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Electronic Spectroscopy and Photoisomerization of *trans*-Urocanic Acid in a Supersonic Jet

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Abstract: *trans*-Urocanic acid (*trans*-UA), a component of the epidermal layer of skin, exhibits wavelength-dependent photochemistry. The quantum efficiency of isomerization to *cis*-UA is greatest when the molecule is excited on the long wavelength tail of its absorption profile in solution (300−320 nm). However, exciting the molecule where it absorbs UV light most efficiently (260−285 nm) causes almost no isomerization. We have used fluorescence excitation and dispersed emission methods in a supersonic jet to investigate the electronic states involved in this complex and interesting photochemistry. Three distinct regions are present in the excitation spectrum. Region I, which is below the isomerization barrier, contains sharp, well-resolved peaks that upon excitation emit from the S_1 state of *trans*-UA. Region II exhibits peaks that increase in broadness and decrease in intensity with increasing excitation energy. Upon excitation these peaks produce dual emission from the S_1 states of both *trans*- and *cis*-UA. The trans to cis isomerization barrier is estimated to be 1400 cm^{-1}. Region III exhibits excitation to the S_2 electronic state and has a broad structure that spans 3000 cm^{-1} and occurs 4000 cm^{-1} above S_1. S_2 excitation results in essentially no trans to cis isomerization.

Introduction

trans-Urocanic acid (*trans*-UA) is formed in the epidermal layer of the skin upon deamination of the amino acid histidine. *trans*-UA absorbs in the UV-A and UV-B regions and is thought to act as a natural sunscreen to protect DNA from UV damage. It was added to sunblocks for a period until the discovery that UV absorption also results in isomerization to *cis*-UA, which has been shown to exhibit immunosuppressive behavior.[1]

This finding generated a number of investigations into the photochemistry and photobiology of UA,[2] which has turned out to be a complex and interesting problem. Urocanic acid exhibits wavelength-dependent photochemistry; the quantum efficiency of isomerization has its maximum value of 0.5 when the molecule is excited on the long wavelength tail of the absorption curve. However, exciting the molecule where it absorbs UV light most efficiently causes almost no isomerization.[3] A handful of organic molecules have this type of wavelength-dependent photochemistry, and two explanations have been proposed to explain this behavior. The molecule may have multiple ground-state rotamers that have distinct electronic structures, or the molecule may have several near lying electronic excited states that have different photophysics.

The Simon group has performed several experiments in the condensed phase that indicate that the wavelength-dependent photochemistry of urocanic acid is due to multiple electronic excited states.[4−6] Fluorescence emission studies[5] show an emission peak near 370 nm when the molecule is excited at 308 nm, on the red tail of the absorption curve. This maximum shifts only slightly when excitation is in the 300 to 320 nm region. Excitation at the absorption maximum (266 nm) results in emission that peaks at 354 nm; this is constant as the excitation wavelength is varied from 260 to 285 nm. The fluorescence quantum yield of *trans*-UA excited at 266 nm is estimated to be 10^{-4}, which is 10 times smaller than the quantum yield resulting from excitation at 310 nm.

Transient absorption experiments[6] show that the state populated when pumping at 308 nm is likely a short-lived (<40 ps) singlet state. Since isomerization occurs in this region, the authors suggest a minimum rate of isomerization of 1.2×10^{10} s^{-1} based on the transient signal observed. The authors conclude that the state populated via pumping at 266 nm is also a very short-lived singlet state that decays with a rate of 1.4×10^{11} s^{-1} by intersystem crossing to a nearby triplet state. Photoacoustic calorimetry experiments[5] have shed further insight into the nature of the electronic states involved by measuring how much energy is released nonradiatively when the molecule is excited in the two regions of interest. At 308 nm, all of the excitation energy is released to the solvent as heat. However, excitation at 266 nm causes 50% of the excitation energy to be retained in the molecule when the solvent is saturated with argon. This suggests the presence of a long-lived (>1 μs) state. When the solvent is saturated with oxygen, 75% of the energy is released implying that the long-lived state is a triplet state. The energy of the triplet state was calculated to be 230 kJ/mol, which is in good agreement with triplet sensitization experiments performed by Morrison et al.[3] The above experiments indicate that there are two different excited states involved at the different excitation wavelengths.

The electronic structures of both *trans*- and *cis*-UA have also been investigated in recent theoretical calculations.[7] The authors perform CASPT2 calculations on the lowest electronic excited

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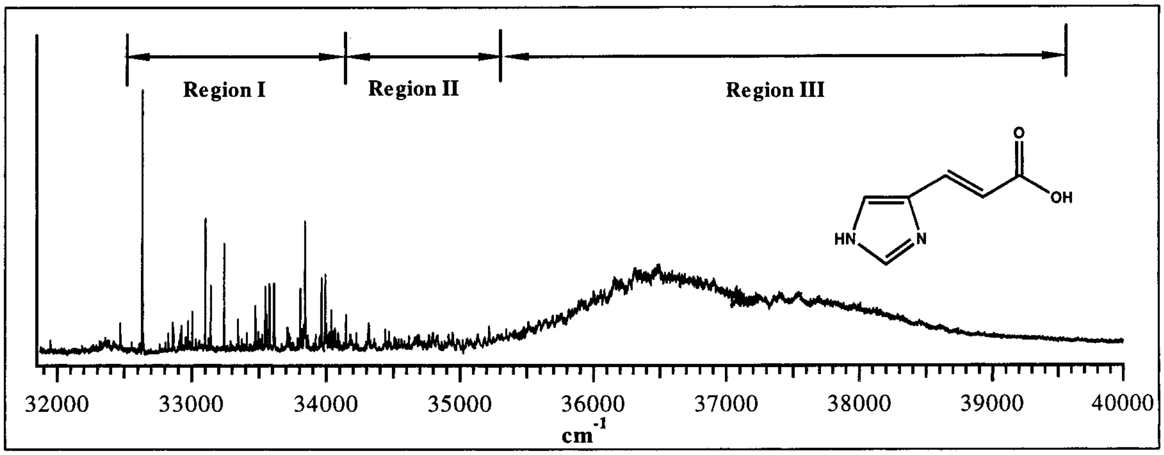

Figure 1. Fluorescence excitation spectrum and structure of *trans*-urocanic acid.

states of the two isomers. For the trans isomer, the calculated vertical excitation energies of the first two electronic excited states correspond to a $\pi-\pi^*$ state at 39 760 cm^{-1} and an n$-\pi^*$ state at 41 292 cm^{-1} with oscillator strengths of 0.1203 and 0.0005, respectively. At the equilibrium geometries of the n$-\pi^*$ and $\pi-\pi^*$ states, the origin transitions were calculated to be 33 000 and 37 600 cm^{-1}, respectively. Note that the n$-\pi^*$ transition is predicted to occur at lower energy in this case, unlike the vertical excitation energy calculations, indicating a surface crossing. The n$-\pi^*$ state was predicted to involve a large change in geometry from the ground to the excited state, with its emission maximum shifted 9600 cm^{-1} from the origin transition. Similarly, the n$-\pi^*$ and $\pi-\pi^*$ states for the cis isomer were calculated to occur at 33 800 and 27 200 cm^{-1}. Again, the emission maximum for the n$-\pi^*$ state was shifted significantly, indicating a large change in geometry from the ground to the excited state.

The prototype molecule for studying trans/cis photoisomerization in a supersonic jet is *trans*-stilbene (1,2-diphenylethylene). Syage et al.[8,9] measured fluorescence lifetimes upon excitation of vibronic levels in S_1. They found the fluorescence lifetimes were constant for excitation energies below the isomerization barrier, but the lifetimes rapidly decreased with increasing energy beyond the isomerization barrier. The decrease in lifetimes above the isomerization barrier was attributed to the competition of the nonradiative isomerization channel with radiative decay. In the fluorescence excitation spectrum which is more relevant to our study, the shortening of vibronic lifetimes due to isomerization was manifested as an increase in broadening and decrease in intensity of the peaks with increasing excitation energy.

To gain further insight into urocanic acid's complicated photochemistry, we have performed fluorescence excitation and dispersed emission studies of *trans*-UA in a supersonic jet.

Experimental Section

trans-Urocanic acid was purchased from Aldrich and used without further purification. The spectra presented were recorded with use of fluorescence excitation and dispersed fluorescence techniques described in detail elsewhere.[10] The molecules were heated to 270 °C to attain a sufficient vapor pressure and the nozzle temperature was kept about 20 °C higher than the sample temperature. The molecules were seeded into helium gas preheated to a temperature of 200 °C and a stagnation pressure of 3−4 atm, and the mixture was expanded into a vacuum chamber through a 50−100 μm orifice. Excitation spectra were measured by monitoring the total fluorescence as a function of excitation wavelength, using a photomultiplier tube. The dispersed fluorescence spectra were measured by dispersing the emission obtained at fixed excitation wavelength through a 1.0 m monochromator and detecting the fluorescence with a photomultiplier tube. Resonance-enhanced multiphoton ionization was also performed to ensure that all of the features occurring in the fluorescence excitation spectrum were due to *trans*-UA.

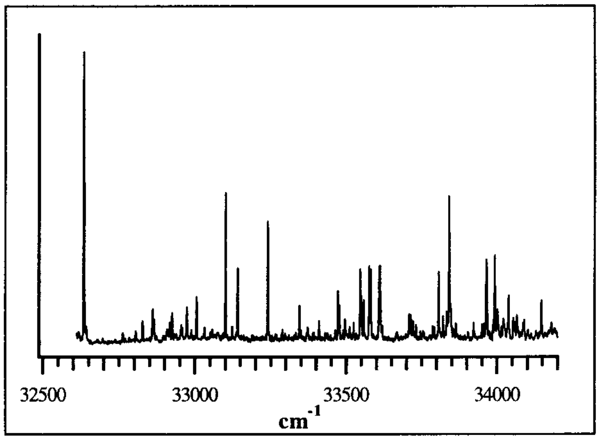

Figure 2. Expanded fluorescence excitation spectrum of *trans*-UA in Region I.

Results

The fluorescence excitation spectrum and structure of *trans*-UA are shown in full in Figure 1. It is useful for discussion purposes to divide the spectrum into three regions: Region I from 32 500 to approximately 34 000 cm^{-1}, Region II from 34 000 to 35 500 cm^{-1}, and Region III from 35 500 to 39 000 cm^{-1}.

Region I. The first region, expanded in Figure 2, is comprised of sharp, well-resolved peaks. The strongest peak in this spectrum is at 32 626 cm^{-1} (307 nm), and is assigned as the S_1 origin. The less intense features to the blue of the origin are vibrational progressions. The emission spectrum resulting from excitation of the origin transition is shown in Figure 3a. The most intense feature occurs at the excitation wavelength, with several less intense vibrational peaks to the red. The fact that the origin transition is the strongest feature in both the excitation

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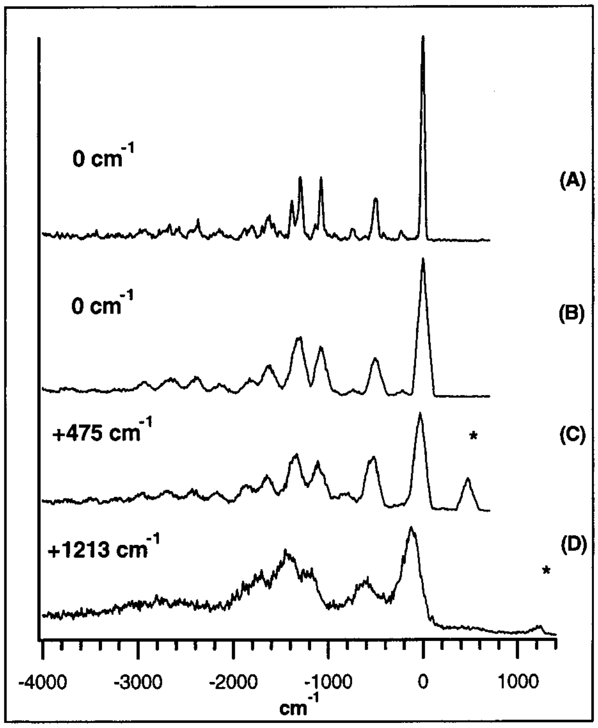

Figure 3. Single vibronic level emission of *trans*-UA excited at (A) origin (32 636 cm^{-1}) at 40 cm^{-1} spectral resolution and (B, C, D) origin, +475, and +1214 cm^{-1}, respectively, at 120 cm^{-1} spectral resolution. The *x* axis is in cm^{-1}, relative to the origin transition 32 626 cm^{-1}. Features marked with asterisks are entirely due to scattered laser light. Less than 15% of the intensity at the excitation wavelength in parts A and B is due to scattered laser light.

and emission spectra implies that the geometry of the S_1 state is not significantly different from that of the ground state.

The spectrum in Figure 3a was taken at 40-cm^{-1} resolution. To obtain sufficient signal upon exciting the less intense features, the monochromator slits were widened such that the resolution in the rest of the emission spectra to be discussed is 120 cm^{-1}; the origin emission spectrum at this resolution is shown in Figure 3b. Exciting the other vibrational peaks in Region I results in almost identical emission spectra (see the +475-cm^{-1} peak in Figure 3C, for example), but a noticeable broadening occurs at higher energies, as illustrated in Figure 3d. This broadened emission appears at excitation energies around +1100 cm^{-1} from the origin; note that the peak in the excitation spectrum is still sharp at this point.

The majority of the vibrations described above exhibited relaxed emission. That is, energy originally contained in a single vibrational mode (or a few vibrational modes in the case of combination bands) has been distributed to many lower frequency modes prior to emission. However, two peaks at +620 and +1180 cm^{-1} above the origin did not relax, as shown in Figure 4a, where a significant portion of the intensity at the excitation wavelength is fluorescence. Figure 4b shows the overlay of the unrelaxed peaks and origin emission, where it is clear that the unrelaxed peaks are vibrational peaks built upon the originally excited level.

Region II. The second region, shown in greater detail in Figure 5, involves peaks that decrease in intensity and increase in width as the excitation energy is increased. Excitation of these peaks results in dual emission, as shown in Figure 6. The emission is comprised of the same features, now broadened, observed in Region I. In addition there are blue-shifted components, the bluest occurring at about 33 800 cm^{-1}. The onset of emission spectra exhibiting dual emission first occurs for excitation around 34 000 cm^{-1} (origin + 1400 cm^{-1}). Note that there are several sharp peaks in the excitation spectrum around the onset of the broad peaks.

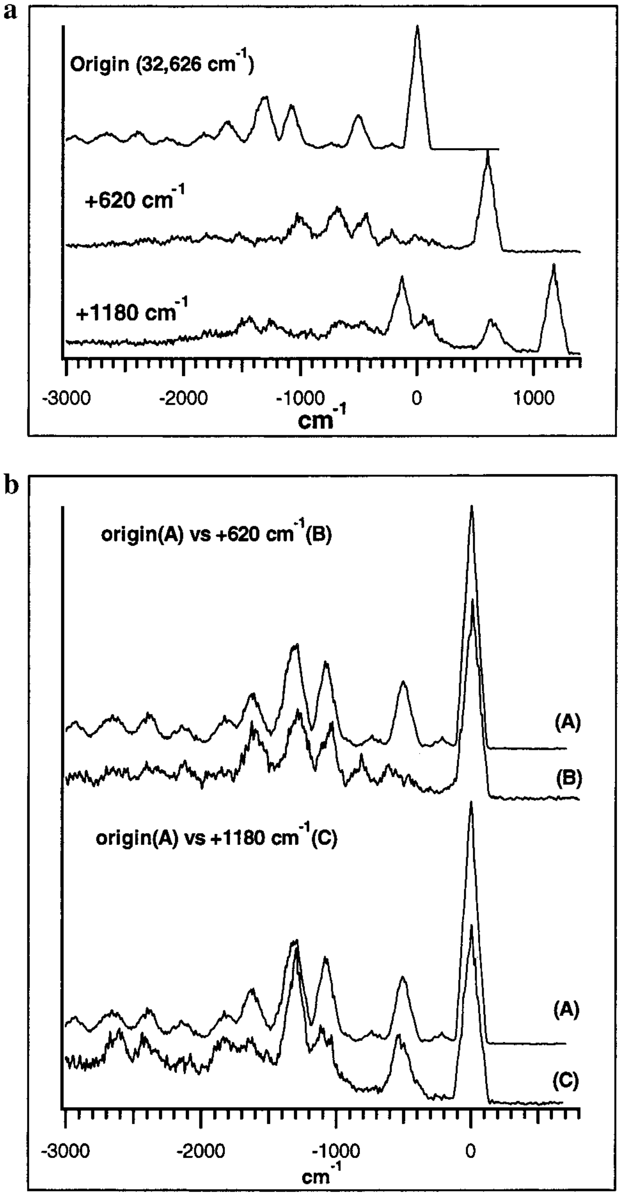

Figure 4. (a) Single vibronic level emission spectra of *trans*-UA excited at (A) origin, (B) +620 cm^{-1}, and (C) +1180 cm^{-1}. Less than 15% of the emission intensity at the excitation wavelengths is due to scattered laser light. (b) Overlays of the +620 (B) and +1180 cm^{-1} (C) emission spectra from Figure 4A with origin emission (A). Spectra B and C were shifted −630 and −1195 cm^{-1}, respectively, to depict overlap with origin emission.

Region III. The bluest region begins with the continuing broad peaks from Region II with a growing in of an extremely broad feature covering over 3000 cm^{-1}. We believe that this is due to the S_2 electronic state. The maximum absorption occurs about 4000 cm^{-1} above the S_1 origin (273 nm). Such a broad absorption signifies that vertical excitation is to a point on the S_2 potential energy surface that contains a large density of states. Furthermore, absorption to a large density of states implies that the S_2 state is shifted in one or more coordinates relative to the S_0 state since absorption to the lowest vibrational level would appear sharp and broadened only by radiationless processes. Emission resulting from excitation of this feature is shown in Figure 7. It appears to be an even further broadened version of

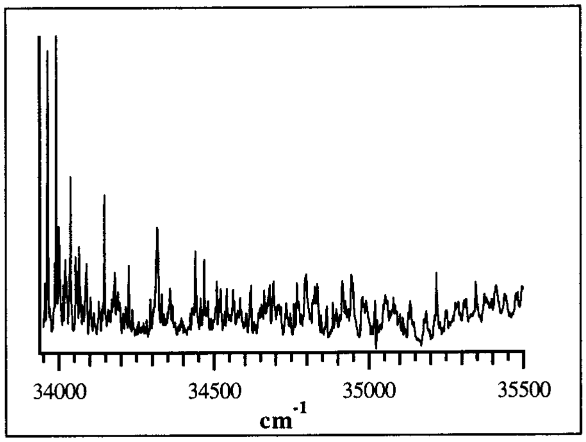

Figure 5. Expanded fluorescence excitation spectrum of *trans*-UA in Region II.

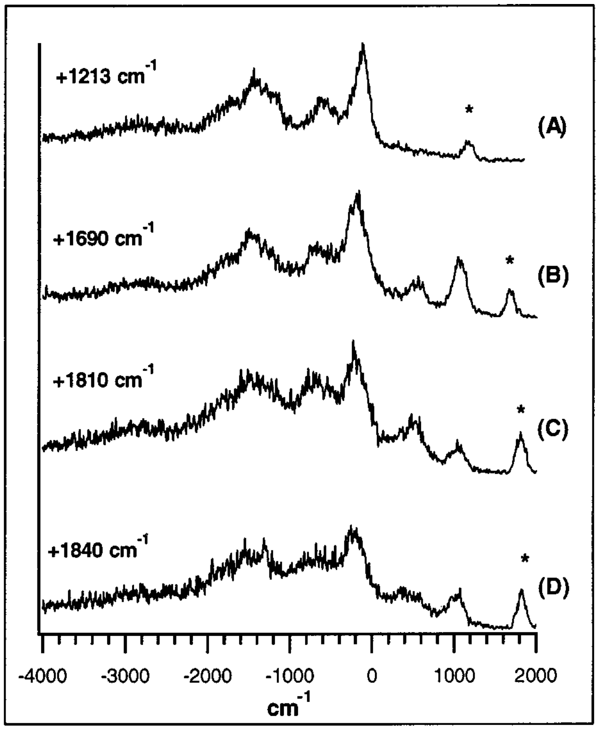

Figure 6. Single vibronic level emission spectra of *trans*-UA excited at (A) $+1213$ cm^{-1} in Region I and (B, C, D) $+1690$, $+1810$, and $+1840$ cm^{-1} in Region II. The *x* axis is in cm^{-1}, relative to the origin transition 32 626 cm^{-1}. Features marked with asterisks are entirely due to scattered laser light.

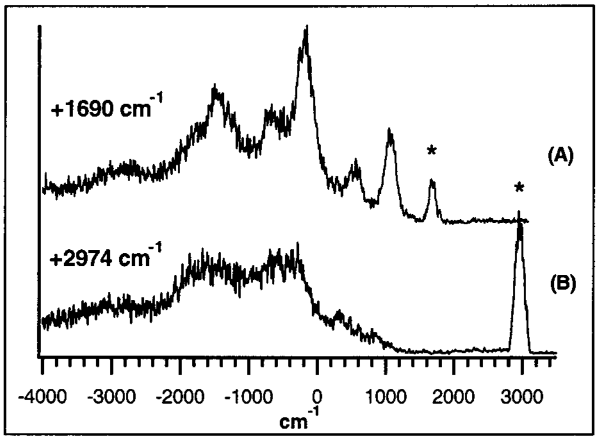

Figure 7. Emission spectra of *trans*-UA excited at (A) $+1690$ cm^{-1} in Region II and (B) $+2974$ cm^{-1} in Region III. The *x* axis is in cm^{-1}, relative to the origin transition 32 626 cm^{-1}. Features marked with asterisks are entirely due to scattered laser light.

the emission spectrum produced by excitation of the S_1 origin transition. A very small amount of emission is observable at wavelengths where the blue features occur in the emission spectra from Region II, but the ratio of blue -shifted emission to origin emission has decreased significantly in this region.

Discussion

trans-Urocanic acid (*trans*-UA) exhibits somewhat rare wavelength-dependent photochemistry in solution. Excitation at low energies results in maximum isomerization to *cis*-UA while excitation where *trans*-UA absorbs most efficiently results in minimal isomerization. The objectives of this supersonic jet study were to elucidate the nature of the electronic states buried under the broad, structureless absorption spectrum of urocanic acid observed in solution. Furthermore, we were very interested in the manifestation of wavelength-dependent photoisomerization in the isolated molecule under the collision-free conditions achieved in the jet.

As seen above, the fluorescence excitation spectrum of *trans*-UA features three distinct regions. The first region, covering about 1400 cm^{-1}, is comprised of many sharp, well-resolved peaks. The second region is characterized by many broad but resolvable peaks that increase in width and decrease in intensity with increasing energy. The third region involves the broad features from Region 2 overlaid on a broad, structureless absorption covering about 3000 cm^{-1}. The three regions will be discussed, followed by comparisons to condensed-phase experiments and theoretical calculations.

Region I. As presented in the Results section, the fact that the $\Delta v = 0$ transition is the strongest in both the excitation and emission spectra implies that the ground and first excited state potential energy surfaces are not shifted much relative to each other. This behavior is indicative of a $\pi-\pi^*$ transition because in large, delocalized π-systems, a change in one delocalized electron usually has little effect on the geometry or force constants of the molecule. High-level ab initio calculations have suggested that the S_1 state is an n$-\pi^*$ transition of miniscule oscillator strength localized on the carbonyl oxygen, with a very different geometry from that of the ground electronic state.[7] If the transition observed here were to an n$-\pi^*$ state, we would expect not only a much less intense transition but also a broadened emission spectrum with a large shift relative to the excitation spectrum.

It is difficult to assign the vibrations in the ground and excited state. Infrared studies have been performed on imidazole and propionic acid separately, but not on urocanic acid as a whole. Furthermore, the electronic spectrum of the imidazole chromophore has not been studied in a jet. Much of the vibrational activity in the emission spectrum of *trans*-UA may be attributed to the normal mode vibrations of the imidazole chromophore. Most of the observed features correlate well with published infrared spectra,[11,12] as seen in Table 1. A few features appear in the emission spectrum that cannot be imidazole vibrations, so we can look to the propionic acid moiety. The feature at 226 cm^{-1} in the emission spectrum is identical to the ethylene bend in propionic acid.[13] There is a corresponding feature in the excitation spectrum at 237 cm^{-1}. Several features in the *trans*-UA fluorescence emission and excitation spectra appear

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Table 1. Vibronic Features in Excitation (S_1) and Emission (S_0) Spectra of *trans*-UA, Compared to a Published Imidazole Infrared Spectrum

S_0 (cm^{-1})	published imidazole IR spectrum[11] (cm^{-1})	S_1 (cm^{-1})[a]	assignments
226		237	ethylene bend
506	538/551	476, 514 (Y)	
606	636/631	620	
736	735/728	719	
1066	1056/1074/1120/1130	924/954/987	imidazole normal modes
1281	1252	1214/1180 (Z)	
1376	1325	1338/1366 (X)	
1576	1518	1519	
1786		1694 (Z + Y)	combination bands?
1876		1814/1842 (X + Y)	other propionic acid vibrations?

[a] The letters X, Y, and Z in parentheses represent possible fundamentals contributing to combination bands, e.g. X + Y.

between 1600 and 1800 cm^{-1}, but the imidazole infrared spectrum does not contain any peaks between 1600 and 3000 cm^{-1}. These features may be combination bands of some of the imidazole fundamental vibrations or vibrations arising from the rest of the molecule, like the carbonyl stretch. A few peaks in the excitation spectrum, labeled X and Z in the table, appear to be combination bands with the +476 cm^{-1} mode, labeled Y.

The emission spectra resulting from excitation of the vibrational peaks in this region are very similar and resemble the emission spectrum obtained by exciting the origin. At higher energies, the spectra become broadened, but retain similar features. This is likely a consequence of intramolecular vibrational relaxation (IVR). The molecule is initially excited to a Franck−Condon allowed bright state. As the excitation energy is increased, the density of dark states originating from other vibrational modes of the molecule increases, which may mix with the bright state via anharmonic couplings. Each of these dark states has large Franck−Condon factors with corresponding ground-state levels, i.e., large $\Delta v = 0$ Franck−Condon factors. The many overlapping transitions with slightly different frequencies result in a broadened emission spectrum. The IVR broadening of the emission spectra occurs around +1000 cm^{-1} above the origin, when the first two features in the emission spectrum appear to merge together. However, the unrelaxed vibrational peaks at +620 and +1180 cm^{-1} suggest that IVR in this region is mode selective.

Region II. The second region in the fluorescence excitation spectrum involves an abrupt appearance of features with increasing width and decreasing intensity as the excitation energy increases. We will discuss two arguments as to why we believe that we are observing trans to cis isomerization in this region.

Initially, the broad excitation features alternate with sharp features, then at about 1600 cm^{-1} all features become broad. Excitation of these broad features results in dual emission which contains the standard IVR broadened *trans*-UA emission with some blue-shifted components. Dual emission signifies coupling to another electronic state, which we believe is the *cis*-UA S_1 state. The blue-shifted emission would then be fluorescence of the *cis*-UA S_1 state back to the *cis*-UA ground state. The presence of some sharp peaks initially means that at the onset of level mixing of the *trans*-UA S_1 with the *cis*-UA S_1, the density of states of acceptor levels has not reached the statistical limit, so accidental degeneracies are observed.

The second argument we have for the occurrence of isomerization in this region is the similarity of this portion of the spectrum to the isomerization region of *trans*-stilbene.[8,9] In the frequency domain, the excitation spectrum of stilbene showed an abrupt broadening of peaks at the isomerization barrier that increased in width and decreased in intensity as the excitation energy increased. Quantitative studies were performed to measure the lifetimes of each vibrational peak, and the conclusion was that the lines broadened due to competition of the radiationless isomerization channel with radiative decay. Furthermore, the onset of IVR occurred a few hundred cm^{-1} before isomerization, which led to the conclusion that the isomerization was not mode selective.

The assumption that isomerization is occurring in Region II allows us to make a few comments on the isomerization process in urocanic acid. The onset of the broad features exhibiting dual emission occurs around 1400 cm^{-1}, or 4 kcal/mol. We approximate this as the isomerization barrier. Emission spectra exhibiting IVR broadened features occurs around 1100 cm^{-1}, which means that like stilbene, isomerization of *trans*-UA is not mode selective. The bluest emission peak of the *cis*-UA emission occurs at 33 800 cm^{-1}. This is likely the *cis*-UA origin transition which is about 1200 cm^{-1} higher in energy than the *trans*-UA origin. Several calculations have shown that the *cis*-UA ground state is more stable than the *trans*-UA ground state because of the intramolecular hydrogen bond that may form between the ring imidazole and the carbonyl oxygen. The calculation of Page et al.[7] assigns a difference of 3 kcal/mol, or about 1000 cm^{-1}, between the *cis*-UA and *trans*-UA ground states. If this is the case, the S_1 state will be about 200 cm^{-1} higher in energy than the trans S_1 state, which means that the cis-to-trans isomerization barrier is a few hundred cm^{-1} lower than the trans-to-cis barrier.

Region III. The third region is comprised of the increasingly broadened peaks from Region II, with a growing in of a broad, structureless feature that covers about 3000 cm^{-1}. The broad structure is likely due to excitation of the S_2 electronic state of *trans*-UA. The emission spectrum resulting from excitation of this state is S_1 emission minus the blue-shifted components characteristic of *cis*-UA emission, which seems to indicate that isomerization is occurring to a significantly lesser extent in Region III than in Region II. According to Kasha's rule, S_2 emission rarely occurs, because the density of states available at higher electronic states is great enough that some other radiationless process will occur much faster than fluorescence. The most likely radiationless processes are internal conversion (IC) to the S_1 state and intersystem crossing (ISC) to a triplet state.

We do not believe we are observing ISC because the emission is shifted at most a hundred cm^{-1} from S_1 emission. The triplet state would have to lie coincidentally close to the S_1 state for ISC to be occurring. Furthermore, we attempted to measure a lifetime for this state but it was shorter than our instrument response of 10−20 ns, which is too short to be a triplet state. Ruling out ISC would lead us to believe that we are observing IC to the S_1 state. The problem with this idea is that if S_2 is

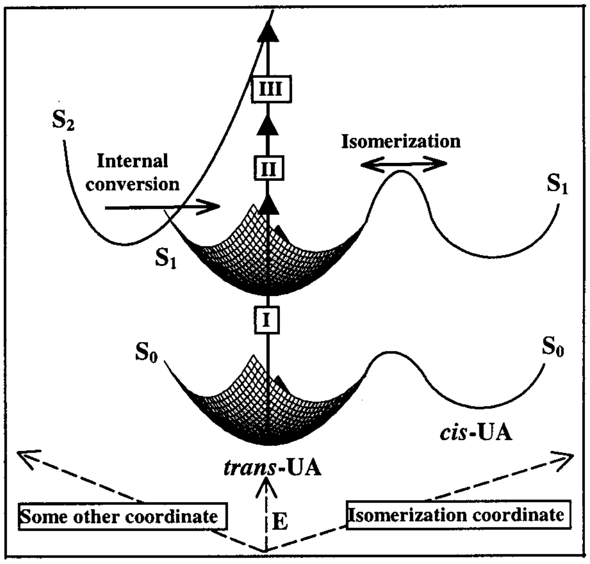

Figure 8. Schematic of electronic states involved in the photodynamics of urocanic acid. The potential energy surfaces of *trans*-UA are shown with respect to two coordinates: the isomerization coordinate (right-hand side) and another coordinate (left-hand side) in which S_2 changes with respect to S_0 and S_1. The arrows labeled I, II, and III depict excitation into Region I (below the isomerization barrier), Region II (isomerization region), and Region III (S_2 electronic state where IC to S_1 competes with isomerization), respectively.

coupling to a large density of states high in the S_1 state, i.e., above the isomerization barrier, we would expect that isomerization would occur after IC. This seems unlikely as the blue-shifted emission characteristic of *cis*-UA is miniscule. However, recall that the broad absorption of S_2 led us to believe that its geometry is shifted from that of the ground state. This being the case, excitation would occur to some high energy vibrational levels in the S_2 manifold, and vibrational relaxation could occur within S_2 before IC to S_1. If the relaxed vibrational state had vibrational energy distributed among many vibrational modes with little or no excitation of the vibrations involved in the trans to cis isomerization reaction coordinate, S_2 would couple to a density of states that would result in only *trans*-UA emission. Figure 8 illustrates this idea. This scheme requires that the coordinate along which S_2 shifts relative to S_1 is different than that of the coordinate change in trans-to-cis isomerization. Unfortunately, the geometry of *trans*-UA in the second $\pi-\pi^*$ electronic state has not been calculated.

The photodynamics observed in the gas phase are similar to those in solution. In both cases, some radiationless process competes with isomerization at high energies to lower the isomerization quantum yield. Unlike the solution results, we do not observe ISC to a triplet state. In addition, in the jet isomerization only seems to be occurring over about 1500 cm^{-1} of excitation energy, while it occurs over at least 3000 cm^{-1} in solution. It is possible that the solvent may lower the isomerization barrier and increase the rate of isomerization. We have begun studies on van der Waals clusters of *trans*-UA with water molecules to address these issues.

As far as comparison with the calculated electronic structure, we do not observe the n$-\pi^*$ state that is supposed to occur at 33 100 cm^{-1}. The origin of the first $\pi-\pi^*$ state is predicted to be 36 700 cm^{-1}, which is close in energy to our S_2 state. However, the origin transitions for higher lying $\pi-\pi^*$ states were not calculated. The difference in vertical excitation energy between the two lowest lying $\pi-\pi^*$ states is calculated to be around 4000 cm^{-1}, which is close to the difference in vertical excitation energy of our S_1 and S_2 states.

Conclusion

The rare wavelength-dependent photochemistry of *trans*-urocanic acid has been observed in the gas phase. Isomerization of *trans*-UA to *cis*-UA occurs in the S_1 electronic excited state after overcoming a barrier of approximately 1400 cm^{-1}. The isomerization quantum yield decreases significantly in the region of the S_2 electronic state, possibly due to fast internal conversion back to S_1 with little excitation in the reaction coordinate.

The S_1 origin of *trans*-UA occurs at 32 626 cm^{-1} and is likely a $\pi-\pi^*$ state. From the blue-shifted emission characteristic of *cis*-UA, we can predict that the *cis*-UA S_1 origin occurs approximately 1200 cm^{-1} higher in energy than the *trans*-UA origin. The S_2 electronic excited state of *trans*-UA occurs about 4000 cm^{-1} above S_1, and is extremely broad, suggesting a change in geometry relative to the S_0 state.

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