

## 3-Ethylindole electronic spectroscopy: $S_1$ and cation torsional potential surfaces

Jonathan D. Pitts, Swarna Basu, and J. L. Knee<sup>a)</sup>

*Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459*

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The tryptophan derivative 3-ethylindole was studied in the first excited electronic state and the cation ground state using resonance enhanced multiphoton ionization (REMPI) and zero electron kinetic energy (ZEKE) spectroscopy. Weakly bound clusters of 3-ethylindole with argon ( $n = 1-3$ ) have also been studied. The monomer spectroscopy revealed that two conformations of the 3-ethylindole exist in the jet cooled sample. Density-functional theory (DFT) calculations have been used to calculate the ground- and ionic-state geometries and energies. The calculations reveal the two conformations to be a planar and a nonplanar orientation of the ethyl substituent relative to the indole plane. The ZEKE spectrum of the nonplanar form has an extensive progression in the vibration associated with ethyl torsion and indicates a significant geometry change in the ethyl chain torsion upon ionization. The ethyl chain torsional potential is mapped out using DFT calculations, and the ion surface is adjusted such that calculated frequencies and Franck-Condon factors reproduce the experimental ZEKE spectra. The conformer interconversion barrier height is calculated in the ground and ion states. This is compared to an experimentally determined barrier height in the ion. The spectroscopy of the argon complexes reveals interesting results with regard to the cooling of the 3-ethylindole conformations. © 2000 American Institute of Physics.

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### INTRODUCTION

Derivatives of indole provide a very interesting class of molecules for spectroscopic studies, particularly derivatives substituted in the three position, which are analogs of the amino acid tryptophan. Several studies have successfully investigated indole derivatives in the  $S_1$  electronic state.<sup>1-8</sup> The focus of much of this work lies in conformational studies of such species. Fluorescence spectral signatures have been used as a probe in understanding protein conformations, but such experiments are often difficult to interpret due to solvent interactions. Tryptophan is a striking example of this difficulty.<sup>9-12</sup> To simplify the problem of solvent interactions gas-phase studies can be performed where supersonic cooling is an additional aid in simplifying the electronic spectrum.

One of the earliest jet expansion studies of substituted indoles, as a model for tryptophan itself, was by Bersohn and co-workers.<sup>1</sup> They studied 3-methylindole, and 3-indole acetic acid, using laser induced fluorescence, and determined the vibrationless origins for these two compounds relative to the parent indole. Additionally, their work studies the electronics of solvation of 3-methylindole with water,  $D_2O$ , and argon. Shortly after, Levy and co-workers<sup>2</sup> published the first electronic spectrum of tryptophan itself expanded in a supersonic molecular beam. They find a rich vibrational spectrum near the origin of tryptophan, with a harmonic vibrational progression suggesting a large geometry change upon electronic excitation.<sup>2</sup> This work also shows evidence for the existence

of multiple conformers of tryptophan. Using power saturation techniques as many as six distinct conformations are detected. This work was continued by Levy *et al.* with the study of several tryptophan analogs.<sup>3</sup> These investigations include the molecules 3-indole acetic acid, 3-indole propionic acid, tryptamine, and *N*-acetyl tryptophan. Similar to the previous work on tryptophan multiple conformations of each molecule are found. The multiple conformations are ascribed to substituent conformations, and the spectroscopy is analyzed in that context.

Previous work from our group has investigated the existence of multiple conformations of isolated molecules.<sup>13,14</sup> We have coupled resonance enhanced multiphoton ionization (REMPI) and zero electron kinetic energy (ZEKE) photoelectron spectroscopy with DFT (density-functional theory) calculations, to predict barriers to interconversion, and transition state structures of large molecules. To that end tryptophan derivatives offer a favorable system due to their multiple conformations, and the relatively well understood and spectroscopically accessible indole moiety. In searching for transition states, and calculating barrier heights, it is advantageous to have a single path connecting only two minimum structures with a single transition state. This requires a high degree of symmetry in the molecule as was the case in 9-ethylfluorene.<sup>13</sup> The next best candidate, and perhaps one that spans a larger class of molecules, is to have only two minima, connected by two pathways, but one pathway is a substantially higher barrier than the other. This in effect will eliminate the higher barrier as a pathway, reducing the interconversion to a single pathway. This is the case in 3-ethylindole.

<sup>a)</sup>Electronic mail: jknee@wesleyan.edu

This study presents the first  $S_1$  and ZEKE spectra of 3-ethylindole. To the best of our knowledge, there is only a single theoretical paper<sup>15</sup> that investigates the vibrations and Raman intensities in the ground state. To support the experimental results extensive calculations have been employed to investigate the relative stability of different conformations and to determine the isomerization potential surface. A limited investigation of the argon solvated 3-ethylindole is also presented primarily because of interesting behavior with respect to the different 3-EI conformers. Our overall goal here is twofold. More narrowly we are interested in understanding the specifics of 3-ethylindole and related molecules with respect to the possible structures and how to characterize them. Our longer term interest is in characterizing not only the equilibrium structures but also the transition states so that we may apply time resolved spectroscopy to the study of the dynamics of barrier crossings in isolated molecules, as done for 9-ethylfluorene.<sup>13</sup> As will be shown below the torsional potential is not only revealed by calculations but the experimental spectra are also analyzed to give information on the potential away from the minima.

## EXPERIMENT

3-Ethylindole (3-EI), and its clusters with argon (3-EI- $Ar_n$ ), were studied in both the  $S_1$  excited state, and the first ionic state. The  $S_1$  state of the parent and cluster were studied using resonance enhance multiphoton ionization (REMPI) spectroscopy. The ionic ground state of the parent was studied using zero electron kinetic energy (ZEKE) spectroscopy<sup>16</sup> and the argon clusters ground ionic state was studied using the mass resolved equivalent of ZEKE, mass analyzed threshold ionization (MATI) spectroscopy.<sup>17</sup>

A detailed description of the theory<sup>18,19</sup> and experimental apparatus has been given elsewhere. Only a brief description will be given here. 3-Ethylindole was synthesized from 3-(2-Bromoethyl)indole and tri-butyl tin hydride (one mole equivalent), with 5 mg of azobisisobutyronitrile (AIBN) as an initiator. The reaction proceeded via a radical mechanism and was carried out in tetrahydrofuran (THF) (reflux at 70 °C, 2 h). The product was separated using flash chromatography (80% hexane/20% ethyl acetate), and excess solvent was evaporated to give white platelets. The product was checked by NMR (nuclear magnetic resonance) and compared to a known spectrum.<sup>20</sup> The 3-ethylindole was heated to 90 °C in the sample container of a pulsed nozzle (general valve). This nozzle, located in a differentially pumped molecular beam apparatus produces a supersonic expansion of the 3-EI, seeded with various gases. For studies on the 3-EI monomer, pure He was used as a carrier gas, but for cluster studies it was found that an Ar-Ne mixture was needed to produce the desired concentration of clusters, as noted below.

The resulting molecular beam is skimmed before entering the second chamber, where the REMPI and ZEKE spectroscopy take place. A set of microchannel plates (MCP) (Galileo Electro-optic Corp.) located perpendicular and below the interaction region is used as an electron detector. Located perpendicular and above the interaction region is a

linear time-of-flight mass spectrometer (LTOF MS). This LTOF MS is used as an ion detector for both the REMPI and MATI experiments. The appropriate electron and ion optics are located in the second chamber for extraction of the resulting electrons and ions.

For the following experiments, a pulsed nanosecond Nd-YAG operating at 20 Hz was used (Lumonics NY-61). This laser pumps two dye lasers, a Lumonics HD 500 with a visible bandwidth of 0.05  $\text{cm}^{-1}$ , and a home built Littman type laser, bandwidth 0.1  $\text{cm}^{-1}$ . The dye lasers output are frequency doubled using KDP crystals, and sent to the chamber under slightly focused conditions. These two lasers are spatially overlapped in the interaction region, and one functions as the pump laser, and the other as the probe.

The REMPI spectra are acquired by fixing the probe laser slightly above the ionization potential and scanning the pump through the  $S_1$  resonances. Care was taken to avoid fragmentation of clusters into the mass channel being monitored.

The ZEKE spectra were obtained by fixing the pump to a desired resonance in  $S_1$  and scanning the probe through the ionization potential (IP). The resulting ZEKE electrons were collected and sent to the electron detector using a series of extraction pulses. The initial extraction pulse was kept as low as possible,  $\sim 0.6$  V/cm, to avoid deep field ionization of the Rydberg manifold, and hence improved the final ZEKE spectra resolution. The ZEKE resolution was on the order of 1–5  $\text{cm}^{-1}$  for these large molecular systems. The extraction pulses were delayed one microsecond relative to laser excitation to allow for prompt electron separation.

The MATI spectra were obtained by collecting the simultaneously created ions in the LTOF MS. The MATI spectra give similar information to the ZEKE spectra, but add mass resolution to the experiment. The MATI spectrometer has been described elsewhere.<sup>18,19</sup> Briefly, it is equipped with a linear pulsed Wiley-McClaren mass spectrometer. This Wiley-McClaren-type of extraction stands to improve the MATI/prompt separation, and hence allows for subtle, near zero background experiments to be completed. The MATI scheme used a delayed discrimination field of  $-2$  V/cm and an extraction pulse of 560 V/cm, which was delayed 15  $\mu\text{s}$ . The ions then traverse the LTOF MS and are detected on a second set of dual stack microchannel plate (MCP).

## RESULTS

### Calculations of conformer structure and energetics

The geometry of possible stable conformations of 3-EI were first determined by a simulated annealing process using the HYPERCHEM program<sup>21</sup> with a simple  $MM+$  force field. Using this low level annealing process, two conformations were found. These are shown in Fig. 1. The nonplanar conformation has the ethyl group rising above the plane of the indole moiety. The planar conformation has the ethyl group in plane (dihedral angle of zero degrees), facing away from the six membered ring.

To refine the geometry and relative energy of the two conformations, several calculations were undertaken using

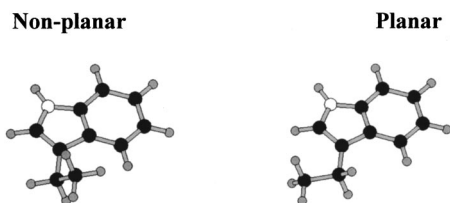


FIG. 1. Structures of the planar and nonplanar forms of 3-ethylindole. The open circles are nitrogen, gray are hydrogen, and black are carbon.

GAUSSIAN 98.<sup>22</sup> All these calculations use the density functional theory (DFT) algorithm B3LYP with a 6-31G(*d*) basis set. The results are shown in Table I. It is immediately noticed that upon ionization, there is only a modest change in geometry for the planar structure, as is typically the case for these large aromatic molecules. The nonplanar conformation though, undergoes quite a large geometry change upon ionization. The major contributor to this change is the 2-3- $\alpha$ - $\beta$  dihedral angle, which goes from 106° in  $S_0$  to 81° in the cation ground state. This change has direct implications for the ion spectroscopy, and will help with conformer assignments, as will be seen below.

The energy of the one-dimensional torsional potential of the ethyl chain was mapped out in its entirety using DFT methods. This was accomplished as follows. First the indole moiety was fixed in its minimum, planar geometry, so as to limit the computational time. The 2-3- $\alpha$ - $\beta$  dihedral angle was then fixed at various values and all other degrees of freedom involving the ethyl chain and its orientation with respect to the indole were geometry optimized using the B3LYP/6-31G(*d*) DFT algorithm. This procedure was conducted for both the ground state and the ionic state of the 3-EI. The dihedral angle was varied by five degrees between each optimization. The resulting potential surfaces are shown in Fig. 2. The solid lines are a cubic spline fit to the data collected from the calculations.

GAUSSIAN 98 has a method for determining the transition state of a reaction simply by entering the initial structure, and the final structure (*qst2*). This method (or *qst3*, allowing for a transition state guess) was also used to predict the transition states of conformer interconversion in the neutral and ionic 3-EI. In the ground state, the barrier to interconversion, starting in the nonplanar conformation, is 338 and 287  $\text{cm}^{-1}$  from the planar conformation. The ion shows, in general, reduced barriers to interconversion relative to the ground

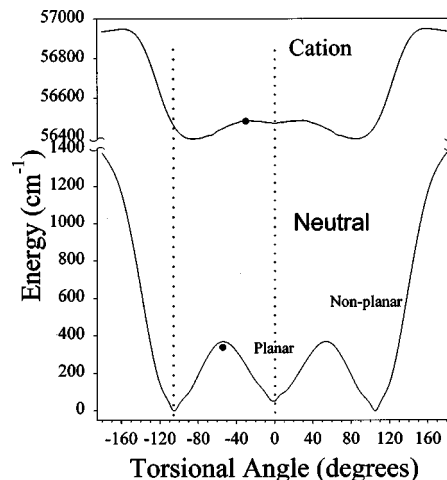


FIG. 2. Plot of calculated energy versus the ethyl group dihedral angle for the cation and ground state of 3-ethylindole. The line is a cubic spline fit of data points calculated every 5 degrees. The calculations used the B3LYP DFT method with a 631-G\* basis set and are referenced to the energy of the nonplanar neutral ground state. The solid circles indicate the energy of the transition states calculated using the QST2 procedure. See text for details.

state. The nonplanar to planar interconversion is calculated to be 87  $\text{cm}^{-1}$ , and the planar to nonplanar is found to be only 11  $\text{cm}^{-1}$ . In Fig. 2, the filled circles represent the *qst2* calculated transition states of the neutral and ionic 3-EI. These are also listed in Table I. One can see that the transition state calculated by varying the torsional angle is in very good agreement with the *qst* calculated values.

## $S_1$ excited-state REMPI spectroscopy

### Monomer

The  $S_1$  excited state of the monomer was investigated using two-color two-photon REMPI. The spectrum from the origin to  $\sim 1200 \text{ cm}^{-1}$  excess energy is shown in Fig. 3. There is very little vibrational structure present in the first 400  $\text{cm}^{-1}$  above the origin band at  $34810 \pm 2 \text{ cm}^{-1}$ . From 400 to 950  $\text{cm}^{-1}$  above the origin there is a moderate amount of resolvable vibrational structure. After 950  $\text{cm}^{-1}$  the structure tends to drop off again. A detailed vibrational analysis has not been attempted on the  $S_1$  state of 3-ethylindole. Rather, the focus is on the origin region, shown in detail in Fig. 4. Here two discrete bands are seen. The reddest and most intense feature is at  $34810 \text{ cm}^{-1}$ . This is assigned as

TABLE I. Calculated relative energies and structural parameters for two conformations and the transition state of the neutral ground state and cation of 3-ethylindole. Calculations using B3LYP with 6-31G(*d*) basis set.<sup>a</sup>

Conformation	Ground state			Cation		
	nonplanar	planar	TS <sup>b</sup>	nonplanar	planar	TS <sup>b</sup>
3- $\alpha$ - $\beta$ angle	114	115	114	112	116	115
2-3- $\alpha$ - $\beta$ dihedral angle	106	0	54	81	0	32
Energy ( $\text{cm}^{-1}$ )	0	50	340	0 <sup>c</sup>	80	90

<sup>a</sup>All angles are in degrees, and all energies are in wave numbers relative to the ground state or cation nonplanar conformation.

<sup>b</sup>The transition state energy and structure are determined by the QST algorithm.

<sup>c</sup>The calculated energy of the nonplanar cation, relative to the neutral, is  $56390 \text{ cm}^{-1}$ .

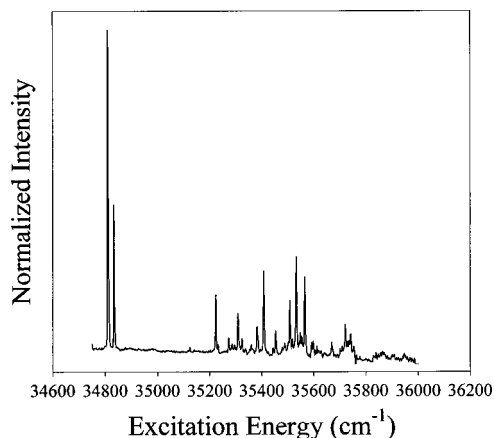


FIG. 3. Two-color REMPI spectrum of the  $S_1$  state of jet cooled 3-ethylindole. This survey scan shows the two prominent origin bands at low energy and only relatively smaller bands at high energy. Further scans to the blue failed to show any significant structure.

the vibrationless origin of the nonplanar conformation of 3-EI.  $23\text{ cm}^{-1}$  to the blue is another band, also assigned to a vibrationless origin, but of the planar conformation of 3-EI. The assignments of the relative conformations will be justified in the Discussion section below. The ratio of the peak intensities of the planar to nonplanar conformation is 1:2.2 in a pure helium expansion. The planar conformation is 45% of the intensity of the nonplanar conformation. If the energies of the two conformers were equal, a ratio of 50% planar to nonplanar would be expected, based on the two identical rotamers of the nonplanar conformation to the single rotamer of the planar conformation. A simple Boltzmann calculation on the conformer ratios suggests that the planar conformer is  $25\text{ cm}^{-1}$  higher in energy than the nonplanar conformation, which is consistent with the calculated value of  $50\text{ cm}^{-1}$ . This assumes that the conformer populations in the beam are ‘‘frozen out’’ at the 363 K temperature of the nozzle. This will be discussed below.

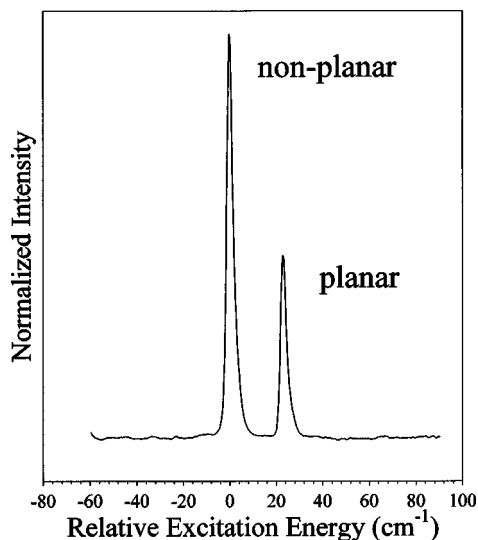


FIG. 4. Two-color REMPI spectrum in the region of the  $S_1$  origin. Laser power was kept constant over the scan under nonsaturating conditions. Each peak is assigned as an origin of a separate conformation as indicated.

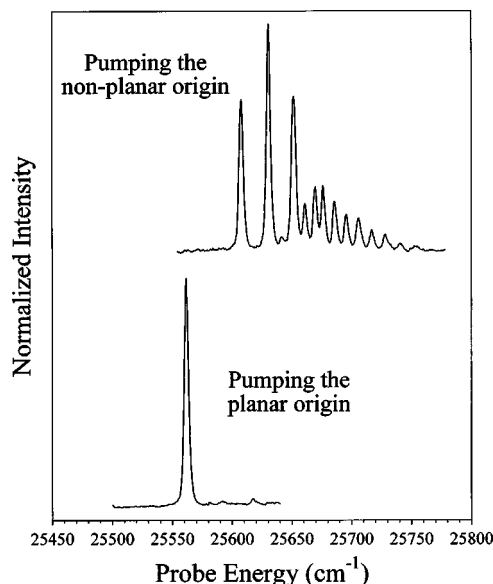


FIG. 5. ZEKE spectra obtained by pumping each of the two main transitions observed in the MPI (multiphoton ionization) spectrum. The top trace is obtained by pumping the origin assigned to the nonplanar structure at  $34\,810\text{ cm}^{-1}$  and the lower trace is that of the planar origin pumped at  $34\,831\text{ cm}^{-1}$ .

### Cation spectroscopy

The cation of 3-EI was studied using ZEKE spectroscopy, and its mass resolved analog, MATI spectroscopy. The monomer was studied primarily with ZEKE spectroscopy. The clusters of 3-EI with Ar were studied most extensively with MATI spectroscopy. MATI spectroscopy introduces mass resolution into the photoelectron experiment, a considerable advantage when studying clustered species. By using MATI spectroscopy it is possible to effectively eliminate any background from the monomer, or higher clusters.

The ZEKE spectra of 3-EI are shown in Fig. 5. The top trace shows the photoelectron spectrum obtained by pumping the nonplanar origin at  $34\,810 \pm 2\text{ cm}^{-1}$ . The IP of this conformation is determined to be  $60\,417 \pm 5\text{ cm}^{-1}$ . The spectrum exhibits two pronounced anharmonic vibrational progressions. The vibrational bands in these progressions are listed in Table II. It is apparent from this spectra that the conformation being excited is undergoing a rather significant geometry change upon ionization. Typically one sees only  $\Delta v = 0$  transitions for these types of molecules, but in this case the cation potential must be shifted from the  $S_1$  potential, giving rise to the Franck–Condon progression observed.

The bottom trace of Fig. 5 is the ZEKE spectrum obtained by pumping the other 3-EI conformation at  $34\,831 \pm 2\text{ cm}^{-1}$ . In contrast to the redder origin this spectrum shows only a single sharp ZEKE feature. This suggests no geometry change upon ionization, and hence the  $\Delta v = 0$  propensity is obeyed. The adiabatic IP is  $60\,394 \pm 5\text{ cm}^{-1}$ . The dramatically different appearance of the intensity distribution in the spectrum and the shift in probe energy confirm that the two  $S_1$  spectral features do in fact correspond to different conformations.

A number of higher energy  $S_1$  bands were used as intermediate states, and the ZEKE spectrum of each was recorded. Typically these spectra were very complicated,

TABLE II. 3-Ethylindole experimental and calculated cation vibrational frequencies.

Nonplanar conformer vibrational frequencies		Planar conformer vibrational frequencies	
Experiment	Calculated	Experiment	Calculated
0	0	0	0
23	24	30.2	37
34	40	55.8	49
45	45		64
62	54		82
69	61		
79	65		
89	73		
99	81		
111	89		
121	98		
134	108		
146	118		
	128		
	138		
	150		
	161		
	173		
	186		

showing large amounts of vibrational structure. No attempt to assign these intermediate states to a specific vibration of an individual conformer was successful. Due to this complication little else was done at higher energy.

### ZEKE frequency and intensity calculations

To better understand the ZEKE spectra of both the planar and nonplanar forms of 3-EI, we calculated the one-dimensional eigenvalues, eigenfunctions, and Franck-Condon (FC) factors for the cation vibrational spectrum using the DFT calculated neutral and cation potential surfaces. The procedure used in the calculations was very similar to the methodology we reported previously.<sup>23</sup> The problem is setup as a one-dimensional Schrödinger equation with the variable being the torsional angle. The potential energy as a function of this angle is obtained from the calculation and the reduced moment of inertia ( $5.377 \times 10^{-39}$  g cm<sup>2</sup>) is determined from the DFT calculated structural parameters. The eigenvalues and eigenfunctions and FC factors were determined by numerical methods using a matrix approach.<sup>23,24</sup>

The FC factors from the calculated potentials gave a qualitative fit to the experimental data but there were clearly significant differences. To improve the fit the potentials were modified to increase the agreement with experiment. It was decided that the ground-state potential would be fixed at the calculated value and the cation potential would be adjusted. This is justified by the fact that all the observed transitions began in the ground vibrational state of the neutral and it is likely that this ground state is better approximated by the calculations. It is also important to remember that the excitation goes through the excited  $S_1$  state which could also effect the observed intensities (although the  $S_0$  to  $S_1$  transition appears very vertical). To modify the cation potential it was first fit to a functional form consisting of a cosine ex-

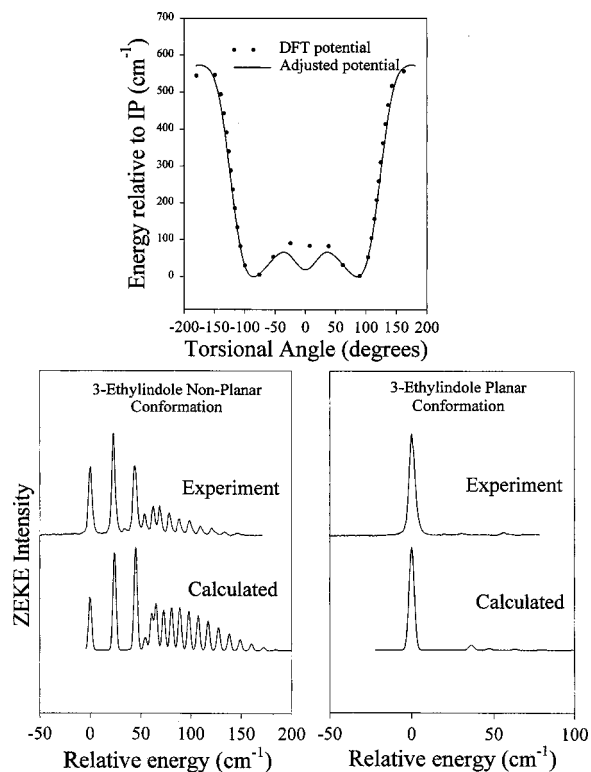


FIG. 6. Upper panel: Dotted curve shows the cation potential as a function of ethyl torsional angle using DFT theory. The solid curve is the adjusted potential which gives a much better fit to the experimental data in terms of torsional frequencies and intensities. Lower panels: Comparison of calculated and experimental spectra using the adjusted potential shown above. See text for details of calculation and a comparison of experiment to theory.

pansion, describing the outer nonplanar wells, and an inverted exponential describing the inner planar well. By adjusting this potential surface, and calculating the eigenvalues, eigenvectors, and Frank-Condon overlap between the ground and ionic state, we were able to reproduce the experimental ZEKE spectrum, to a reasonable approximation. This fit, and the resulting calculated spectra of both the nonplanar and planar conformations are shown in Fig. 6, and the calculated frequencies are given in Table II. The calculated spectra agree reasonably well with the experiments for both the planar and nonplanar forms. The fit of the nonplanar, more complicated, spectrum is not perfect. The fit fails to precisely match the intensities within the first major progression and the frequency and number of peaks in the second progression are not quite right. Still, both progressions are evident and the threshold for the second progression appears to be correct. While a better fit may be obtained by further adjusting the potential used in the calculation, it has been found to be rather difficult to minimize this discrepancy. Further refinement is probably not warranted since we have not adjusted the ground-state potential and perhaps most limiting is that fact that the intermediate  $S_1$  state is not taken into account at all in these calculations.

### Argon clusters

The  $S_1$  spectra of 3-EI-Ar<sub>n</sub> ( $n = 1-3$ ) are shown in Fig. 7. All the argon spectra shown in Fig. 7 use a mixture of

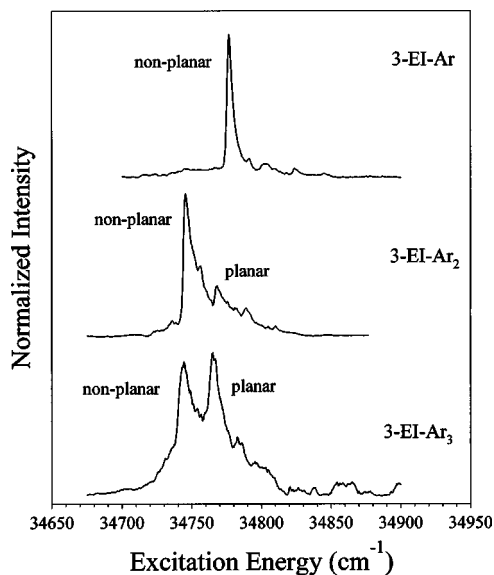


FIG. 7. REMPI spectra of 3-EI-Ar<sub>n</sub> with mass gating on the  $n=1, 2,$  and 3 species as indicated. The spectra were taken using an expansion gas mixture of 20% argon and 80% helium. Note the appearance of only one 3-EI conformer for the  $n=1$  cluster.

20% Ar in He at a backing pressure of 6 psi. The  $n=1$  cluster seems to show only a single conformation of the 3-EI, not the two that are seen in the case of the monomer. For the  $n=2$  and  $n=3$  clusters the appearance of both conformations is apparent, and the origin spacing of  $\sim 23$   $\text{cm}^{-1}$ , that is seen in the monomer, is retained.

Due to fact that two conformations of 3-EI-Ar were not observed this system was investigated further by recording the  $S_1$  spectra in a variety of carrier gasses. 10% Ar-He, 20% Ar-He and pure Ar all gave similar  $S_1$  spectra. In contrast the  $S_1$  spectrum recorded using a 10% Ar-Ne mixture produced both the nonplanar and planar conformers of the  $n=1$  complex. The spectra recorded using the various expansion gasses are collected in Fig. 8. No evidence for a second isomer of the nonplanar conformation is seen although it is possible since the argon may bind on the same or opposite side of the out-of-plane ethyl group.<sup>18,19</sup>

Ruoff and co-worker<sup>25</sup> found that heavier carrier gas atoms, such as Ar and Kr, are more effective at relaxing high-energy molecules and clusters, while lighter carrier gases such as He and Ne, are not as effective. Additionally they note that if the barrier to interconversion is greater than 350  $\text{cm}^{-1}$  no relaxation is observed. In the case of 3-EI-Ar, we see relaxation into both conformers of the 3-EI only in Ne. This is most likely due to improved cooling of the molecular beam when Ne is used as a carrier gas.

The only 3-EI cluster studied in the ion was 3-EI-Ar. The MATI spectra for 3-EI-Ar are shown in Fig. 9. The top spectrum is the MATI signal obtained when pumping the origin at  $34\,777 \pm 2$   $\text{cm}^{-1}$ . It is similar to the equivalent monomer conformation ZEKE seen in Fig. 5 and the IP of nonplanar 3-EI-Ar conformations is determined to be  $60\,338 \pm 5$   $\text{cm}^{-1}$ . Interestingly the vibrational progression in the Ar complex is changed subtly from the monomer. The frequency of the first progression increases slightly in the

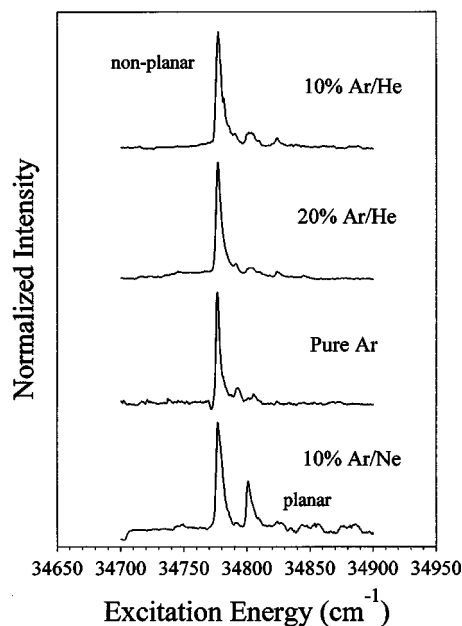


FIG. 8. REMPI spectra of the 3-EI-Ar complex with different carrier gas mixtures. Only in the case of an Ar-Ne mixture do both conformations of the 3-EI become visible. In comparison to the monomer the Ar complexes red-shift 33  $\text{cm}^{-1}$  for the planar conformation and 31  $\text{cm}^{-1}$  for the nonplanar conformation.

complex. Also it appears that the second vibrational progression that is prevalent in the monomer is not seen in the Ar case. This suggests that there is some change in the shape of the ethyl torsional potential after complexation with an argon.

The bottom of Fig. 9 shows the 3-EI-Ar MATI signal collected by pumping the planar conformation of 3-EI-Ar at  $34\,800 \pm 2$   $\text{cm}^{-1}$ . As mentioned above the planar conformation is only seen when Ne is used as the carrier gas. We have found repeatedly that the overall signal level drops by as much as a factor of ten when Ne is used rather than He.

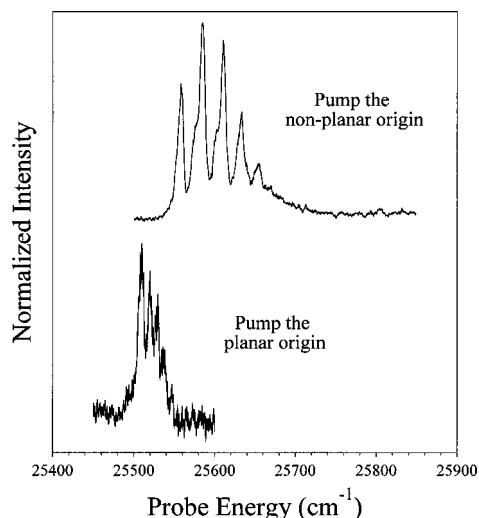


FIG. 9. MATI spectra of the 3-EI-Ar complex pumping the planar and nonplanar origin bands. The probe transition of the nonplanar form is red-shifted by 44  $\text{cm}^{-1}$  relative to the monomer while the planar form is red-shifted by 47  $\text{cm}^{-1}$ .

Because of this, the MATI spectrum collected for the planar conformation has a decreased signal to noise ratio. Still it is clear that this spectrum is significantly different than the nonplanar origin, again confirming that the excitation bands do indeed belong to two different conformers. The IP of the planar 3-EI-Ar complex is determined to be  $60\,309 \pm 5 \text{ cm}^{-1}$ .

## DISCUSSION

### Monomer

#### Conformer assignments

ZEKE spectroscopy has been used to determine the existence of two conformers of 3-EI. The question then becomes, can one unambiguously assign a specific conformation to each origin peak? The *ab initio* calculations introduced above predict two stable conformations of 3-EI, with the nonplanar being more stable by  $50 \text{ cm}^{-1}$ . See Table I. Two observations can be used to assign conformations to specific spectral features. The first is a simple intensity argument. Since there are two rotamers of the nonplanar 3-EI versus only a single conformation for the planar structure it would seem likely that the nonplanar intensity in  $S_1$  would be greater than the planar intensity. Figure 4 shows the two origins in the  $S_1$  excited state, and the intensity of the reddest origin is approximately twice as large as the bluer origin. This leads to an assignment of the red  $S_1$  origin at  $34\,810 \text{ cm}^{-1}$  as belonging to the nonplanar conformation.

This simple population argument and the more detailed Boltzmann analysis in the results section are not necessarily conclusive. Several factors affect the observed peak intensities, including beam conditions, laser power, and others. For this reason it is impossible to rely on simple peak intensities for conformer assignments. Further evidence for the assignment is obtained from the details of the ZEKE spectroscopy. As seen in Fig. 5, the ZEKE spectrum of the 3-EI monomer, pumping the origin band at  $34\,810 \text{ cm}^{-1}$  shows a relatively large vibrational progression. Spectroscopically, progressions such as these are seen when a large geometry change occurs upon ionization. This changes the shape of the potential well, relative to the  $S_1$  state, and hence the  $\Delta v = 0$  propensity is lost. Instead, overlap with higher vibrational levels gain intensity, and a vibrational progression is seen in the spectrum. The geometries of the ground state (this is similar to the geometry of the  $S_1$  state) and the ionic state of 3-EI have been calculated and the results shown above (see Table I). These calculations predict that upon ionization, the nonplanar 3-EI undergoes a large change in the 2-3- $\alpha$ - $\beta$  dihedral angle. The torsional potential has also been calculated and is shown in Fig. 2. It is seen that the nonplanar ion minimum shifts substantially from the ground-state nonplanar minimum (dotted line in Fig. 2). It is this geometry change that give rise to the vibrational progression seen in the ZEKE spectrum. Equivalently, Fig. 2 shows that the planar ground ionic state minima line up exactly. This suggest that the  $\Delta v = 0$  propensity rule will again be followed, and the ZEKE spectrum will show only a single peak. This is indeed the case as can be seen in the bottom of Fig. 5.

This argument for the assignment of the reddest  $S_1$  peak to the nonplanar conformation is by itself a very convincing argument for the proposed conformer assignment. This coupled with the population argument and relative energy argument, confirms that the origin at  $34\,810 \text{ cm}^{-1}$  belongs to the nonplanar conformation and the bluer origin at  $34\,833 \text{ cm}^{-1}$  belongs to the planar conformation of 3-EI.

#### Vibrational calculation and the torsional potential

Calculation of the ethyl chain torsional potential (Fig. 2) helps to provide insight into the spectroscopy of 3-EI. It was noted above that the nonplanar conformation undergoes a geometry change upon ionization while the planar conformation does not. The calculated potential shows a shift in the nonplanar ionic state wells relative to the ground state. This shift in the potential minimum is what gives rise to the observed Frank-Condon progression in the nonplanar ZEKE. In contrast, the calculated well for the planar conformation does not shift relative to the ground state. This is consistent with the observed ZEKE spectrum that shows a single sharp feature corresponding to the vertical  $\Delta v = 0$  transition.

As seen in Fig. 2 there is a very small barrier for interconversion between the planar and nonplanar conformations in the ion ( $11 \text{ cm}^{-1}$ ). Still the ZEKE spectrum of the planar conformation suggests that there is a discrete level residing in this small well.

To explain the experimental observations it is helpful to incorporate the calculated torsional potential and ion spectrum. The first observation that must be made is that the potential obtained using the DFT methods, described above, does not accurately represent the real potential. The calculated spectrum is considerably different than the experimental if only the unadjusted surface is used. By adjusting the potential and using a functional fit, to predict the ion spectrum, a more accurate barrier height is obtained. It is found that interconversion on the ionic surface from the nonplanar to the planar conformation is  $\sim 60 \text{ cm}^{-1}$ , not the originally calculated  $87 \text{ cm}^{-1}$ . While this difference is small, it has a direct influence on the observed spectroscopy, and provides insight into the accuracy of the DFT methods used.

Finally the calculated spectra allows us to interpret the rather complicated ZEKE spectra obtained. Consider first the nonplanar conformation that showed a large Frank-Condon progression. The shift of the potential upon ionization has already been discussed, but the interpretation of the progression can be better understood with the calculated spectra. First it is seen that there are actually two progression, a major and minor progression, in the nonplanar ZEKE. The calculations show that the minor progression arises, as a result of degeneracy loss, when the top of the interconversion barrier is approached ( $\sim 60 \text{ cm}^{-1}$ ). By noting when the experimentally observed minor progression turns on, we can reasonably predict the experimental barrier height in the ion. The start of this progression is seen in Fig. 5 and is at  $34 \text{ cm}^{-1}$  relative to the nonplanar  $\Delta v = 0$  transition. By adding in the calculated zero-point energy ( $14 \text{ cm}^{-1}$ ), and knowing that the splitting of vibrations occurs just below the barrier, we can estimate the experimental barrier to be  $\sim 50 \text{ cm}^{-1}$ , in good agreement with the calculated barrier. The shape of the

adjusted ion potential also allows the planar conformation to comfortably have a bound level in its well. This explains the existence of the observed planar 3-EI ZEKE.

## Argon clusters

### Isomer assignment

As was noted in the Results section, 3-EI-Ar<sub>n</sub> ( $n = 1-3$ ) shows a single argon isomer for each monomer conformation. The excitation spectra of these clusters are shown in Figs. 7 and 8. The MATI spectra of the  $n=1$  cluster unambiguously confirms the existence of the individual isomers as opposed to hot bands or vibrational structure. By using standard additivity rules, it is possible to assign isomeric structures to the various  $S_1$  origins. The  $n=1$  cluster has the nonplanar origin at  $34\,877\text{ cm}^{-1}$  and the planar origin at  $34\,800\text{ cm}^{-1}$ . The shift in the  $S_1$  spectra relative to the respective monomer for both the nonplanar and planar conformations is red by  $33\text{ cm}^{-1}$ . This  $S_1$  shift is similar to that of the indole-Ar system, of  $-27\text{ cm}^{-1}$ .<sup>26</sup> In the indole system, the argon is determined to reside over the bond common to the five and six membered rings. The similarity in the 3-EI-Ar and indole-Ar  $S_1$  shift leads to the conclusion that the argon is in a similar position as in indole. Atom-atom calculations (described in detail elsewhere)<sup>18,19</sup> also suggest that the argon resides over the bond fusing the five and six membered rings. The final question is whether, in the case of the nonplanar conformation, is it on the side of the indole moiety with or without the ethyl chain, i.e., “top” or “bottom” of the rings. This question is not easily answered, since as will be seen shortly, the  $n=2$  has a conformation with one argon on each side, with no side dependent difference in the  $S_1$  shift. Preliminary atom-atom calculations have been run, and they suggest a slightly higher binding energy for the argon on the side with the ethyl chain of the nonplanar 3-EI. This may suggest that the most favorable isomer of the nonplanar conformation has the argon on the side with the ethyl chain.

In the  $n=2$  case, both isomers again show a  $33\text{ cm}^{-1}$  shift in  $S_1$  relative to the  $n=1$ . This would suggest, according to the additivity rules, that the argon occupies the side opposite the first argon. In the case of the planar conformation this suggests a conformation with one argon on each side. The nonplanar conformation can also be assigned using the additivity rules. Similar to the planar 3-EI, additivity would suggest a conformation with one argon on each side of the planar ring system. This assignment is consistent with other molecular clusters that primarily show two sided conformations for small argon clusters.<sup>18,19,26</sup>

The  $n=3$  complex does not shift at all relative to the  $n=2$  3-EI-Ar<sub>n</sub>. This causes the additivity rules to break down, and makes isomer assignments difficult without further experiments and calculations. It should be noted that in the case of  $n=2$  and  $n=3$  3-EI-Ar<sub>n</sub> complexes, the  $S_1$  spectra become broader and more complicated than the  $n=1$  complex. This is taken to suggest that other isomers exist in the molecular beam that we are not able to resolve with these experiments.

### $n=1$ MATI interpretation

The 3-EI-Ar MATI spectra are shown in Fig. 9. The planar conformation of the  $n=1$  complex shows a progression of  $\sim 10\text{ cm}^{-1}$  that may be assigned to the 3-EI-Ar bending vibration in the cation. This assignment comes from direct comparison to the indole-Ar system.<sup>24</sup> The nonplanar conformation MATI (Fig. 9) is quite different than the planar MATI. Just as in the monomer studies, the 3-EI-Ar MATI shows a pronounced Frank-Condon progression in the ion. This is presumably arises from the same change in the ethyl chain torsional angle that is observed in the monomer. There is one striking difference though. In the monomer there were two progressions observed in the ion (see above and Fig. 9), referred to here as the major and minor progression. The major progression in the monomer arose from the vibrational levels localized in the nonplanar conformation potential well. The minor progression turns on only when the barrier to conformer interconversion is approached. In the nonplanar 3-EI-Ar MATI, only the major progression is observed. This is taken to suggest that upon solvation of the 3-EI with argon, the barrier to conformer interconversion is increased. The direct cause for this barrier increase has not been studied, but preliminary molecular mechanics calculations show that the barrier to conformer interconversion increases by  $\sim 35\text{ cm}^{-1}$  when the argon is located on the ethyl chain side of the 3-EI. Presumably this increase arises from the new Ar-C $\beta$  interaction that must be broken when the ethyl chain rotates toward planar. Whatever the specific interactions are it seem safe to assume that the argon is on the same side as the ethyl chain since it influences so directly the ethyl chain potential.

## CONCLUSION

3-ethylindole, a derivative of tryptophan, has been shown to have two distinct conformations in a jet expansion. Density functional calculations are used to determine the geometry of the two local minimums in the ground and ionic state, and the relative energies of each. These two conformations, termed planar, and nonplanar, exhibit two distinctly different ZEKE spectra, unequivocally confirming the existence of multiple conformer. The ZEKE for the planar conformation shows a “normal”  $\Delta v=0$  transition to the ion, while the nonplanar shows a large, complicated Franck-Condon progression. The DFT calculations performed show a large geometry change in the nonplanar conformer ethyl chain torsion upon ionization. It is this geometry change that give rise to the complicated ion spectrum.

DFT calculations have been used to map out the ethyl torsional potential surface in the ground and ionic state. The ion potential has been adjusted to reproduce the nonplanar and planar ZEKE spectra to a good approximation. By noting the onset of the minor progression in the nonplanar ZEKE, we are able to approximate the barrier to conformer interconversion in the ion. This is compared directly to the theoretical determination of the barrier height, and theory is found to vary significantly from experiment.

3-ethylindole solvated with as many as three argon atoms has also been investigated. In the case of  $n=1$  and 2,

the isomeric structure could be determined using additivity rules. The  $n=1$  complex has an argon located on the side with the ethyl chain in the nonplanar 3-EI. The  $n=2$  shows a conformation with one argon on each side for both the planar and nonplanar 3-EI. The  $n=1$  cluster was studied in the ion using MATI spectroscopy, and the nonplanar conformer is found to show similar geometry changes upon ionization, as was the case in the monomer. Although the cluster torsional potential was not investigated directly, it is noted that the nonplanar PES reduces to a single progression, suggesting that the barrier to conformer interconversion is increased upon addition of a single argon.

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