Conformational Analysis and Dynamics of 9-Propylfluorene and 9-Ethylfluorene

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Received: February 21, 2001; In Final Form: March 30, 2001

The S_1 excited state and cation ground state of jet-cooled 9-propylfluorene have been studied using resonance enhanced multiphoton ionization (REMPI) and zero electron kinetic energy (ZEKE) photoelectron spectroscopy. Three conformations of 9-propylfluorene have been experimentally identified. Quantum chemical calculations have been used to calculate the ground state and cation energies of each conformer as well as the barrier to conformer interconversion via a bond rotation. ZEKE spectroscopy has also been used to search for conformer interconversion upon vibronic excitation to S_1, but no evidence for a dynamic barrier crossing has been found, even at the highest energy probed (3210 cm^{-1}). Similar studies previously carried out on 9-ethylfluorene were also extended to higher energy, and no evidence of dynamic barrier crossing was found at energies as high as 3525 cm^{-1}. Statistical density of state calculations have been carried out to predict the relative populations of each conformer as a function of excess energy, and the Rice−Ramsperger−Kassel−Marcus (RRKM) isomerization rates have also been calculated.

Introduction

Electronic spectroscopy in supersonic jets has been successfully used to identify and characterize multiple conformations of large aromatic molecules. In the past, conformational analysis has been carried out on various alkylbenzenes,[1−4] alkylphenols,[5,6] naphthols,[7−10] indole derivatives (tryptophan,[11,12] 3-ethylindole,[13] and tryptamine[12,14]), and fluorene derivatives such as 9-ethylfluorene,[15−17] 9-phenylfluorene,[18] 2-propylfluorene, and 9-fluorene acetic acid.[19] The identification of separate conformers of these compounds has been accomplished with a combination of quantum chemical calculations and different experimental techniques such as dispersed fluorescence,[1−4,11,12] hole-burning spectroscopy,[10] resonance enhanced multiphoton ionization (REMPI) spectroscopy, and zero electron kinetic energy (ZEKE) spectroscopy.[9,13,15−19]

Quantum chemical calculations are widely used today to determine the relative energetics of ground-state conformations, including the barrier to interconversion between conformers. On molecules of the size considered here, these calculations have a theoretical accuracy of less than 1 kcal/mol.[20] These calculations, combined with electronic spectroscopy, have been used to study 9-propylfluorene (9-PF) as well as the higher energy region of 9-ethylfluorene (9-EF), whose conformational analysis had been previously carried out by our group.[15]

The choice of these alkyl-substituted fluorenes for study is based on the fact that they exhibit conformations and barrier heights best-suited to our dynamical studies. Also, they have desirable spectral properties which provide excellent sensitivity in the excitation and probing processes.

In addition to identifying and characterizing molecular conformations, we attempt to measure dynamic isomerization, which is expected to occur upon vibronic excitation to energies above the barrier. ZEKE spectroscopy, with a time delayed probe (nominally 15 ns), is used to monitor the excited-state dynamics and is a sensitive probe of the S_1 conformation. The selectivity is derived from the distinct ionization potential and unique ZEKE spectra. Previous studies have shown that photoelectron spectroscopy can be effectively used to measure vibrational dynamics, in particular, intramolecular vibrational redistribution (IVR), which has been identified by a significant broadening of the ZEKE features.[15−17,21−22] Here we attempt to measure the much more specific process of conformer isomerization. This was done previously on 9-EF with no direct observation of the isomerization. In this work, 9-PF has been studied and additional studies on 9-EF have been carried out, where we have extended the excess energy range from the previous upper limit of 2648 cm^{-1} to 3575 cm^{-1}.

Experimental Section

Two color 1 + 1′ resonance enhanced multiphoton ionization (REMPI) spectroscopy with mass-resolved detection has been used to study the spectroscopy of the S_1 electronic state of 9-PF. Zero electron kinetic energy (ZEKE) spectroscopy has been used to measure the photoelectron spectroscopy of the ion ground state.

9-PF was synthesized by the Grignard reaction of 9-fluorenone with ethylmagnesium bromide. The resulting alcohol was reduced with a mixture of hypophosphorous acid and iodine.[23] 9-EF was obtained from Aldrich.

The experimental apparatus has been described previously.[19,24−25] A nanosecond laser system has been used in these experiments, consisting of two dye lasers, each pumped by the second harmonic of a pulsed Nd:YAG laser (Continuum NY-61 and Quanta Ray DCR-3). The visible output of each dye laser has a pulse width of 6 ns and a bandwidth of 0.04 cm^{-1}. One dye laser (Quanta Ray PDL-2) functions as the pump, while the other one (Lumonics HD-500) functions as the probe, and both lasers are frequency doubled. The pump and probe lasers are temporally overlapped by an appropriate optical delay by external triggering which allows precise control of the pulse timing to within 1 ns. The temporal overlap was set by a photodiode and confirmed by the appearance of pump−probe signals. This unambiguously established the “time zero” of these experiments. The lasers were also spatially overlapped in the

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10.1021/jp010684c CCC: $20.00

vacuum chamber under mildly focused conditions. Care has been taken to ensure that the signal was 100% dependent on both the pump and the probe.

A pulsed supersonic beam originates in the first of two differentially pumped vacuum chambers. The nozzle (General Valve) has an external sample container which is heated to 115 °C (for 9-PF) and 120 °C (for 9-EF). The temperature of the nozzle is set 10 °C higher to prevent clogging. The exact vapor pressure of this compound is unknown but is estimated to be significantly below 1 Torr at this temperature. The carrier gas for the expansion is He, at a nominal backing pressure of 1.3 bar. The pulsed beam is skimmed, and it enters the second chamber where it is intersected perpendicularly by the ionizing laser.

The REMPI spectra of 9-PF were obtained by fixing the probe laser energy to be slightly higher than the S_1−ion transition energy of this compound, and the pump laser was scanned over a wide range from the origin region to an excess energy of 3200 cm^{-1}. The higher energy REMPI spectrum of 9-EF was also obtained from 2100 cm^{-1} above the origin to 3600 cm^{-1}.[15]

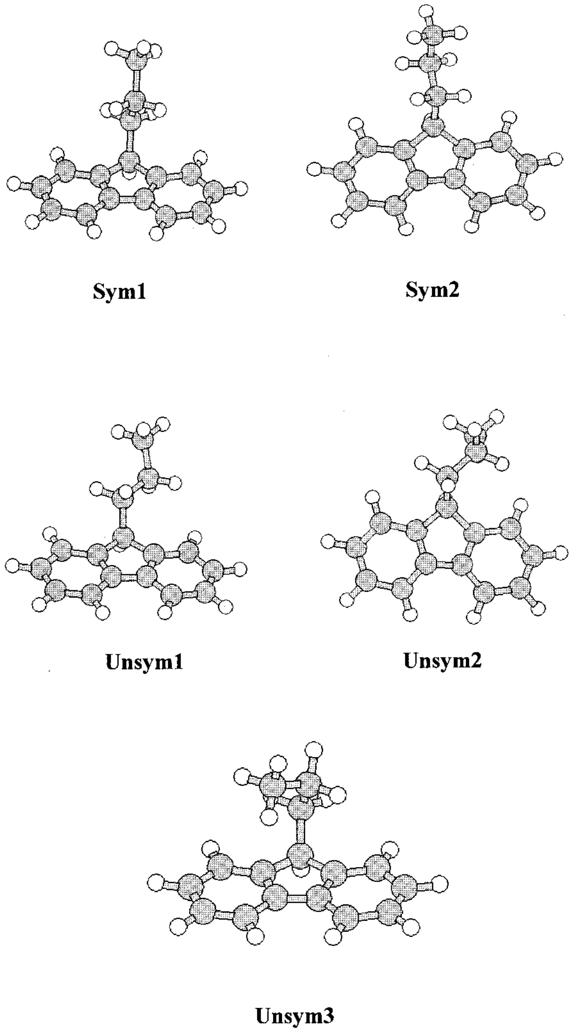
The ZEKE spectra for both of these compounds were obtained by fixing the pump to the S_1 vibronic band of interest and scanning the probe through the ionization potential. The electrons were collected on a microchannel plate detector, and the interaction region was held field-free while the pump and the probe laser excitation occurred. A pulse was applied after a 1−2 μs delay to field ionize the remaining high Rydberg states and accelerate the resulting electrons to the detector. The spectra were scanned over a relatively narrow spectral range, centered on the $\Delta\nu = 0$ transition to the cation, as scans covering this region generally provide the most important spectral information.

Quantum chemical calculations using the Gaussian 98 program were carried out on the ground state and the cation of 9-PF. The overall procedure and calculations for 9-EF have been reported previously and will be discussed in the following sections.[15]

Results and Discussion

A. 9-Propylfluorene Quantum Chemical Calculations. 9-PF has a flexible side chain which gives rise to several possible conformations at relatively low energy. Calculations were performed to determine which conformations might be significant at room temperature and would, therefore, contribute to the observed spectra. The population of the conformers is not expected to change dramatically in the expansion, because the barriers between conformers are large (~2000 cm^{-1}). The work of Baer and co-workers[28,29] and Ruoff and co-workers,[30] as well as our own experience, suggests that when barriers exceed 350 cm^{-1}, the room temperature populations are frozen out in the expansion. Thus, intensities of jet-cooled spectral peaks should at least be indicative of room temperature populations. These results would then help identify and assign the experimentally observed spectral peaks to a particular origin.

A total of five unique conformations were identified by a preliminary molecular mechanics search. These structures were further refined by higher level calculations. The Gaussian 98 program was used for these calculations.[26] A structural optimization was carried out using the B3LYP hybrid density functional theory method[27] with a 6-31G* basis set. A summary of calculated results is shown in Table 1. The cation ground states were calculated with the same method with the charge set to +1 and the multiplicity set to 2. A spin unrestricted calculation was then carried out. We have adopted the same naming convention that we used in 9-EF, for which we categorized and labeled the conformers as symmetric (where the carbon atoms of the side chain are contained in the perpendicular symmetry plane bisecting the fluorene moiety through C_9) and unsymmetric (where C_β and C_γ are rotated out of the same symmetry plane).


Sym1 **Sym2**

Unsym1 **Unsym2**

Unsym3

Figure 1. Structures of five conformations of 9-propylfluorene obtained by molecular mechanics. The structures were refined using quantum chemical calculations, and the ones labeled sym1 and unsym1 were observed experimentally.

TABLE 1: Summary of Quantum Chemical Calculations for 9-Propylfluorene

	neutral			cation			
	torsion angle			torsion angle			
9-PF conformer	C_1C_9	C_9C_α	relative energy (cm^{-1})	C_1C_9	C_9C_α	relative energy (cm^{-1})	calcd IP (cm^{-1})
sym1	55°	180°	0	58°	180°	0	58 680
unsym1	178°	171°	195	174°	173°	120	58 604
unsym2	180°	60°	480	176°	60°	355	58 557
unsym3	69°	−71°	740	68°	−70°	718	58 659
sym2	−118°	180°	985	−81°	180°	400	58 098

On the basis of the above description, two of the conformations are classified as symmetric (sym) and three as unsymmetric (unsym). These conformers are shown in Figure 1. The conformer labeled sym1 has a $C_1-C_9-C_\alpha-C_\beta$ dihedral angle of 55°, while the same dihedral angle in the conformer labeled unsym1 is 178°. Molecular mechanics and quantum chemical

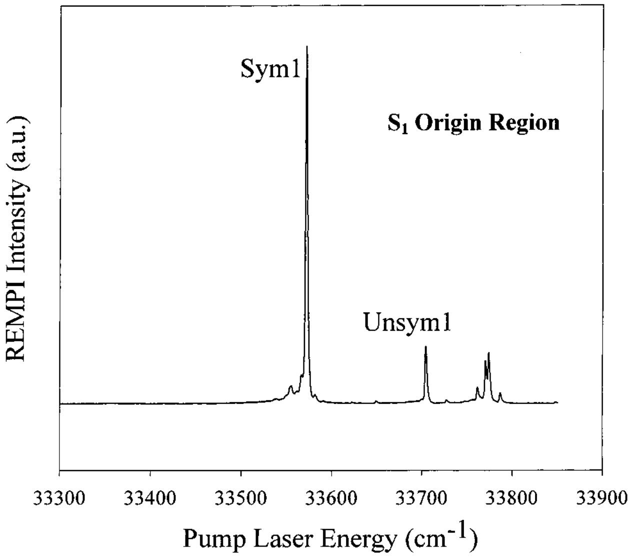


Figure 2. REMPI spectrum of the S_1 state of 9-propylfluorene, showing both sym1 (33 543 cm^{-1}) and unsym1 (33 663 cm^{-1}) origins.

calculations indicate that these are the two conformers with the lowest energy in the ground state, with sym1 lower than unsym1 by 195 cm^{-1}. In the case of 9-EF, there was only one sym and one unsym conformer. The conformer labeled sym was lower in energy by 180 cm^{-1}.

The main objective of these studies is to attempt to observe conformer interconversion when vibronic transitions are pumped with energies greater than the barrier to interconversion between the conformers. Therefore, knowing the barrier as accurately as possible is important. The ground-state barrier was calculated using the QST3 method, and a stable transition state based on an initial guess of the transition state was found. This was also performed using the B3LYP method and a 6-31G* basis set. This transition state was found at 1875 cm^{-1} above the sym conformer and 1690 cm^{-1} above the unsym conformer. The $C_1-C_9-C_\alpha-C_\beta$ dihedral angle for this structure turned out to be 123°, while the $C_9-C_\alpha-C_\beta-C_\gamma$ angle was almost unchanged at 180°.

Gaussian 98 was also used to determine the vibrational frequencies of the neutral and cation states of the two conformers of 9-PF. These were determined at the HF level of theory and scaled by a factor of 0.893. The resulting frequencies were applied to statistical calculations which will be discussed in a later section.

B. 9-Propylfluorene Electronic Spectroscopy. The jet-cooled REMPI spectrum of the origin region of 9-PF is shown in Figure 2. The S_1 spectrum was obtained from the electronic origin to 3230 cm^{-1} excess energy. We have assigned spectral features primarily to two main conformers with one additional small origin being observed. On the basis of the results of our calculations, we identify the two main conformers with sym1 and unsym1. With this assignment, the experimentally observed energy differences fit nicely for the ground-state energies as well as the ionization potentials. The origin of the sym1 conformer is located at 33 571 cm^{-1}, and that of the unsym1 conformer is at 33 704 cm^{-1}. This measured energy difference indicates that the sym1 conformation is stabilized by an additional 133 cm^{-1} in the S_1 state relative to the ground state. Coupled with the quantum chemical calculations, the S_1 energy difference between the two conformers is approximately 330 cm^{-1}. These assignments are based on comparing the experimentally observed intensities and assigning the strongest band to the most stable conformer from the quantum chemical calculations.[15] This assignment is by no means unequivocal, but much of our interest is in the dynamics where the absolute assignment of the conformations is not critical.

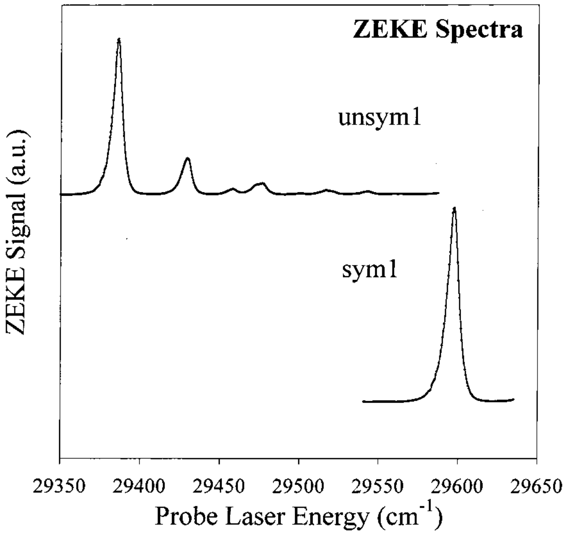


Figure 3. ZEKE spectra obtained by pumping the origins of the sym1 and unsym1 conformers. The peaks are the origins of the cation spectra and, together with the S_1 wavelength, give the IP of each conformer.

TABLE 2: Summary of Experimental Results for 9-Ethylfluorene and 9-Propylfluorene

compound	conformer	obs rel intensity	S_0-S_1 (cm^{-1})	S_1−ion (cm^{-1})	IP (expt) (cm^{-1})
9-ethylfluorene	sym	6	33 543	29 688	63 231
	unsym	1	33 663	29 490	63 153
9-propylfluorene	sym1	24	33 571	29 584	63 155
	unsym1	4	33 704	29 386	63 090
	unsym2	1	33 761	29 289	63 050

ZEKE spectroscopy was used to determine which S_1 bands corresponded to conformer origins. As demonstrated in previous studies, each conformer is expected to have a unique ZEKE spectrum, including distinct ionization potentials.[13,15,19] By pumping each S_1 band and then recording the ZEKE spectrum, the band can be categorized as belonging to one of the identified origins (and, hence, conformations). Figure 3 shows the ZEKE spectra obtained by pumping the S_1 origins of sym1 and unsym1. It is observed that, while sym1 has the redder S_1 transition energy, its overall ionization threshold (63 155 cm^{-1}) is greater than that of unsym1 (63 090 cm^{-1}) by approximately 65 cm^{-1} (Table 2). The well-separated ZEKE spectra of the two conformations help us to categorize each of the excited-state bands as belonging to one or the other of the two conformers.

A third conformer was also observed with an origin at 33 761 cm^{-1} and an S_1−ion transition which is significantly different from those of the two main conformers, as shown in Table 1. However, no higher energy bands of this conformer were observed in the S_1 spectra. On the basis of the quantum chemical calculations and the spectroscopic data, we believe that this conformer is most likely the unsym2 conformer.

ZEKE spectra were obtained for a number of S_1 bands of both conformations of 9-PF. Because of its significantly higher population in the beam, the sym1 conformer bands were predominant at higher energy, whereas the unsym1 bands were lost in the generally busy baseline at higher vibrational energy. A number of intermediate S_1 bands were selectively pumped, and the probe laser was scanned to obtain the ZEKE spectrum. 9-PF, like 9-EF and other similar molecules, exhibits a strong

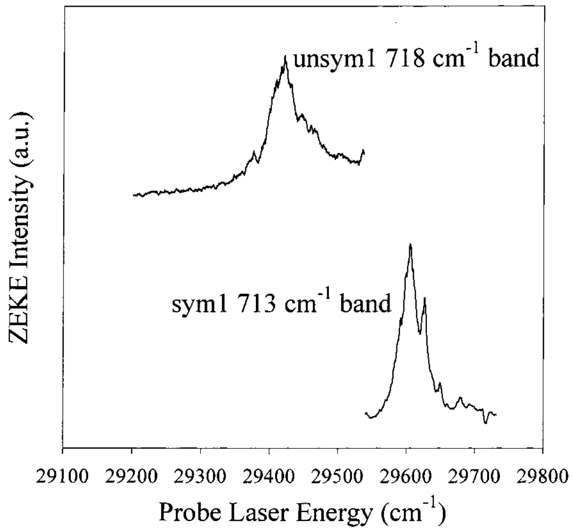


Figure 4. ZEKE spectra of intermediate energy (700 cm^{-1}) S$_1$ bands of sym1 and unsym1 showing broadening due to restrictive IVR.

$\Delta\nu = 0$ propensity in the S$_1$−cation transition, and most scans were concentrated in the narrow region around the $\Delta\nu = 0$ transition. Therefore, if a 1000 cm^{-1} S$_1$ band were pumped, the probe laser would scan through the region 1000 cm^{-1} above the adiabatic ionization potential. An example of ZEKE spectra of higher energy bands is shown in Figure 4 for the 718 cm^{-1} S$_1$ band of the sym1 conformer and the 713 cm^{-1} band of the unsym1 conformer. These ZEKE spectra retain the characteristic positions of the origins of their respective conformations, 29 584 cm^{-1} for sym1 and 29 386 cm^{-1} for unsym1. The ZEKE peaks are significantly broader at higher S$_1$ energy. This has previously been established to be the result of IVR in the intermediate state, wherein a number of coupled levels in S$_1$ contribute to the ionization and the broadening is due to the distribution of $\Delta\nu = 0$ transition frequencies.[15]

C. S$_1$ Dynamics. The primary goal in this study was to investigate the conformational dynamics resulting from vibronic excitation. This work is a very close follow-up work on 9-EF in which almost identical experiments were performed.[15] It was hoped that 9-PF would provide another test system to compare to 9-EF and perhaps exhibit isomerization which was not observed in that case. As mentioned before, IVR is observed in this compound at excess energies as low as 718 cm^{-1}, which is consistent with observations in similarly sized molecules. This indicates that a number of coupled vibrational modes are involved in the excitation. However, rather than just observing vibrational mixing, we have attempted to measure isomerization when the vibrational excitation exceeds the barrier to isomerization. As discussed in our previous studies on 9-EF, it is expected that isomerization between the sym1 and unsym1 forms of 9-PF should be observed by probing via ZEKE spectroscopy, because the spectra of each of the two forms are quite different. Our work on 9-EF did not show such isomerization at an S$_1$ energy as high as 2648 cm^{-1}, 750 cm^{-1} above the calculated barrier. The experiments on both 9-EF and 9-PF were carried out with a 15 ns delay between the pump and probe lasers. Larger delays could not be used because of the short excited-state lifetimes. Some additional results for 9-EF are presented here, where we extended experiments to 3525 cm^{-1} excess energy in S$_1$.

For 9-PF, ZEKE spectra were obtained for a number of bands with up to 3210 cm^{-1} excess energy, which is significantly above the calculated barrier of 1875 cm^{-1}. Sym1 is the dominant conformer at higher energies, and the ZEKE spectra of several of these bands are shown in Figure 5. It is quite evident that the ZEKE spectrum becomes broader as we go to higher energy. The positions of the broadened peaks are consistent with the $\Delta\nu = 0$ transition of the sym1 conformer. This is interpreted as a signature of extensive IVR in sym1.

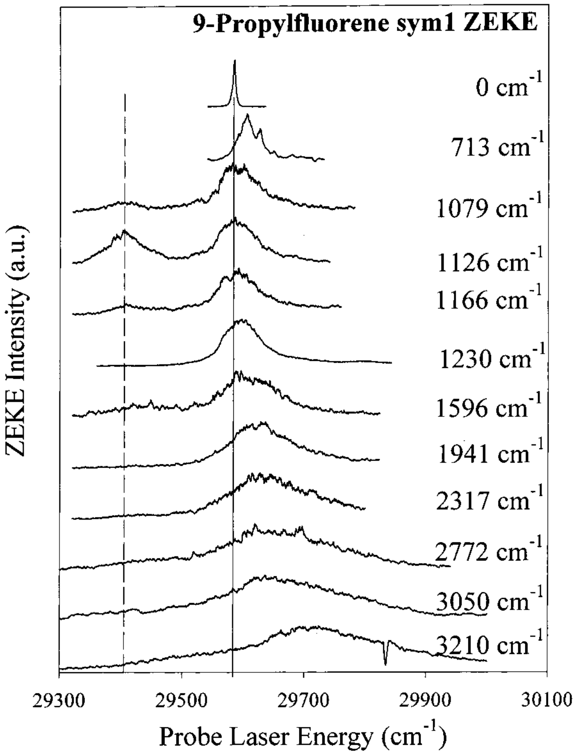


Figure 5. ZEKE spectra of origin and selected higher energy bands of the sym1 conformer. The spectral region covered is the $\Delta\nu = 0$ transition in each case. The broadening at higher energy is due to vibrational redistribution. The dashed line is at the S$_1$−ion energy of the unsym1 conformer.

A possible indication that isomerization has taken place would be the appearance of a broad ZEKE peak at the position of the other conformer. When the 1126 cm^{-1} band of sym1 is pumped, a broadened peak appears at the region where the unsym1 ZEKE peak is expected. But this S$_0$−S$_1$ transition of sym1 is well below the barrier to isomerization, and as bands higher than 1126 cm^{-1} are pumped, the broad peak around 29 386 cm^{-1} disappears while the ZEKE peak at 29584 cm^{-1}, attributed to sym1, becomes broader. The peak observed in the ZEKE spectrum of the sym1 1126 cm^{-1} band is therefore attributed to background excitation of small bands of unsym1.

Overall, there is very little spectral evidence that unsym1 is being formed even at the highest excess energy of 3210 cm^{-1}. There is, however, a steady increase in the full-width at half-maximum (fwhm) with increasing energy. This increased width reflects the larger number of vibrations contributing to the excited state, each of which has its own characteristic frequency shift upon ionization. As part of this study, the previous higher energy studies on 9-EF were extended to 3525 cm^{-1} as shown in Figure 6. Even at this high energy, evidence of isomerization is absent, and the sym ZEKE peak simply gets broader.

An important parameter to keep in mind for these dynamics experiments is the probe delay time, which is approximately 15 ns here. Further probe time delay would be valuable to search for isomerization, but the probe window was limited by the

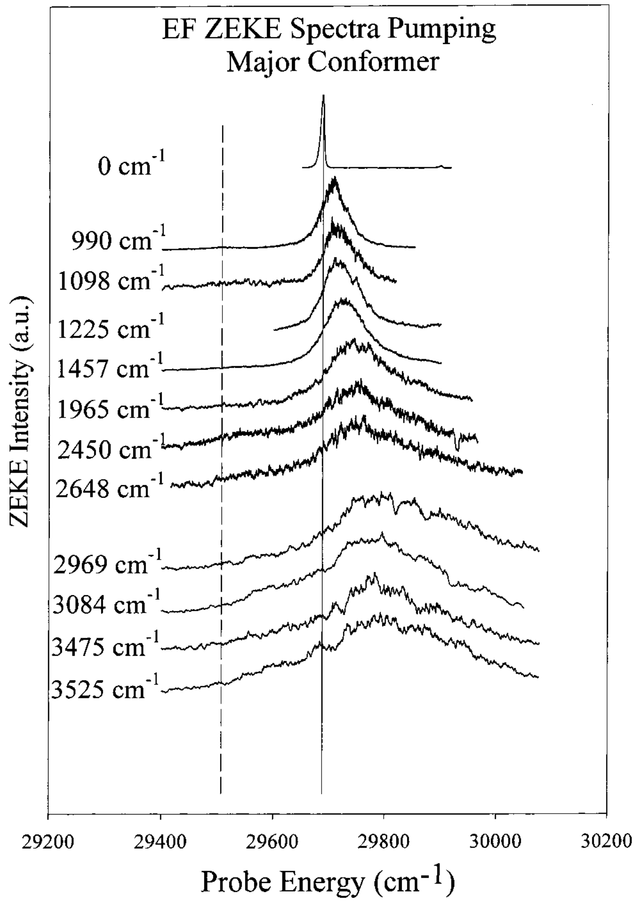


Figure 6. ZEKE spectra of origin and selected higher energy bands of the major (sym) conformer of 9-ethylfluorene, covering the $\Delta v = 0$ transition in each case. The dashed line is at the S_1–ion energy of the minor (unsym) conformer.

excited-state lifetime of 9-PF. The choice of 15 ns was a trade-off between the largest possible delay and an acceptable signal level.

We have performed some calculations based on a statistical contribution of vibrational states at the energies pumped. This was also done in our previous work on 9-EF and provides a point of comparison to the experimental observations.[15] The two parameters of major interest were the statistical ratio of the sym1 and unsym1 forms of 9-PF as a function of excess energy and the rate of interconversion as a function of excess energy above the barrier. These calculations then guide us as to how much of each conformer we might expect to observe and how long the isomerization might take relative to our observation window of 15 ns. The statistical population ratios are given by the energy dependent microcanonical equilibrium constant,[28]

$$\frac{[\text{sym1}]}{[\text{unsym1}]} = \frac{\rho_s(E_{\text{sym1}})}{2\rho_u(E_{\text{unsym1}})} \qquad (1)$$

where $\rho_s(E_{\text{sym1}})$ is the density of states of the sym1 conformer and $\rho_u(E_{\text{unsym1}})$ is the density of states of the unsym1 conformer. The energy values are related to the 195 cm^{-1} difference in energy between the two conformers on the basis of the quantum chemical calculations and then adjusted to 330 cm^{-1} on the basis of the S_1 spectral shift. The density of states of unsym1 is multiplied by 2 to account for the fact that there are two equivalent unsym conformations compared to one unique sym conformation.

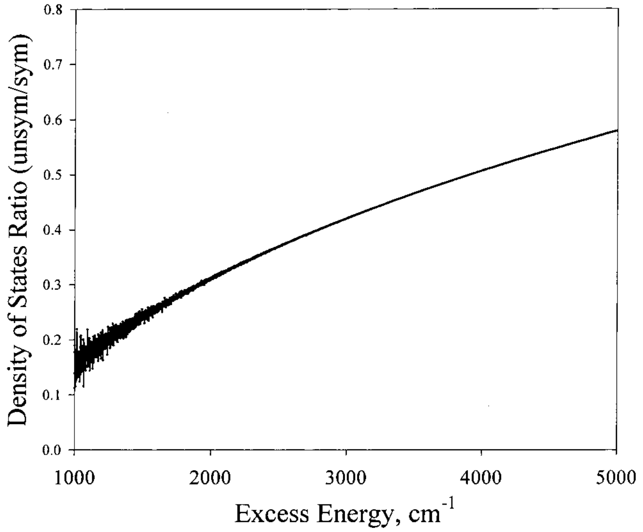


Figure 7. Plot of density of states ratio for the unsym1 and sym1 conformers of 9-PF as a function of excess energy in S_1. This is the microcanonical equilibrium constant as shown in eq 1.

The density of states is calculated using a direct state counting method which includes all the normal-mode frequencies of sym and unsym, with only the $j = 0$ rotational states being considered. The frequencies were obtained from the quantum chemical calculations described earlier in this section. Both harmonic and anharmonic state counting algorithms were used with a generic anharmonic factor of 0.15 used for all modes. Figure 7 shows the plot of the anharmonic microcanonical equilibrium constant as a function of excess energy. This calculation ignores the presence of other higher energy conformations, but it should accurately reflect the ratio of sym1 and unsym1, irrespective of possible contributions from other conformations. At the energies that we are considering (2000–3200 cm^{-1}), the ratio of unsym1 to sym1 varies from 0.4 to 0.5, which should be more than sufficient to be observed experimentally. Given this ratio and the signal-to-noise ratio in the ZEKE spectra, we conclude that the observed populations are not statistical and that little or no isomerization is taking place, on the time scale of our probing process. A similar plot for 9-EF is shown in Figure 8.

The rates for interconversion from sym1 to unsym1 are calculated as a function of excess energy using Rice–Ramsperger–Kassel–Marcus (RRKM) theory, where the rates are given by[28]

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

E is the total energy above the origin of sym1, E_a is the activation energy, $N^{\ddagger}(E - E_a)$ is the sum of states of the transition-state structure at an energy of $E - E_a$ above the transition state minimum, and $\rho_s(E)$ is the density of states of sym1. The sum of states of the transition state is obtained from the density of states on the basis of the frequencies obtained from the quantum chemical calculations. A plot of the rate, or isomerization lifetime, versus excess energy is shown in Figure 9. This calculation is a sensitive function of the barrier height. If the barrier height in S_1 is significantly greater than the calculated S_0 barrier (1875 cm^{-1}), then the rates might be slow enough to explain our lack of observation of the unsym conformer (unsym1). Figure 10 shows the corresponding plot for 9-EF.

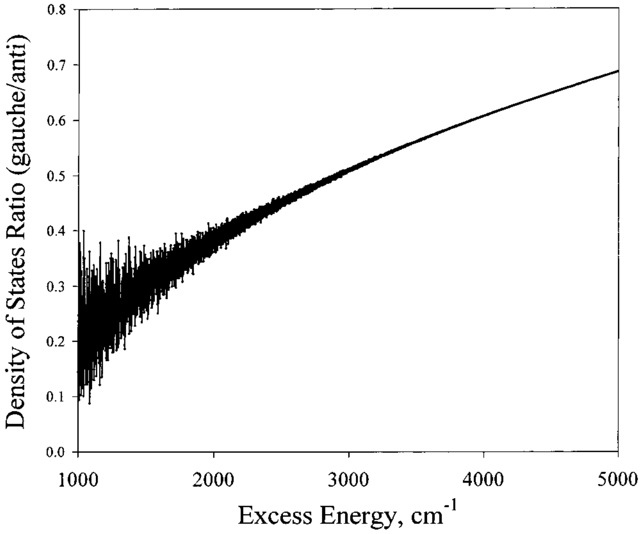


Figure 8. Plot of the density of states ratio for the sym and unsym conformers of 9-EF as a function of excess energy in S_1. The graph is smoothed.

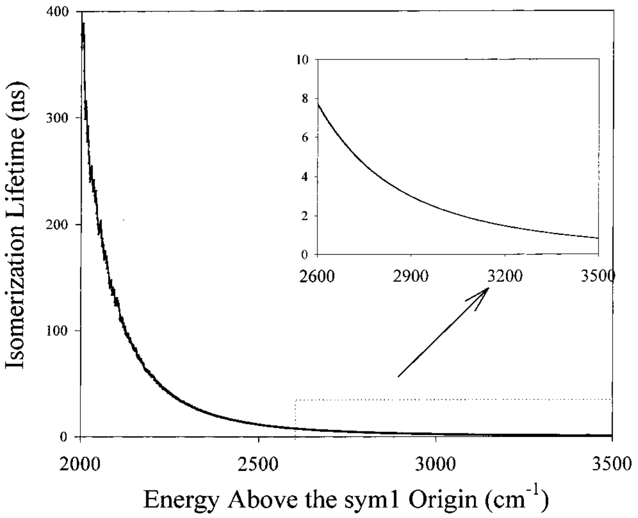


Figure 9. Calculated RRKM lifetime for isomerization of 9-PF from sym1 to unsym1 as a function of S_1 energy. The plot assumes a barrier height of 1875 cm^{-1} obtained from quantum chemical calculations. The 2600−3500 cm^{-1} region is enlarged and shown in the inset.

This work can be compared to previous studies on *trans*-stilbene and related compounds.[31−33] In that case, the cis/trans isomerization is easily observed in fluorescence because of the rapid fluorescence quenching of the cis form. For that compound, the isomerization was clearly observed, the barrier was located, and the rates compared favorably to statistical RRKM calculations. In comparison with 9-PF, one can argue that, in stilbene, the barrier is formed from an avoided curve crossing, and it is expected that significant electronic effects may be at play to mix the vibronic states of each conformer. Recent infrared−microwave double resonance experiments by Pate and co-workers studied ground-state isomerization by measuring eigenstate spectra and determining the optical accessibility of “isomerization states”.[34] The conclusions drawn from that work indicate that there were “isomerization states” which had a wave function spanning both configurations and which were optically accessible from the ground state. A categorization of the states at a particular energy was performed, and this revealed that, although the isomerization states exist, their density was not very great. It was concluded that an optically prepared superposition of the states would in fact lead to a very slow isomerization process, much slower than predicted by statistical theories. Our results are for the excited state, where one may expect more state mixing, but overall are consistent with this slow or limited isomerization which is nonstatistical. This can be seen as a restricted phase space argument, because there is clearly extensive vibrational mixing, as indicated by the very broad ZEKE peaks, yet little or no isomerization. In this study, as compared to our previous work on 9-EF, we are much more confident of our conclusions because we were able to go to such high energies in S_1.

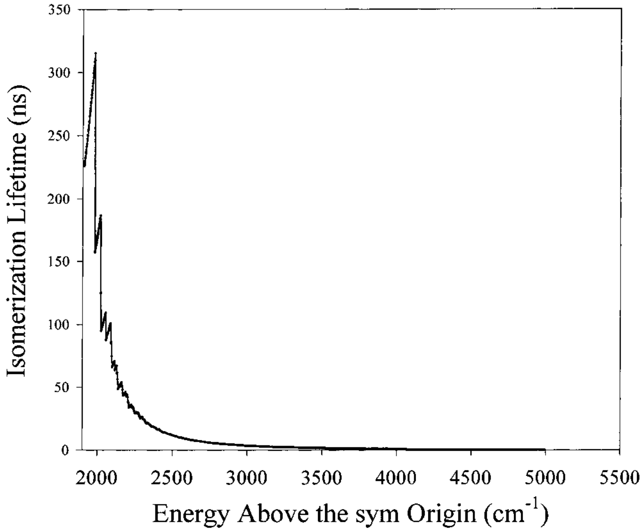


Figure 10. Calculated RRKM lifetime for isomerization from the sym to unsym conformation of 9-EF as a function of S_1 energy. The plot assumes a barrier height of 1910 cm^{-1} obtained from quantum chemical calculations.

Conclusion

The electronic spectroscopy of 9-PF has been studied with the goal of elucidating possible isomerization dynamics in the S_1 state using ZEKE spectroscopy. Multiple conformations of 9-PF have been identified by measuring S_1 and cation spectra and assignments of the absolute configurations made with the help of quantum chemical calculations. Two major and one minor conformations are shown to exist in the beam, and these were the subject of further dynamical studies.

The ZEKE spectra of the two major 9-PF conformers, sym1 and unsym1, are measured and are shown to be distinct such that the ZEKE spectra are diagnostic for the identity of the conformer. Vibronic bands are pumped from the origin to 3210 cm^{-1} excess energy in S_1, and ZEKE probing showed extensive IVR as revealed by the significantly broadened peaks. However, the ZEKE spectra reveal no discernible isomerization on the 15 ns time scale determined by the probe delay. This is similar to previous results on 9-EF, but these results extend to significantly higher energy. As part of the current work, 9-EF was also studied again, but now the experiments were extended to 3525 cm^{-1} excess energy, about 1600 cm^{-1} above the calculated barrier. Even at this high energy no isomerization is observed.

The statistical calculations predict much faster isomerization, and so we conclude that with the optical excitation employed the state distribution is decidedly nonstatistical. This is consistent with the recent work of Pate et al.[34]

Currently we are undertaking infrared experiments on related molecules where a vibrational mode is excited with a significant amount of energy well in excess of the isomerization barrier.[35] Because the ground-state vibrations have much longer lifetimes, we hope to characterize the time scale and extent of the isomerization.

Acknowledgment. The authors wish to thank Ja-Kyung Han and Professor Albert Fry of Wesleyan University for synthesizing 9-PF. We gratefully acknowledge the NSF for financial support of this project under Grant CHE-9523575.

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