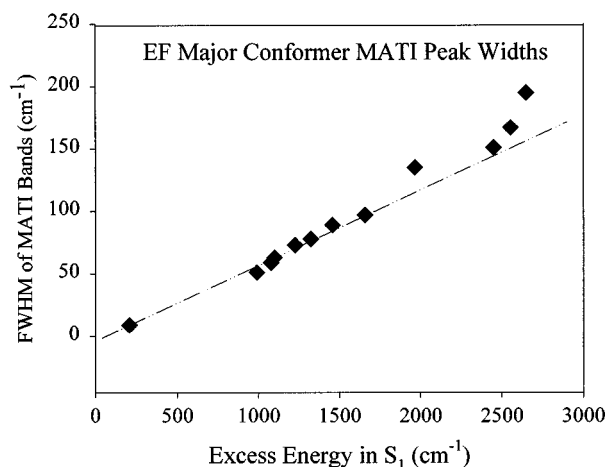


FIG. 11. Plot of the MATI peak widths, in the $\Delta v=0$ region, as a function of excess energy in S_1 for the sym conformer. The dashed line is not a fit but is included for a visual reference.

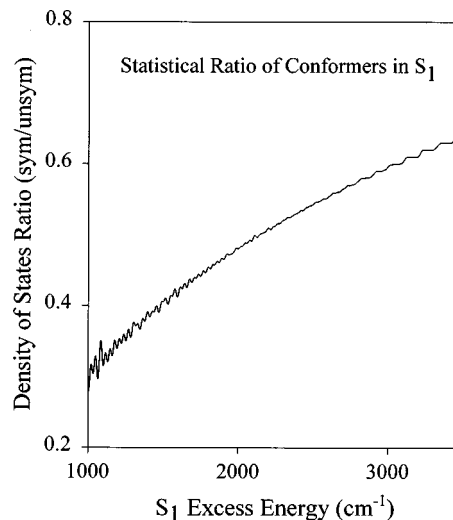


FIG. 12. Plot of the density of states ratio for the sym and unsym conformations as a function of excess energy in S_1 . This is the microcanonical equilibrium constant as shown in Eq. (1). The unsym conformation is assumed to be 300 cm^{-1} above the sym conformation. The ratio takes into account the fact that there are two identical unsym structures. The graph is smoothed as explained in the text.

sentation purposes. The actual calculated ratio oscillates dramatically at lower energy but becomes quite regular at around 2000 cm^{-1} excess energy.

The microcanonical equilibrium constant is valid only in the statistical limit in which all of phase space is sampled. In the experimental state preparation this is clearly not going to be the case when excitation is below the barrier for interconversion. Above the barrier it may or may not be a valid assumption. Figure 12 can be used as a guide for interpreting what population ratios one might expect for a statistical population of conformers when excitation is above the barrier.

Using similar input data the rates for interconversion from sym to unsym are calculated as a function of excess energy using RRKM theory. The RRKM rates are given by:³⁸

$$k(E) = \frac{N^\ddagger(E - E_a)}{h\rho_s(E)}, \quad (2)$$

where E is the total energy above the origin of the sym conformer, E_a is the activation energy, $N^\ddagger(E - E_a)$ is the sum of states of the transition state structure at an energy $E - E_a$ above the transition state minimum, $\rho_s(E)$ is the density of states of the sym conformer, h is planck's constant, and $k(E)$ is the energy dependent microcanonical rate constant. The density of states of the reactant (sym conformer) is obtained as described above using both harmonic and anharmonic state counting. $N^\ddagger(E - E_a)$ for the transition state is obtained from the *ab initio* frequencies of the transition state structure. The barrier height is obtained from the DFT calculations and is 1910 cm^{-1} . In order to assess the sensitivity of the rates to the barrier height calculations were also performed at 2100 and 2300 cm^{-1} . A plot of the rates versus excess energy is presented in Fig. 13 with data for the anharmonic calculations presented for all three barrier heights.

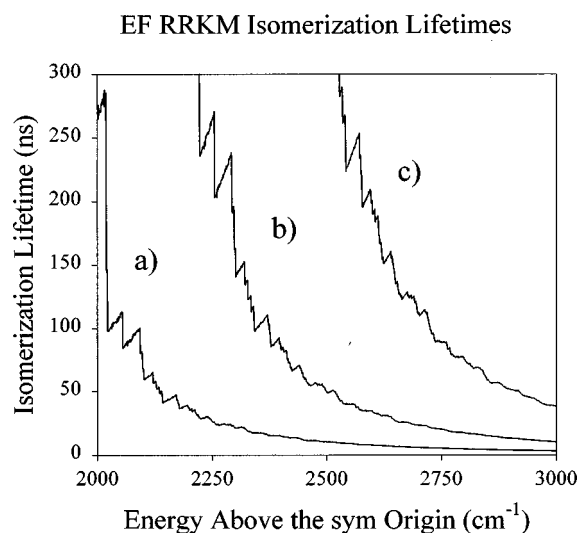


FIG. 13. Calculated RRKM lifetimes for isomerization from the sym to unsym conformation as a function of S_1 energy. Each plot assumes a different barrier height of (a) 1900, (b) 2100, and (c) 2300 cm^{-1} .

It is important to remember that the calculations are for the ground state, whereas the experiment is performed in the excited S_1 electronic state. Thus any calculated values, particularly the energy difference between the conformers and the barrier height, are subject to additional error. As a reference the calculated energy of the barrier height goes from 1920 cm^{-1} in the neutral ground state to 1710 cm^{-1} in the cation. This is an indication of the changes which may occur in S_1 but is not a predictor.

IV. DISCUSSION

A. Assignment of conformations

The spectral assignment of the observed S_1 and cation origin bands to particular conformations is based on the *ab initio* calculations and reference to similar compounds.¹⁻⁹ The calculations determined that the sym conformation is the most stable and suggests the largest origin be assigned thus. There is further supporting evidence for this assignment. First, the stability of the two conformations in the cation, relative to the ground state, is determined exactly by the photoelectron spectroscopy. The conformer associated with the 33 543 S_1 band has an IP *greater* by 80 cm^{-1} than the conformer associated with the S_1 33 663 band. The *ab initio* calculations (Table I) show that the sym conformation is destabilized by 80 cm^{-1} in the ion relative to the unsym, again supporting the 33 543 S_1 band as sym. (The close agreement is certainly fortuitous and in fact using a larger basis set the difference reduces to 56 cm^{-1} but the direction and magnitude should be reliable at this level of theory.)

A less quantitative argument for the assignment is derived from Smalley *et al.* in their work on alkylbenzenes¹ and alkylanilines.⁵ In these cases the origin which was shifted more to the red was assumed to have the alkyl chain bending back toward the chromophore which stabilized the more diffuse, polarizable excited state, and thus led to a red

shift. This is consistent for our case where the sym configuration brings the alkyl chain slightly closer to the chromophore.

B. Vibrational redistribution

As mentioned in Sec. III the photoelectron data show that all bands above 990 cm^{-1} show rapid vibrational redistribution. This can be compared to fluorene where the vibrational dynamics have been studied with picosecond time resolved stimulated emission pumping³⁴ and picosecond time resolved ZEKE spectroscopy.⁴⁰ In fluorene the consistent appearance of irreversible vibrational dynamics does not occur until $\sim 1700 \text{ cm}^{-1}$. Thus, as one might expect, addition of the ethyl group, and its low frequency vibrations, leads to a significant lowering of the threshold for irreversible redistribution. The measured lifetimes for redistribution in EF are in the 10's of ps regime which is similar to fluorene in the higher energy region where irreversible redistribution occurs.^{34,40}

An additional issue of some consideration is the width of the photoelectron peaks which result from redistribution. The peaks widths are due to the distribution of frequency changes between the S_1 and cation ground state for the modes populated by the redistribution. In general redistribution measured with photoelectron spectroscopy yields narrower peaks than dispersed fluorescence, presumably due to smaller changes in the potential between S_1 and the cation compared to S_1 and S_0 . For instance the 1707 cm^{-1} band in fluorene has a ZEKE width of 150 cm^{-1} ⁴⁰ whereas the dispersed fluorescence peak has a width of $\sim 300 \text{ cm}^{-1}$.³⁴ The narrower peak widths are useful when trying to identify two separate conformers which each may have a broadened photoelectron spectrum due to redistribution. It appears that the presence of the alkyl chain leads to an additional narrowing of the redistribution because the EF peaks are considerably narrower than peaks at a similar energy in fluorene. The 1707 cm^{-1} band in fluorene mentioned above has a ZEKE width of 150 cm^{-1} whereas peaks in the similar range for EF have a width near 100 cm^{-1} as can be seen in Fig. 11. Smalley *et al.* attributed a similar narrowing in the fluorescence of the alkylbenzenes¹ and alkylanilines⁵ to significant vibrational energy in the alkyl chain which inherently would have a smaller change in frequency between two electronic states since its potential is less likely to be influenced by electronic excitation in the chromophore.

C. Conformer interconversion

A great deal of effort was directed toward measuring the threshold for conformer interconversion and the rate of interconversion as a function of excess energy. In fact we were not able to confidently measure either of these values. How does one then interpret this negative result?

The most obvious explanations for not observing the conformer interconversion are: (a) the barrier for interconversion is actually higher than we have assumed based on calculations, (b) the rate for interconversion is much slower than the time window afforded by the fluorescence lifetime, (c) the expected ratio of sym and unsym after redistribution

is wrong and in fact the dynamically produced unsym population is too small to measure in the noise, and (d) the experiment is really not effectively measuring the populations of the two conformations.

Point (d) can be addressed first. It is expected that the experiment can measure the dynamic production of each conformer since both conformers can be independently observed and are shown to have distinct photoelectron spectra even upon extensive broadening due to vibrational redistribution. This is further confirmed by the cases in which simultaneous excitation of each conformer occurred with the resulting contamination easily observed in the spectra. Thus we are confident that any dynamically produced products should be measured as well.

Point (c) is a serious consideration which was addressed by the calculation of the microcanonical equilibrium constant. In the statistical limit these calculations should be reliable at least qualitatively. In many of the high energy photoelectron spectra of the sym conformer the signal in the region of the unsym conformation is only approximately 10% or less of the sym peak which is most likely due to simultaneous pump excitation of the unsym species. Also the small shoulder ascribed to unsym shows no dynamic evolution, at least on the picosecond time scale. As shown in Fig. 12 at the excess energies probed one expects at least 30% or more of the unsym conformer if there is a statistical distribution of states. One expects the energy difference between the two conformers, 300 cm^{-1} in S_1 , to be quite reliable because it is based on ground state calculations and spectral shift measurements (as opposed to the S_1 barrier height for which no shift data is available). By extrapolation the calculation of the population ratios should also be reliable such that it is unlikely that the actual ratio is less than the 10% limit observed.

Points (a) and (b) can be considered together and in fact are the most likely explanation of the results. If in fact the barrier is above the highest energy accessed, 2650 cm^{-1} , of course no isomerization would be observed. It seems unlikely that the barrier is that high, particularly given that the ethyl chain is bonded not directly to the aromatic carbons but to the bridging aliphatic carbon. However, looking at Fig. 13 the barrier does not have to be that large to make the lifetime for isomerization prohibitively long for experimental observation of isomerization. For instance a barrier of 2300 cm^{-1} produces a lifetime of close to 150 ns at 2650 cm^{-1} excess energy. At the latest delay time we could access, 15 ns, this would only allow <10% of the molecules to decay, a value which is within our noise limits, particularly at high excess energy and late delay time.

Of course it is also possible that the rate processes are not described by the statistical models. In this case the statistical calculations presented cannot be used as a guide in predicting the expected experimental behavior. Based on results for stilbene and related molecules we do not expect this to be the case.⁴¹ Experiments are currently underway on similar molecular systems in which it is hoped that the rates for isomerization will be measured as a function of excess energy. These experiments should give more insight into interpreting the current results.

V. CONCLUSIONS

EF is shown to exhibit two distinct conformations in the molecular beam which are not effectively equilibrated by the supersonic cooling. The distinct nature of these conformations is established by their unique ZEKE photoelectron spectrum. *Ab initio* calculation similarly show two low energy conformation and help establish the assignment of the peaks in the electronic spectrum. The symmetric conformation with the ethyl chain pointing back toward the fluorene moiety is shown to be lower in energy. Calculations on the cation show changes in conformer stability which closely agree with the experimental photoelectron measurements.

Dynamics experiments were performed using pump-probe ZEKE photoelectron spectroscopy and measured vibrational redistribution beginning at 990 cm^{-1} and measured up to 2650 cm^{-1} excess energy. The photoelectron spectral signature of redistribution was significantly broadened peaks which increased in width with increasing excess energy. Although the peaks were broad there was still a clear distinction between the two conformations. These distinct spectra were used to try and measure conformer interconversion in real time. Even at the highest energy probed, 2650 cm^{-1} , no convincing experimental evidence for conformer interconversion was seen.

Density of states calculations and RRKM rate calculations were performed to model the behavior of the two conformers at higher excess energies. The input for these calculations were the conformer energies, barrier height, and vibrational frequencies obtained from the *ab initio* calculations. The results suggested that the rates of conformer interconversion may be too slow to measure at the excess energies probed.

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