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TECHNICAL REPORT #17

SPECTROSCOPY, STRUCTURE AND CATIONIC FORMS OF 2-ETHYL-2-AMINO-3-
ANILINOL WITH STUDIES ON THE ACTION OF AMMONIA

by

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Spectroscopy, Structure and Proton Dynamics of 2-hydroxypyridine and its Clusters With Water and Ammonia

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Abstract: The two tautomeric forms of 2-hydroxypyridine (2-HP) have been studied in a supersonic jet expansion. Time-of-flight mass spectroscopy (TOFMS) and emission spectroscopy of the lactim and lactam tautomers have been studied and are reported here. The lactim spectrum is similar to an earlier TOFMS spectrum and has its origin at $36,136 \text{ cm}^{-1}$. Evidence of mixing of the $n\pi^*$ and $\pi\pi^*$ electronic states is seen in the lactim spectrum. The mixing is removed in the disolvate water cluster but not in monosolvate clusters of ammonia or water. The lactam is shown to be nonplanar giving rise to two origins in the excitation spectrum at $29,832 \text{ cm}^{-1}$ and $29,935 \text{ cm}^{-1}$. The ammonia and water lactim cluster spectra show significant shifts to the red while the cluster spectra of the lactam show large shifts to the blue. Experimental evidence for strong hydrogen bonding in these clusters is discussed. Intramolecular and intermolecular proton transfer in 2-HP and its clusters is discussed in the context of these data.

pyridine. form

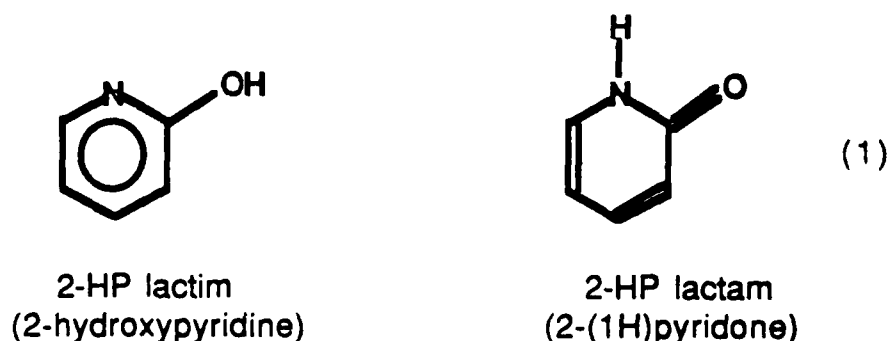


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† Alfred P. Sloan Fellow.

1. Introduction

Tautomerization in N-heterocycles is important in organic chemistry and biochemistry. For example, tautomeric structures can determine the chemistry and biological activity for species such as nucleic acids and, may play a role in spontaneous genetic mutation.¹ One of simplest molecules having stable tautomeric structures is the nominal 2-hydroxypyridine (2-HP). The two stable forms of this molecule are the lactim tautomer (correctly called 2-hydroxypyridine) and the lactam tautomer (correctly called 2-(1H)pyridone):



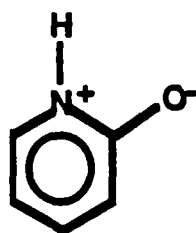
As is shown in (1), tautomerization in 2-HP is accomplished by an intramolecular proton transfer between the molecule's oxygen and nitrogen atoms. 2-HP is an attractive molecule with which to study the processes of tautomerization and proton transfer chemical reactions. The reactants (-OH and -N-) are fixed in space by the structure of the molecule, complications due to diffusion are eliminated and, as the vibrations of both tautomers are well characterized, the possibility of vibrational state-to-state chemistry in this reaction can be studied. One can also easily imagine solvents which should inhibit or promote proton transfer in this system. The fact that 2-HP has a π electron system, also allow proton transfer to be studied in the excited $\pi\pi^*$ electronic state. For instance, if the lactim form of the molecule is excited (276.94 nm)² and proton transfer occurs, emission may be seen from the lactam form (337.5 nm).³ Finally, with the use of picosecond spectroscopy,⁴ the temporal evolution of the excited state reaction can be monitored and the rates and mechanisms of tautomerization investigated.

Supersonic jet spectroscopy is particularly well suited for the study of proton transfer in 2-HP. With this technique,⁵ one can selectively excite specific tautomers⁶ and characterize the emission spectra of each species. Excitation of

various vibronic transitions may then be used to explore the effect of excess vibrational energy upon proton transfer. Supersonic expansions are also ideal for the study of solvation, as individual microclusters involving chromophores and solvents are easily prepared and identified.⁵ Thus, the specific influences of solvation (structure and stoichiometry) upon tautomerization in 2-HP can be investigated.

A number of experimental⁷⁻¹² and theoretical¹³⁻²⁷ studies of 2-HP tautomerization have been undertaken in recent years. In the gas phase, the two structures displayed in scheme (1) are nearly equal in energy,^{8,10} but ground state proton transfer is prohibited by a large potential energy barrier (20,000 cm⁻¹).²¹ In the excited S₁ electronic state, the large exothermicity (~ 6500 cm⁻¹)^{2,3} of the lactim → lactam reaction should decrease the barrier of proton transfer. Like other excited state proton transfer systems,²⁸⁻³⁰ the lactim form can be excited at short wavelengths and evidence of proton transfer would be seen in the long wavelength emission characteristic of the lactam. To date no such evidence has been reported for 2-HP and further investigation is warranted.

Solvation is thought to play an important role in the tautomerization of 2-HP, and a substantial number of studies have investigated the effects of solvents.¹⁰⁻²⁰ In polar solvents, the lactam is known to be lower in energy than the lactim,¹⁶ presumably due to the 2-HP zwitterion resonance structure,



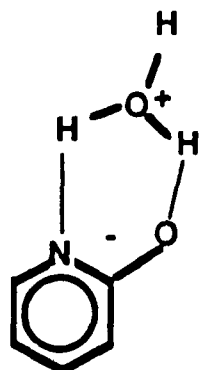
(2)

2-HP Zwitterion

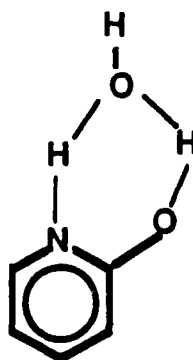
which would be stabilized by polar molecules. No reasonable zwitterion structure can be drawn for 2-HP lactim. In protic solvents, the rate of tautomerization is increased due to the stabilization of the transition state of the proton transfer reaction. Tautomerization of 2-HP in water may proceed *via* a cyclic ionic intermediate in which 2-HP transfers a proton to the solvent which then transfers a proton back to the

solute, or it may proceed via a concerted mechanism in which there is a neutral cyclic intermediate.

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ionic intermediate



neutral intermediate

(3)

The ionic intermediate would consist of a hydronium ion in which the three O-H bond lengths are equal and a 2-HP anion. The neutral intermediate is the transition species in a concerted double proton transfer. In this intermediate, the two O-H bonds of the water involved in reaction are equal in length but are longer than the other solvent O-H bond length. Electronic structure calculations^{13,18} have shown that the real intermediate is a mixture of the two structures in scheme (3). Both intermediates shown above are thought to cause a considerable reduction in the ground state (S_0) potential energy barrier for proton transfer (8,000 cm^{-1} for monosolvate¹³ and 3,000 cm^{-1} for disolvate¹⁸). This barrier reduction is believed to account for the increased proton transfer rate found in such systems.

Protic solvents are believed to affect the amount of ionic character in the transition state according to their proton affinities. Ammonia, for example, has a higher proton affinity than water³¹ and should form a transition state with more ionic character than that formed with water. In fact, in clusters with many ammonia molecules, the ionic intermediate may become a stable species, which would amount to an intermolecular proton transfer from 2-HP to the ammonia solvent. In this case, absorption and emission spectra of the solvates would be characteristic of the 2-HP anion. Solution phase studies³² have shown that the 2-HP anion is indeed formed under basic conditions. Absorption and emission spectra shows absorption and emission maxima at 34,400 cm^{-1} and 28,600 cm^{-1} , respectively. In the excited electronic state, the formation of the 2-HP anion in ammonia clusters should be even more facile,

due to the increased acidities of the O-H and N-H group relative to their acidities in S_0 .³³ It is therefore reasonable to expect that in some 2-HP/ammonia clusters, excitation of the neutral cluster may yield emission characteristic of the 2-HP anion.

Similar intermolecular proton transfer reactions have been investigated in the excited state of naphthol/ammonia clusters.³⁴⁻³⁶ These studies have found that excited anion formation occurs in clusters involving four or more ammonia molecules. Several spectroscopic features characterize excited state proton transfer events. These are large shifts in the excitation spectra upon solvation, broadening in the excitation spectra and broad Stoke's shifted emission characteristic of the anion.

In this paper, we report spectroscopic studies of supersonic jet cooled 2-HP and its water and ammonia clusters. Both the lactam and the lactim tautomers and their ammonia and water clusters are identified. Cluster structures and binding energies are deduced from these spectra and the possibility of both intramolecular and intermolecular proton transfer is addressed based on these findings. Ground state geometries and binding energies for various clusters are estimated using atom-atom potential calculations. Results of this work suggest that excited state intermolecular proton transfer occurs in 2-HP ammonia clusters. The possibility of excited state intramolecular proton transfer in 2-HP/water clusters is also addressed.

II. Experimental Procedures

The experimental apparatus used in this study has been described in detail in other reports³⁷ and will only be discussed briefly here. Supersonic expansions are created in a vacuum chamber using a pulsed nozzle with a 0.5 mm diameter orifice, or a cw nozzle with a 0.1 mm diameter orifice. Samples of 2-HP are placed in the head of the nozzle, enabling the samples to be heated to 110 °C in the pulsed nozzle, and 150 °C in the cw nozzle. The expansion gas is typically helium and the backing pressure is typically about 4 atm. Clusters are prepared by mixing solvent vapor with the expansion gas (about 2 % solvent in He). In order to access higher order clusters with the pulsed nozzle, the timing of the nozzle is set so that the laser interrogates the expansion late in the pulse. With the cw nozzle, higher order clusters can be made by increasing the concentration of the solvent in the expansion gas (ie. 10% ammonia in He).

The experimental procedure consists of crossing the molecular beam with a pulsed Nd/YAG pumped dye laser beam and detecting the absorption or emission of light. The time-of-flight mass spectroscopy (TOFMS) experiment is a two photon technique in which the first photon (pump) excites the molecule of interest and the second photon (probe) ionizes it from the excited state. Ions with the mass-to-charge ratio of interest are then monitored at the end of a 1.5 m flight tube perpendicular to the molecular and laser beams. The energy of the pump photon is scanned, and when it comes into resonance with a vibronic transition of a particular molecule or cluster the signal intensity in the appropriate mass channel increases. Thus, a trace of the ion signal as a function of the laser energy gives an excitation spectrum. In fluorescence excitation (FE) experiments, a single laser is used to excite the molecules in the expansion and all of the emission is monitored. When the laser is tuned to a vibronic transition, the total emission increases, and thus, FE spectra are plots of total emission intensity versus excitation energy. Like the TOFMS experiment, this experiment also yields an excitation spectrum, but without mass selection. Dispersed emission (DE) spectra are obtained by exciting a transition and passing the emitted light through a monochromator. A DE spectrum thus gives the intensity of the emitted light as a function of its energy.

III. Calculations

Geometries of 2-HP/water clusters are important with respect to intramolecular proton transfer, in that some structures should more easily lend themselves to this reaction. In order to estimate these structures, we have utilized empirical atom-atom potential energy calculations developed by Scheraga *et al.*³⁸ These calculations are based on the assumption that the interaction energy between two molecules is the sum of the interaction energies between the atoms on one molecule and the atoms on the other. A simple, empirical potential energy function is assumed to describe this atom-atom interaction. The potential consists of a Lennard-Jones component,

$$U_{ij} = A_{ij}/r_{ij}^6 - B_{ij}/r_{ij}^{12} \quad , \quad (4)$$

a hydrogen bonding component

$$U'_{ij} = C_{ij}/r_{ij}^{12} - D_{ij}/r_{ij}^{10} \quad , \quad (5)$$

and a partial charge component

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$$U^*_{ij} = 167.5 \, q_i q_j / r_{ij} \quad (6)$$

In equation (6), the number 167.5 is a conversion factor from atomic unit charges and Å to kcal/mol and the q 's are partial charges generated from *ab initio* calculations.²⁶ Although the atom-atom potential shown in equations (4) - (6) is only partially adequate for the description of strong hydrogen bonds, it nonetheless gives a qualitative understanding of the energy and structure of clusters. Partial charges generated by CNDO^{3,27,38} calculations are also tested and found to give the same qualitative results. Calculated geometries and energies of 2-HP monosolvate water clusters are compared with results obtained from *ab initio* calculations^{13,18} (Table I) and the two results are found to be in qualitative agreement.

Minima in the potential energy surface discussed above are found using the conjugate gradient and golden section searching methods.³⁹ In these calculations, starting cluster configurations are randomly generated, and translational and rotational degrees of freedom of the molecules are allowed to vary so as to minimize the cluster's energy. This method produces local as well as global potential energy minima. In a supersonic expansion it is often possible to form energetically unstable cluster species corresponding to the local minima. In order to determine the probabilities of forming local and global minima, a large number of starting configurations are randomly generate. From these configurations, the minimization routine locates the nearest local minimum energy structure. The results of many calculations give approximate statistical probabilities of forming the various possible cluster geometries.

IV. Results

Lactim

The TOFMS spectra of the $\pi^* \leftarrow \pi$ transition for 2-HP lactim and the d_1 deuterated lactim are shown in Fig.1, together with the FE spectrum of the nondeuterated lactim. Like earlier TOFMS work,² the origin in the d_0 spectrum is chosen as the most intense feature in the spectrum at an energy of 36,136 cm^{-1} . Upon deuteration of the hydroxyl group, the origin shifts to 36,140 cm^{-1} as is shown in the bottom spectrum of Fig. 1. These spectra, together with the FE spectrum, demonstrate the anomalous peak spacing and intensities which are indicative of the mixing of $n\pi^*$

and $\pi\pi^*$ electronic states.⁴⁰ One would expect this mixing to occur in the 2-HP lactim as the $n\pi^*$ electronic state is about 2500 cm^{-1} lower in energy than the $\pi\pi^*$ electronic state. Unsuccessful attempts were made to locate the origin of the $\pi^* \leftarrow n$ transition in the supersonic jet cooled sample. This suggests that the $\pi^* \leftarrow n$ transition is much weaker than the $\pi^* \leftarrow \pi$ transition as is usually the case.⁴⁰ The intensities and spacings of the peaks in these spectra are collected in Table I and their relevance to electronic state mixing will be discussed later. The DE spectrum which results when the origin is excited is shown in Fig. 2 and its peak spacings are also in Table II.

Lactam

TOFMS spectra of the $\pi \leftarrow \pi^*$ transition for 2-HP lactam are displayed in Fig. 3 and the peak spacing are collected in Table I. The top of this figure shows the spectrum of the d_0 lactam taken at two different backing pressures, demonstrating the pressure dependence of the two intense peaks (A and B) in the spectra. Peak A shows a decrease in relative intensity with increasing pressure but can never be completely diminished by increasing the backing pressure. Several other weak peaks are identified as having the same pressure dependence as A and B and these are listed in Table I beneath the peak (A or B) whose pressure dependence they match. In the d_1 spectrum at the bottom of the figure, peaks A and B are shifted 36 cm^{-1} to the blue but have the same relative spacing as in the d_0 spectra. The DE spectra which result when peaks A or B are selectively excited are identical as is shown in Fig. 4. Table II contains the peak spacing of these DE spectra. Peaks A and B are identified as origins with energies of $29,832\text{ cm}^{-1}$ and $29,935\text{ cm}^{-1}$, respectively. This is consistent with the value of the origin ($29,630\text{ cm}^{-1}$) found in solution phase studies.³ As will be shown below, these spectra suggest the presence two ground state conformations for the lactam.

Clusters

Figures 5 - 7 present TOFMS and DE spectra for various ammonia and water clusters of 2-HP. The TOFMS cluster spectra of the lactim are displayed in Fig. 5, with the monosolvate and disolvate water clusters at the top of the figure and the ammonia monosolvate spectrum at the bottom. No sharp excitation spectrum for the ammonia disolvate could be found. Emission from the lactim clusters is very weak and

DE spectra are not reported here. TOFMS spectra for mono and disolvate ammonia and water clusters of the lactam are shown in Figs. 6. All of these spectra show sharp, well resolved origins. The excitation spectra of the disolvate ammonia cluster shows a broad background which is similar to that seen in reactive ammonia clusters of 1-naphthol.³⁴⁻³⁶ Sharp excitation spectra (either TOFMS or FE) could not be observed in higher order lactim or lactam/ammonia clusters.

The DE spectra of the lactam clusters in Fig. 7 are obtained by exciting the origins found in the TOFMS spectra. Emission peaks in the DE spectra are sharp and not significantly shifted from the excitation energy. The same well-resolved emission lines are observed, even if the region of broad absorption of the lactam(NH₃)₂ is excited. Table III collects the peak positions of the TOFMS and DE spectra of 2-HP clusters while Table I lists the solvent shifts of the origins of the cluster TOFMS spectra relative to the bare molecule origin (peak B in Fig. 3).

The possibility of intermolecular proton transfer can be investigated in higher order 2-HP/ammonia clusters. As mentioned above, no sharp excitation features could be found for the lactim/ ammonia clusters with two or more ammonia molecules, or for the lactam clusters with three or more ammonia molecules. For the latter clusters, broad excitation spectra are observed. The stoichiometry of these larger clusters is difficult to determine, even in TOFMS experiments, due to photofragmentation and low ionization potentials. These clusters always yield broad emission with a maximum at 28,600 cm⁻¹, regardless of whether excitation occurs in the lactim or lactam region. The DE spectrum in Fig. 8 shows the emission generated by excitation of higher order lactam/ammonia clusters.

Clusters of the lactam which are formed with deuterated water and ammonia seeded into the expansion gas yield spectra which are suggestive of hydrogen bonding in 2-HP ammonia and water clusters. Rapid exchange of the deuteria with the 2-HP lead to the formation of clusters with varying degrees of deuteration. Figure 9 displays a mass spectrum showing the various deuterated water clusters of the lactam, while Figs. 10 and 11 show TOFMS spectra of deuterated lactam/water and lactam/ammonia monosolvate clusters. The spectral shifts of the origins of these cluster transitions are listed in Table IV. These results, as they relate to cluster structure, will be discussed below.

The results of atom-atom potential energy calculations provide approximate structures and estimates of the binding energy of water clusters of 2-HP. The most probable cluster structures which arise from these calculations are cyclic (such as that pictured in equation (3) for the water monosolvate) and have two hydrogen bonds. Table I lists estimates of the binding energies of these cyclic structures determined from our calculations and compares them to the *ab initio* results¹³ for the water monosolvates.

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V. Discussion

A. Isolated Molecules

2-HP lactim

As was mentioned above, mixing of the $\pi\pi^*$ of $n\pi^*$ electronic states in the 2-HP lactim is manifested in the excitation spectra shown in Fig. 1. The anomalously large number of transitions observed, as well as the irregularity of the peak spacings are similar to what is found in quinoline and isoquinoline systems for which $n\pi^*/\pi\pi^*$ mixing is well documented.⁴⁰ To emphasize the anomalous features in the spectra, one can compare the intense features in these spectra to the excitation spectrum of phenol,⁴¹ for which no low-lying $n\pi^*$ electronic state is expected. Only one intense peak is found within 500 cm^{-1} of the origin in the phenol spectrum, while for the 2-HP lactim several intense features, as well as many weak ones, are found within 500 cm^{-1} of the origin. This difference is explained as the result of mixing between the vibrational levels of the $\pi\pi^*$ and $n\pi^*$ states of the lactim, giving rise to new levels which do not have spacings characteristic of the $\pi\pi^*$ state. Since the $\pi^* \leftarrow n$ transition is much lower in energy than the $\pi^* \leftarrow \pi^*$ transition, a large number of levels from the $n\pi^*$ state can mix with the few $\pi\pi^*$ vibrational levels. It is thus expected that deuteration of the lactim would increase the density of vibrational levels at a given energy in the $n\pi^*$ electronic state by decreasing the vibrational frequencies. However, Fig. 1 shows that for the d_1 lactim, the effect of deuteration upon the TOFMS spectrum is slight.

The relative intensities of many of the common features in the TOFMS and the FE spectra of the 2-HP lactim are quite different (See Fig. 1). This difference in the intensity of the vibronic transitions is due to the methods of detection and is probably

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a reflection of either selective intersystem crossing or selective $n\pi^*/\pi\pi^*$ state mixing in vibrational levels of the $\pi\pi^*$ electronic state. The $\pi\pi^*$ and $n\pi^*$ vibrational states mix, allowing intersystem crossing to the triplet state. Triplet states typically have longer emission lifetimes than singlet states, and thus, yield weaker emission signals in jet experiments, in which light is collected perpendicular to the molecular beam. The ionization efficiency, on the other hand, should be similar for singlet and triplet states. It is therefore expected that the vibrational states of the $\pi\pi^*$ electronic state which intersystem cross before emission would yield lower FE signals than TOFMS signals. In effect, these spectra demonstrate the propensity of different vibrational levels to intersystem cross.

Unlike the TOFMS and FE spectra of 2-HP lactim, the DE spectrum of this molecule (Fig. 2) is very similar to the emission spectrum of phenol.⁴² This indicates that the emission originates from the excited state of the lactim and not the lactam. Furthermore, all of the vibronic transitions in the FE spectrum in Fig. 1 give DE spectra characteristic of the lactim; no emission from the lactam tautomer is seen. This suggests that excited state intramolecular proton transfer does not occur in the bare molecule. Similar behavior is found for 2-hydroxyquinoline,⁶ for which intramolecular proton transfer in the excited state of the bare molecule is not observed even with excess vibrational energy of greater than 2000 cm^{-1} . Thus, the DE spectrum in Fig. 2 is a signature of the lactim and is useful when discussing proton transfer in 2-HP.

2-HP lactam

Both the pressure dependence of the two strong features in the TOFMS of 2-HP lactam (peaks A and B in Fig. 3) and the similarity of the DE spectra which results when exciting A and B (Fig. 4. and Table II) indicate that two conformers of this molecule exist in the expansion. If peaks A and B were to arise from different vibrational levels, they would give rise to qualitatively different DE spectra. Peak A cannot be a vibrational hot band built on peak B because the DE spectrum which results upon excitation of this feature shows no emission at a higher energy than that of peak A. If A were a hot band and B were the true origin of the system, one would expect to

see emission at the energy of peak B when A is excited. This is not the case and it is concluded that there are two stable conformations of the lactam in the ground state.

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The two conformers which give rise to peaks A and B in the excitation spectra are likely to have nonplanar structures, as one cannot draw two reasonable planar conformers. Since early x-ray crystal studies⁴³ showed the lactam to be planar, this conclusion is surprising. The exact reason for this discrepancy is unclear, but the planar structure in the crystal may be a result of packing forces that are absent in the gas phase. Furthermore, a more recent x-ray crystal study⁴⁴ has suggested that the lactam may be slightly nonplanar. One might initially guess that the two nonplanar conformers result from a puckering of the ring at the nitrogen and an orientation of the amine hydrogen with respect to the ring. This would seem favorable as the nitrogen atom would have pyramidal bonding, allowing the lone pair to decouple from the π electron system. However, if the two conformers correspond to two orientations of the amine hydrogen, one might expect to see a change in the spacings of A and B upon deuteration. Figure 3 and Table II show that this is clearly not the case. Another possibility for nonplanar conformers would involve puckering the carbonyl group, also allowing the nitrogen to have pyramidal bonding. Furthermore, this structure would agree with more recent x-ray crystallographic studies⁴⁴, which suggest that the carbonyl group is nonplanar and that the nitrogen is planar, although again, crystal packing forces could determine the molecular structure. It is difficult to determine which of these ring puckering mechanisms gives rise to the two conformers in the jet. The correct structure may even result from a puckering at both the carbonyl and the nitrogen. In any event, the lactam is apparently nonplanar in the ground electronic state.

Inferences about the electronic structure of the lactam may be made based on the spectroscopic observation of two conformers in the jet. Since the relative intensity of peak B in Fig. 3 increases with increasing backing pressure (and thus, decreasing effective internal molecular temperature), this peak must arise from the more energetically stable configuration. The fact that A could not be cooled out completely, suggests that the two conformations are close in energy, a conclusion which is confirmed by the similarity of DE spectra arising from excitation at the energies of peaks A and B. Further, since A is shifted to the red of B by 103 cm^{-1} , the structure giving rise to B is roughly 103 cm^{-1} more stable in the excited state than the structure corresponding to A. As Table II shows, the excitation spectra of the two

structures are different, suggesting that the electronic structure and energy of these two species in their excited states are dissimilar. This is an indication that the molecule is even more nonplanar in the excited state than it is in the ground state. It is expected that the degree of planarity of the molecule is a reflection of the extent of mixing with the zwitterion structure (2). Since the ground state is more planar than the excited state, it mixes to a larger degree with the zwitterion structure. The extent of this zwitterion mixing will also be discussed below. 13

B. Clusters

Binding energies and structures for 2-HP clusters can be estimated from the spectra and calculations discussed above. The large solvent shifts (500 to 1000 cm^{-1}) shown in Table I are indicative of strong hydrogen bonding in the clusters. This is confirmed by the results of atom-atom potential calculations for 2-HP water clusters, listed in Table I, which show large binding energies for the doubly bonded cyclic clusters. Excited state binding energies for clusters may be determined from the ground state binding energies and the spectral shifts of the cluster origins. Table I also lists the excited state binding energies of 2-HP/water clusters determined in this way. The solvent shifts show that binding energies for water clusters of the lactim are smaller in the ground state than in the excited state while the reverse is true for the lactam. That the binding energy for lactam water clusters decreases upon excitation suggests the zwitterionic structure displayed in (2) contributes more to the ground state than to the excited $\pi\pi^*$ state. That is, polar solvents should stabilize the zwitterion resonance form and lower the energy of the cluster. This contribution of the zwitterionic form to S_0 and $S_1(\pi\pi^*)$ states is also consistent with the bare lactam spectra discussed above. The lactam is more nonplanar in the excited state and thus the excited state should contain less of a contribution from the planar, zwitterion resonance structure than the ground state. A red shift for lactim clusters (i.e., stabilization of the excited state clusters relative to the ground state clusters) is also consistent with data for phenol/water clusters.⁴⁵

Information about how intermolecular bonding shifts the excited electronic states in 2-HP clusters can also be experimentally determined from cluster spectra. For instance, the TOFMS spectra of the lactim monosolvates (Fig. 5) show evidence of $n\pi^*/\pi\pi^*$ electronic state mixing much as is seen in the bare molecule; many features

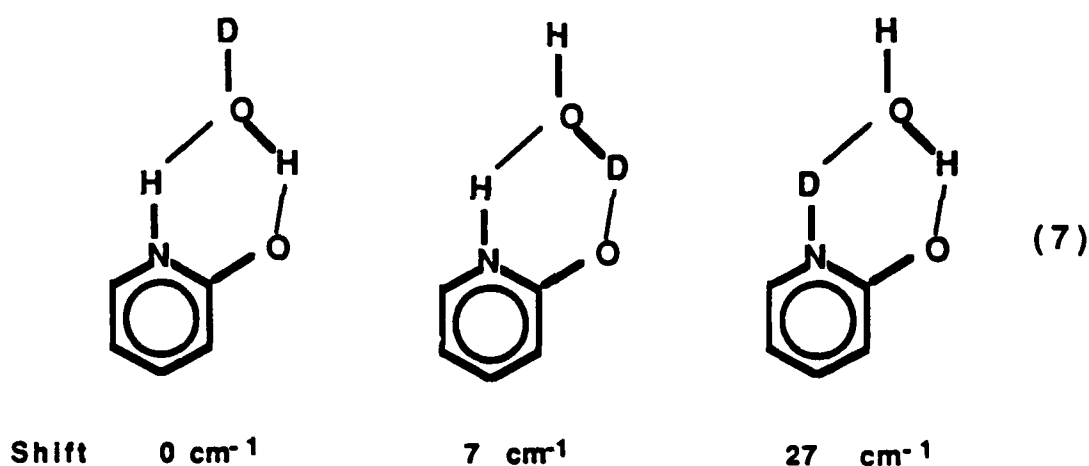
present in these spectra cannot be fit assuming reasonable vibrational levels for a $\pi\pi^*$ cluster state. The fact that this mixing exists in the monosolvates indicates that the $n\pi^*$ electronic state is still lower in energy than the $\pi\pi^*$ electronic state. On the other hand, the excitation spectrum of the disolvate water cluster of the lactim (Fig. 5) contains a number of evenly spaced peaks, 20 cm^{-1} apart. Because these peaks can be identified as vibrational levels of van der Waals (vdW) modes, the $n\pi^*/\pi\pi^*$ mixing would seem to have been removed. One can therefore assert that in the lactim(H_2O)₂ cluster a strong hydrogen bond exists between the solvent and the lactim nitrogen atom.

The $n\pi^*/\pi\pi^*$ state mixing found in both the bare lactim and the lactim clusters is unlike that found for isoquinoline (IQ), for which the $n\pi^*/\pi\pi^*$ mixing is removed in the monosolvate.⁴⁶ In bare IQ, the $n\pi^*$ electronic state is 1900 cm^{-1} lower in energy than the $\pi\pi^*$ state and the IQ excitation spectrum is similar to that of the 2-HP lactim. In monosolvate clusters of IQ with methanol and water, the solvent hydrogen bonds to the chromophore's nitrogen atom, dramatically raising the energy of the $n\pi^*$ state and thereby removing the mixing. Based on *ab initio* calculations and our atom-atom calculations, the monosolvate lactim clusters apparently involve a nominal hydrogen bond between the solvent and the lactim's nitrogen. However, this bond is apparently not strong enough to remove the $n\pi^*/\pi\pi^*$ mixing. Thus, the lactim 2-HP(NH_3)₁ and 2-HP(H_2O)₁ clusters are weakly hydrogen bonded and $n\pi^*/\pi\pi^*$ state mixing is still present.

Hydrogen bonding in lactam monosolvate and disolvate clusters with water and ammonia appears to be somewhat stronger than in the lactim clusters. As the lactam cluster spectra in Figure 6 and 7 show, the two origins observed in the bare molecule spectrum have been replaced by a single cluster origin in all cases. This may reflect strong hydrogen bonding in the lactam clusters, which could potentially stabilize of the zwitterion resonance structure and force the molecule to be more planar in the ground state.

From the excitation spectra (Figs. 10 and 11) of the various deuterated monosolvate lactam clusters, the type of intermolecular bonding can be inferred. As the mass spectrum in Fig. 9 shows, H/D exchange between the deuterated solvent and the solute occurs rapidly in the backing region of the pulsed nozzle. In the bare lactam, only the amine hydrogen is labile enough to exchange. In water monosolvate clusters, a total of three hydrogen atoms may be exchanged. All possible deuterated species are

seen in the mass spectrum. The excitation spectra show one origin for the undeuterated (d_0) and perdeuterated (d_3) monosolvates and three origins for the partially deuterated (d_1 and d_2) monosolvates. The three origins in the partially deuterated species can be understood in terms of their *ab initio* structures, shown in scheme (7).



Each cyclic structure has a unique site for H/D exchange and should therefore, give rise to a different origin. Exchange of a solvent hydrogen which is not involved in hydrogen bonding should lead to a negligible shift in the origin of the excitation spectrum relative to the d_0 monosolvate origin. On the other hand, exchange of a hydrogen which is involved in hydrogen bonding should lead to a significant shift relative to the d_0 spectrum. Finally, exchange of the hydrogen on the chromophore should lead to a shift relative to the undeuterated monosolvate, which is similar to the deuterium shift of the bare molecule (36 cm^{-1}). As anticipated, the three origins in Fig. 10 are shifted from the origin of the undeuterated monosolvate by 0, 7 and 29

cm^{-1} (Table IV), respectively. In a similar way, the shifts of the three origins of the d_2 spectrum may be assigned.

16

Four distinct hydrogens can undergo exchange in the $2\text{-HP}(\text{NH}_3)_1$ cluster but only three of them are unique if a hydrogen bond is formed involving only one of the ammonia's hydrogens. Thus, the partially deuterated species have spectra with three origins for d_1 and d_3 and four origins for d_2 (Fig. 11 and Table IV). This apparent hydrogen bonding in which the ammonia molecule is a hydrogen donor is interesting in light of studies of the microwave spectroscopy⁴⁷ of the ammonia dimer. These studies showed that no hydrogen bond is formed in the ammonia dimer and that the ammonia molecule is a poor hydrogen donor. It is unclear then, why ammonia should be a hydrogen donor in a hydrogen bond with the lactam. This may result from a partial negative charge on the lactam's oxygen due to mixing with the zwitterion structure. The partial charge may be compelling enough to form a hydrogen bond with the ammonia's hydrogen. It may be argued that in the lactam/ammonia monosolvate, one of the ammonia's hydrogens bonds to the π electronic system. Such a structure could give rise to the same number of origins seen in Fig. 11 and Table IV. However, that the deuteration shifts (Table IV) for ammonia clusters are similar to those for water clusters suggests that similar bonding exists for both solvents.

C. Proton Transfer

The DE spectrum shown in Figure 8 is suggestive of 2-HP anion formation in isolated lactam/ammonia clusters due to its similarity to solution phase emission spectra of the 2-HP anion, which like the spectrum in Fig. 8, also has a maximum at $28,600\text{ cm}^{-1}$. In addition, the spectroscopy of 2-HP/ammonia clusters is also similar to that of 1-naphthol/ammonia clusters, for which proton transfer has also been postulated.^{34,35} That is, the 2-HP lactam/ammonia disolvate has excitation spectra which contains broad features in addition to sharp features while the excitation spectra of higher order clusters show no sharp features. Similarly, for the lactim, no sharp features are seen for clusters with more than two ammonia molecules. Excitation of this broad background yields broad emission with a maximum at $28,600\text{ cm}^{-1}$, regardless of whether excitation occurs in the lactim region or in the lactam region. The exact stoichiometry of the clusters that give anion formation is unclear, but since normal emission is seen for monosolvates of the lactim and mono- and disolvates of the lactam, the anion emission must arise from lactim clusters with

more than one solvent and from lactam clusters with more than two solvents. Most likely, the anion is preferentially formed in the excited state because the excited state pK_a of 2-HP is smaller than its ground state pK_a .³³ However, the possibility exists that for larger clusters, the anion can be formed from the ground electronic state of 2-HP.

As discussed above, tautomerization in 2-HP is facilitated by solvation^{13,18} and may occur in isolated clusters. In the excited state, tautomerization from the lactim to the lactam should be even more facile, as the lactim's excited state is much higher in energy than that of the lactam. Table I shows energies of tautomerization in the ground and excited state as determined from calculations and spectral shifts. While the ground and excited electronic state tautomerization energies for the lactim $\rightarrow$ lactam reaction are qualitative, the general predicted trends are correct: tautomerization is much more favorable in the $\pi\pi^*$ electronic state than in the ground state. Moreover, the potential barrier to tautomerization is lowered by increasing the reaction exothermicity in the excited state and by stabilizing the cyclic transition state. Potential energy surface calculations (atom-atom, based on equations (4), (5) and (6) and *ab initio*) demonstrate that these solvents form the cyclic cluster geometries that can lead to tautomerization. This is confirmed by our experimental results which show strong hydrogen bonding in these clusters. The vibronic profile of the excitation spectra of the lactim(H₂O)₂ cluster (Fig. 5) is also indicative of excited state tautomerization, or at least significant geometry displacement upon excitation. Such a displacement is often an indication of excited state dynamics³⁰ as it reflects a dramatic change in the potential energy surface of the reaction coordinate. Tautomerization in the lactim(H₂O)₂ cluster has not been confirmed by DE spectroscopy due to weak emission intensity.

V I. Conclusions

Tautomerization and intermolecular proton transfer in 2-HP have been studied in a supersonic expansion using laser spectroscopic techniques. The $\pi^* \leftarrow \pi$ transition of the lactim has its origin at 36,136 cm⁻¹, while the $\pi^* \leftarrow \pi$ transition of the lactam has two origins at 29,832 cm⁻¹ and 29,935 cm⁻¹. Electronic state mixing is observed in the lactim and is removed in the disolvate water cluster. The two origins of the lactam suggest that this molecule is nonplanar. No evidence of excited state

tautomerization is seen in the bare molecule. Anion formation is likely in $2\text{-HP}\cdot(\text{NH}_3)_n$ clusters with $n \geq 3$ and may occur in *lactim* clusters with $n \geq 2$. Excited state tautomerization is likely in the disolvate water cluster of the *lactim*. 18

Acknowledgment

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Figure Captions

22

Figure 1: Excitation spectra of 2-HP lactim. The top and middle traces are the TOFMS and FE spectra of the d_0 lactim, while the bottom trace is a spectrum of the d_1 lactim. The intense feature at $36,136\text{ cm}^{-1}$ is assigned as the origin. All spectra show several intense features within 500 cm^{-1} of the origin and a large number of weaker features. A dramatic difference in the relative intensities of some of the peaks in the TOFMS and FE spectra of the d_0 compound is observed. The peak spacings of the d_0 TOFMS spectrum and d_1 TOFMS spectrum are similar. See Table II.

Figure 2: The DE spectrum of 2-HP lactim obtained when exciting at the energy of the origin ($36,136\text{ cm}^{-1}$) of the excitation spectrum. No emission is observed further to the red, which would be characteristic of lactam emission. See Table II.

Figure 3: TOFMS spectra of 2-HP lactam. The top two spectra are of the d_0 lactam at different backing pressures. The relative intensities of peaks A ($29,832\text{ cm}^{-1}$) and B ($29,935\text{ cm}^{-1}$) change with backing pressure. The weak features in the spectra show a pressure sensitivity similar to A or B and are thereby associated with these origins (see Table II). In the spectrum of the d_1 lactam at the bottom of the figure, peaks A and B are shifted by 36 cm^{-1} to the blue relative to the d_0 origins.

Figure 4: DE Spectra of the lactam obtained exciting at the energy of peaks A (top) and B (bottom). See Fig. 3. The spectra show identical peak spacings (see Table II). These spectra show that peak A in Fig. 3 is not a hot band built on peak B.

Figure 5: The TOFMS spectra of various water and ammonia clusters of the lactim. The monosolvate spectra show irregular spacings characteristic of $n\pi^*/\pi\pi^*$ electronic state mixing, while the water disolvate spectrum shows harmonic progressions with 20 cm^{-1} spacings, indicating the removal of $n\pi^*/\pi\pi^*$ mixing. No sharp TOFMS spectra of the ammonia disolvate could be found. The large amount of vdW vibrational activity in the water disolvate is suggestive of excited state intramolecular proton transfer. See Table III for peak spacings and Table I for solvent shifts.

Figure 6: The TOFMS spectra of various water and ammonia clusters of the lactam. For the mono- and disolvate water clusters (top two spectra) and the ammonia monosolvate cluster (second from bottom), sharp vdW features are seen. For the ammonia disolvate (bottom) an additional broad excitation is present. See Table III for peak spacings and Table I for solvent shifts.

Figure 7: The DE spectra of various water and ammonia clusters of the lactam which result when the origins of the TOFMS spectra (Fig. 6) are pumped. All spectra are similar to the DE of the bare molecule, with the addition of peaks due to excitation of vdW vibrational modes. For the ammonia disolvate cluster, similar spectra with sharp, unshifted emission results, regardless of where the pump laser is tuned in the TOFMS spectrum (Fig. 6).

Figure 8: The DE spectrum of higher order lactam(NH₃)_n clusters ($n \geq 3$) which results from excitation at 30,888 cm⁻¹. This spectrum is obtained using a cw nozzle with an 10% ammonia/He carrier gas mixture. The broad red shifted emission is characteristic of 2-HP anion emission. Similar emission is also observed upon excitation of higher order ammonia clusters of the lactim.

Figure 9: The time-of-flight mass spectrum showing 2-HP(H₂O)_{0,1,2}, which results upon addition of D₂O to the carrier gas (He). The spectrum shows that rapid H/D exchange occurs in the stagnation chamber of the nozzle yielding all possible deuterated clusters. This mass spectrum is obtained with the laser tuned near the disolvate origin. Excitation spectra obtained when the monosolvates channels are monitored are shown in Fig. 10.

Figure 10: The TOFMS spectra of the various d_n lactam(H₂O)₁ clusters of Fig. 9. The arrows indicate origins (see equation 7) of the various possible d_n configurations. The spectral shifts are shown in Table IV and discussed in the text. These spectra suggest that hydrogen bonding is observed in the lactam(H₂O)₁ cluster.

Figure 11: The TOFMS spectra of the various d_n lactam(NH₃)₁ clusters similar to those displayed in Fig. 10 for the d_n lactam(H₂O)₁ clusters. The arrows indicate the origins. The spectral shifts are shown in Table IV and discussed in the text. These spectra suggest that hydrogen bonding is observed in the lactam(NH₃)₁ cluster.

2-HP Lactim

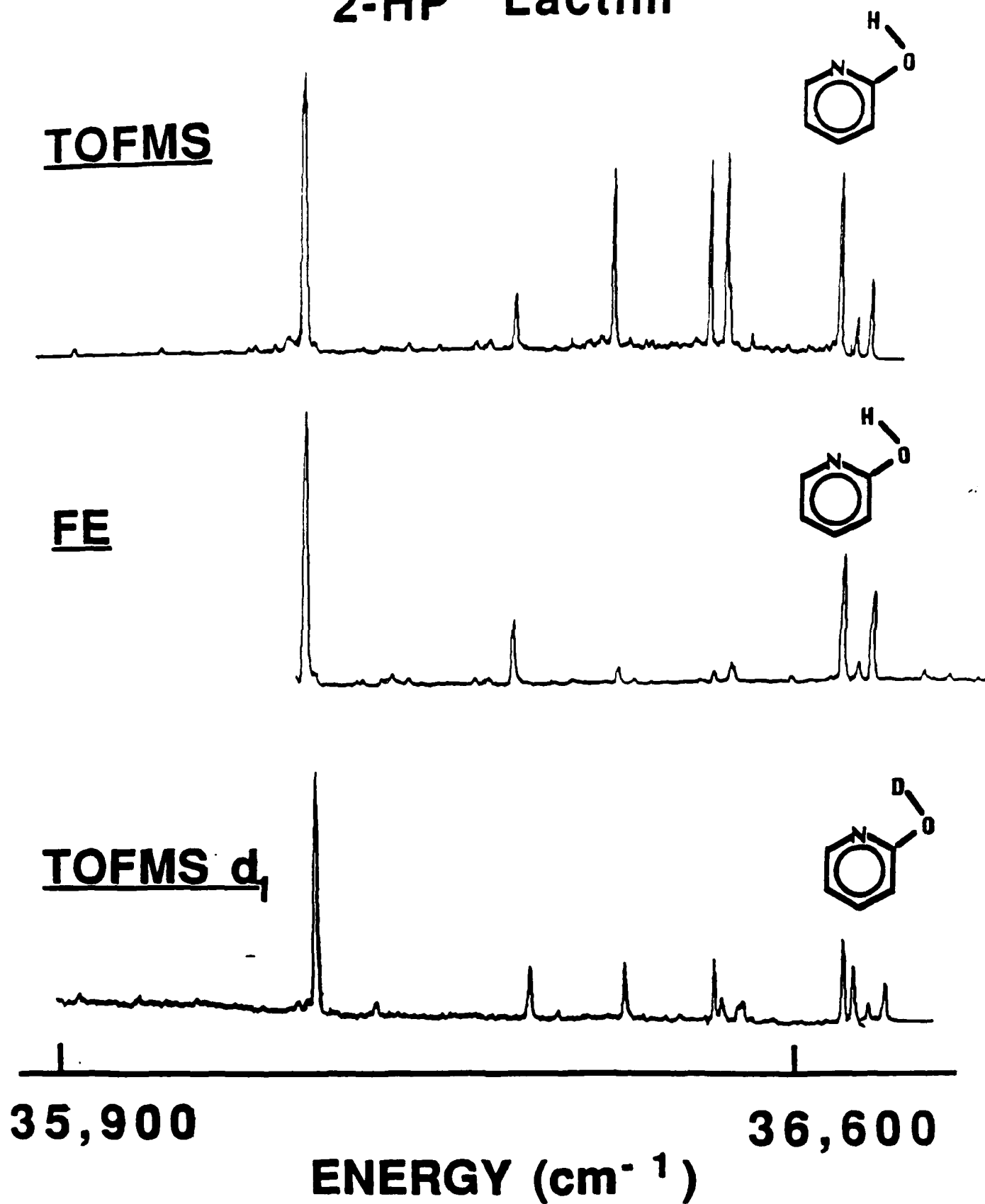
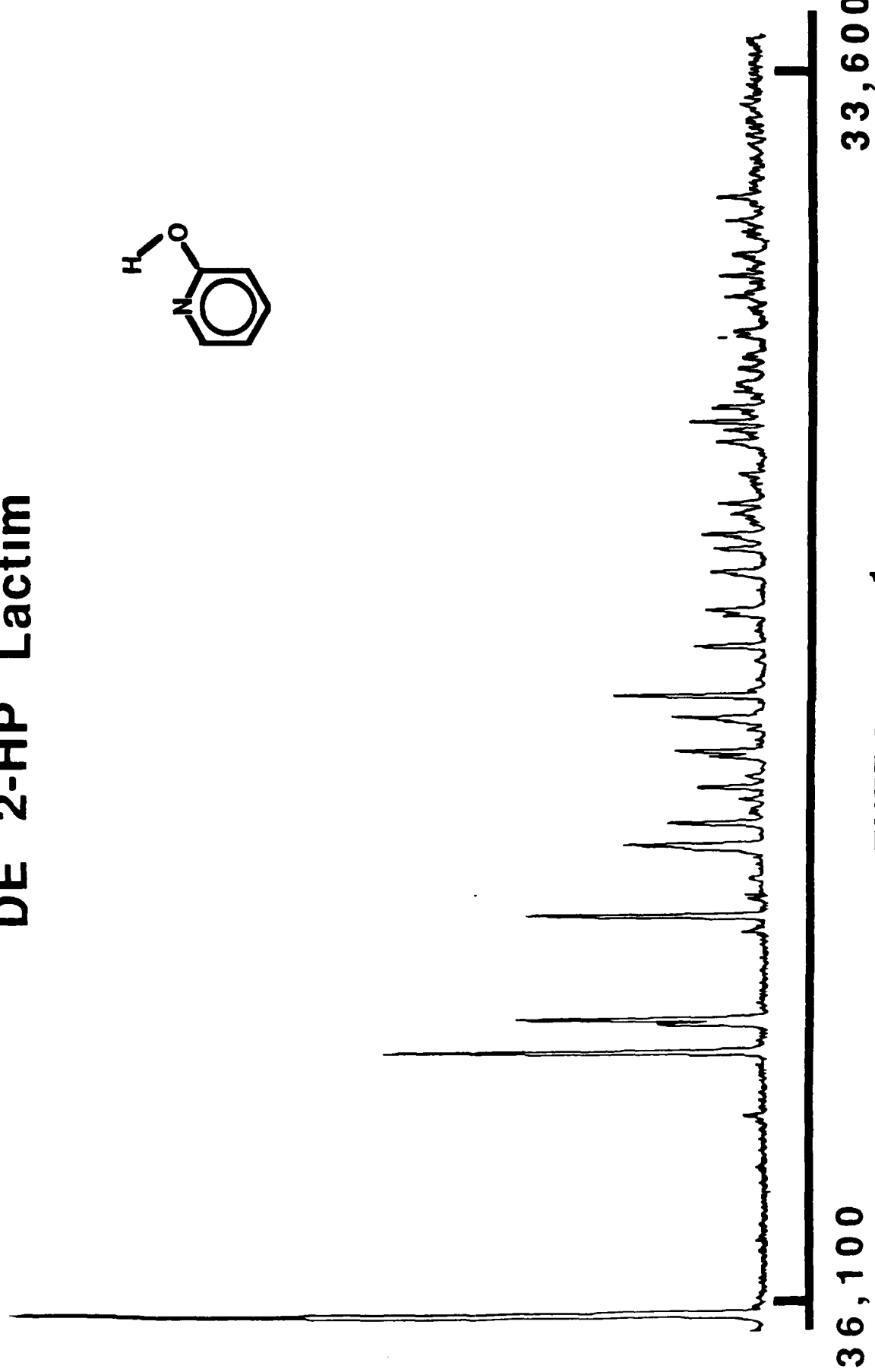
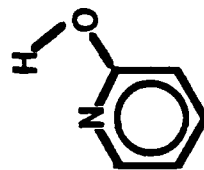


Figure 1

DE 2-HP Lactim



ENERGY (cm^{-1})

Figure 2

TOFMS of 2-HP Lactam

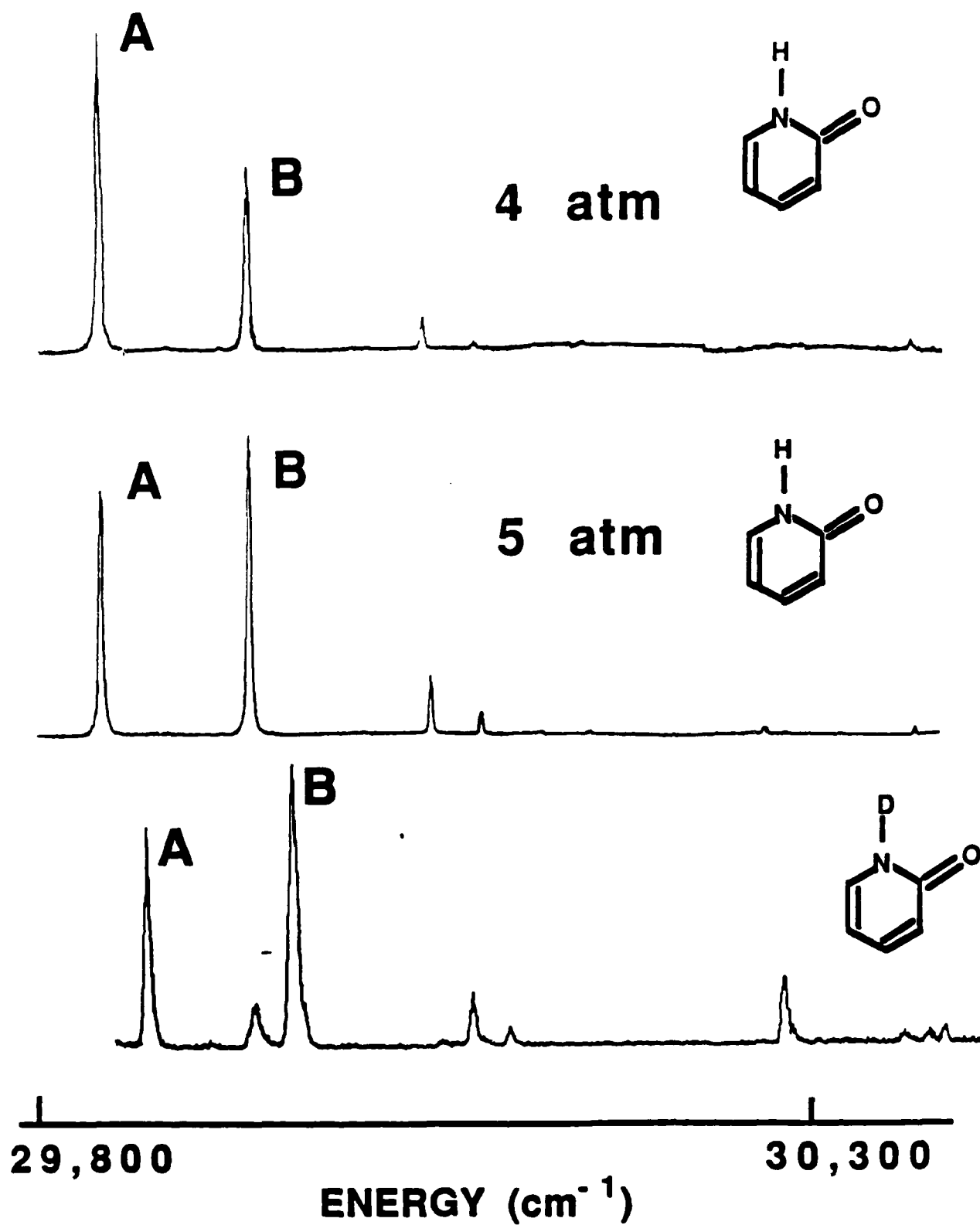


Figure 3

DE 2-HP Lactam

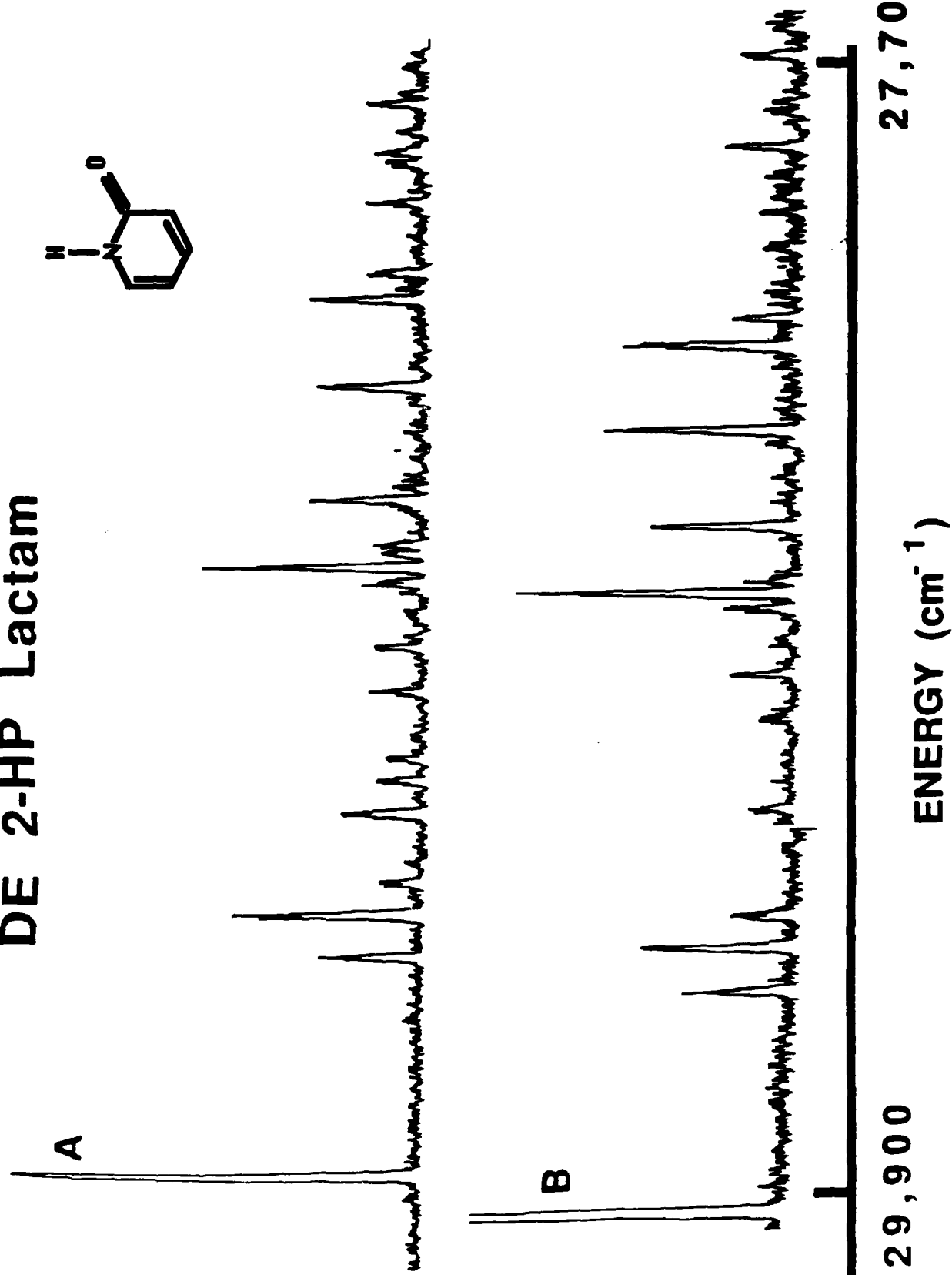
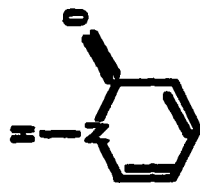


Figure 4

TOFMS of 2-HP Lactim Clusters

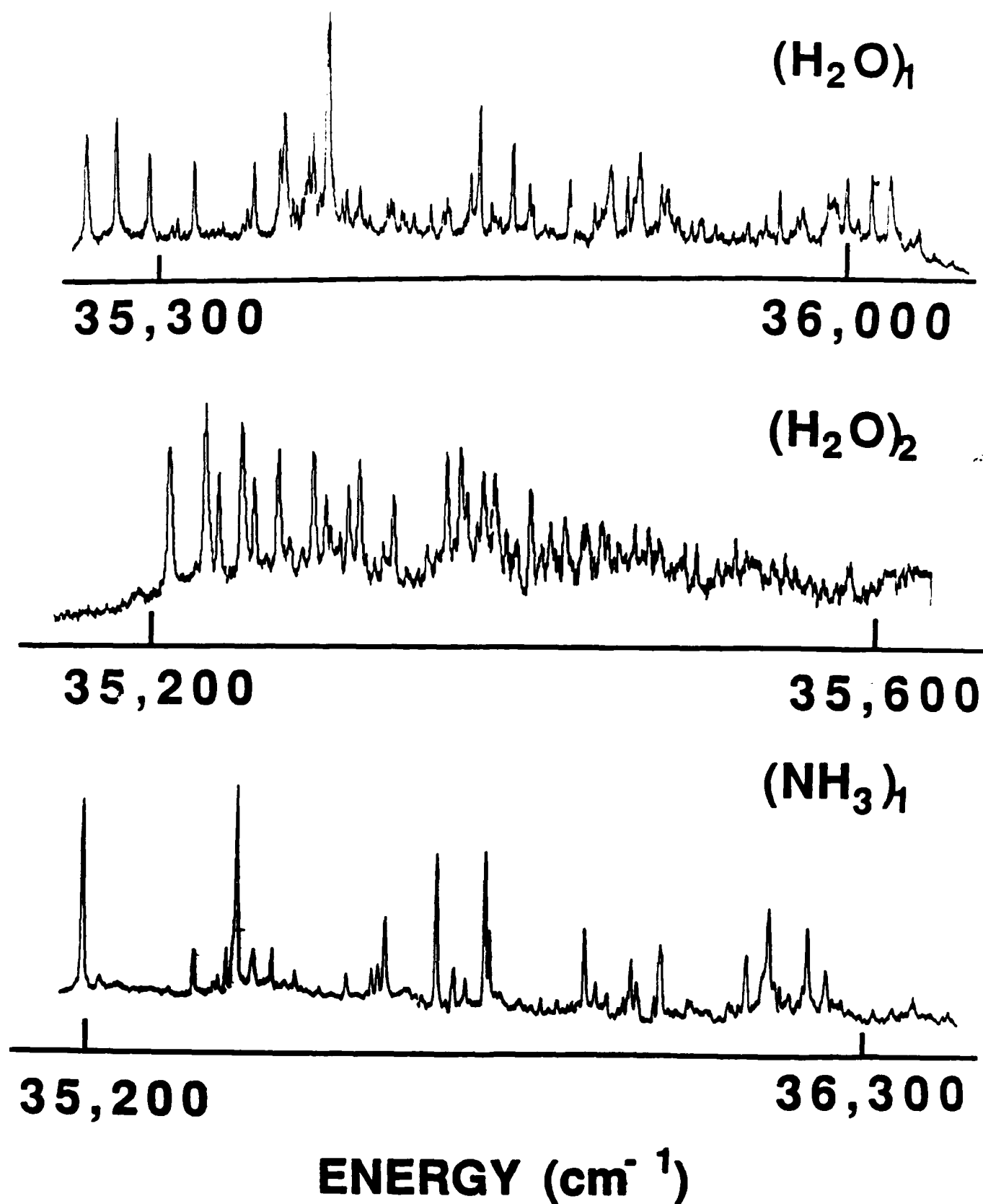


Figure 5

TOFMS of 2-HP Lactam Clusters

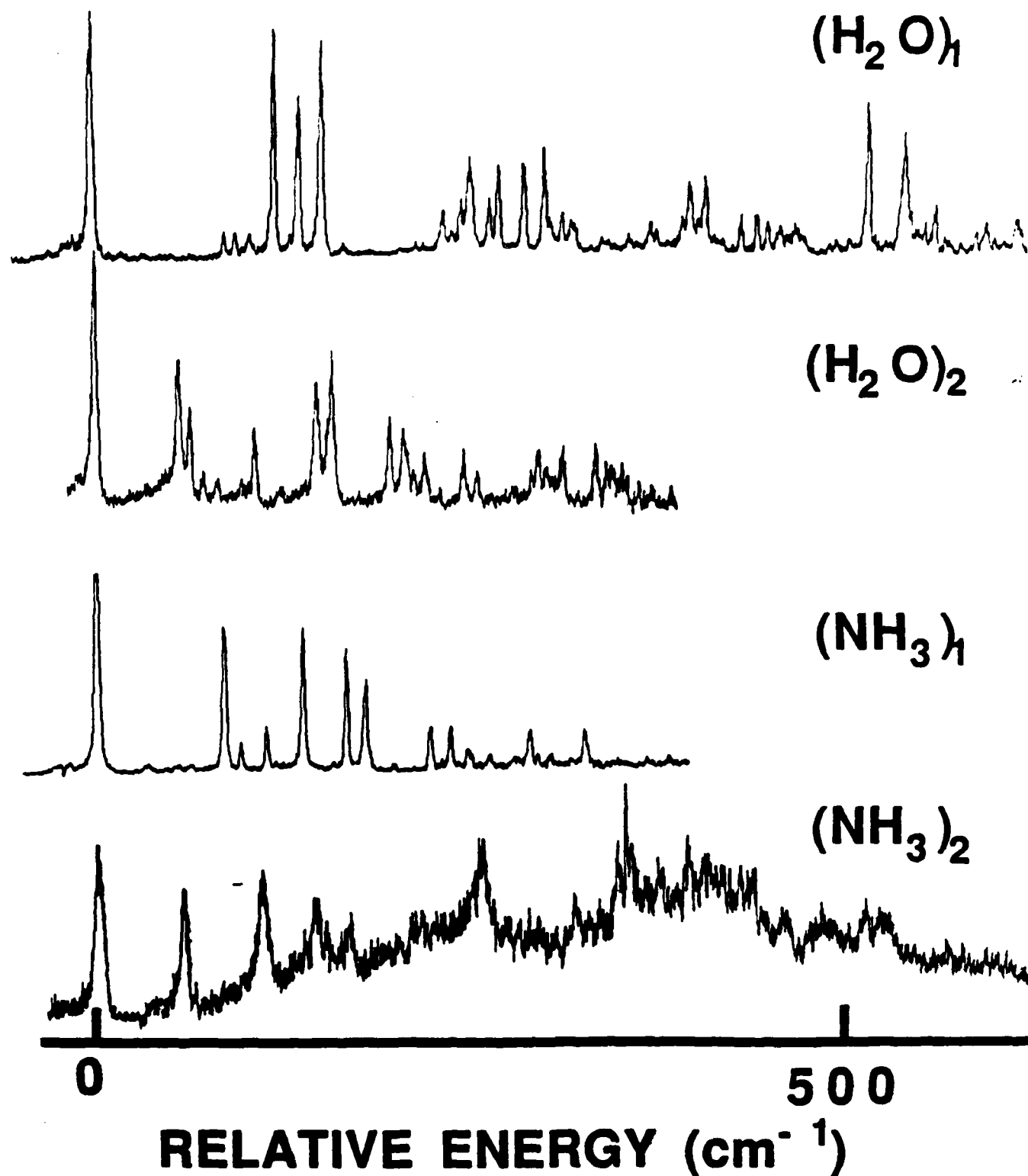


Figure 6

DE of 2-HP Lactam Clusters

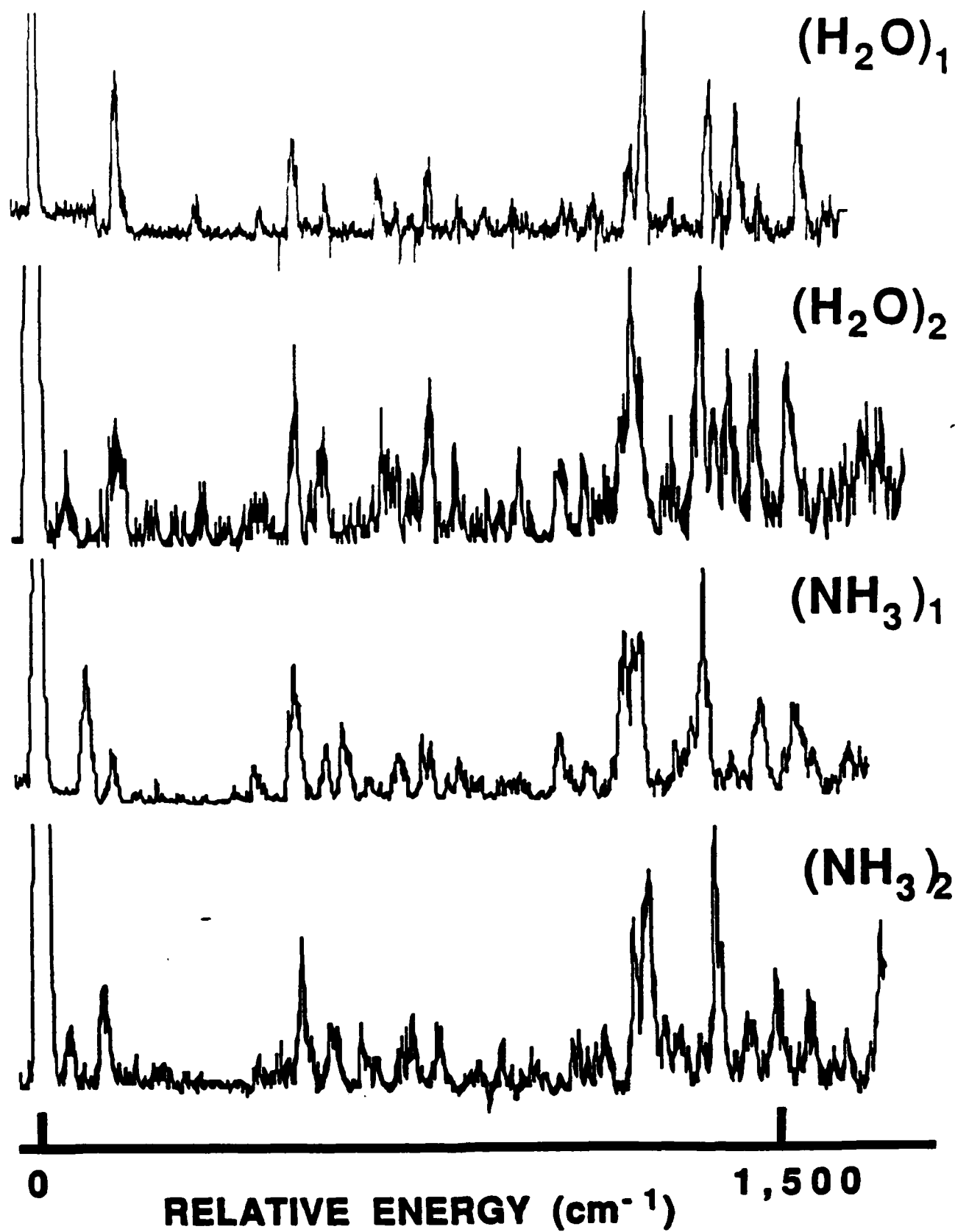


Figure 7

DE of 2-HP(NH₃)_n

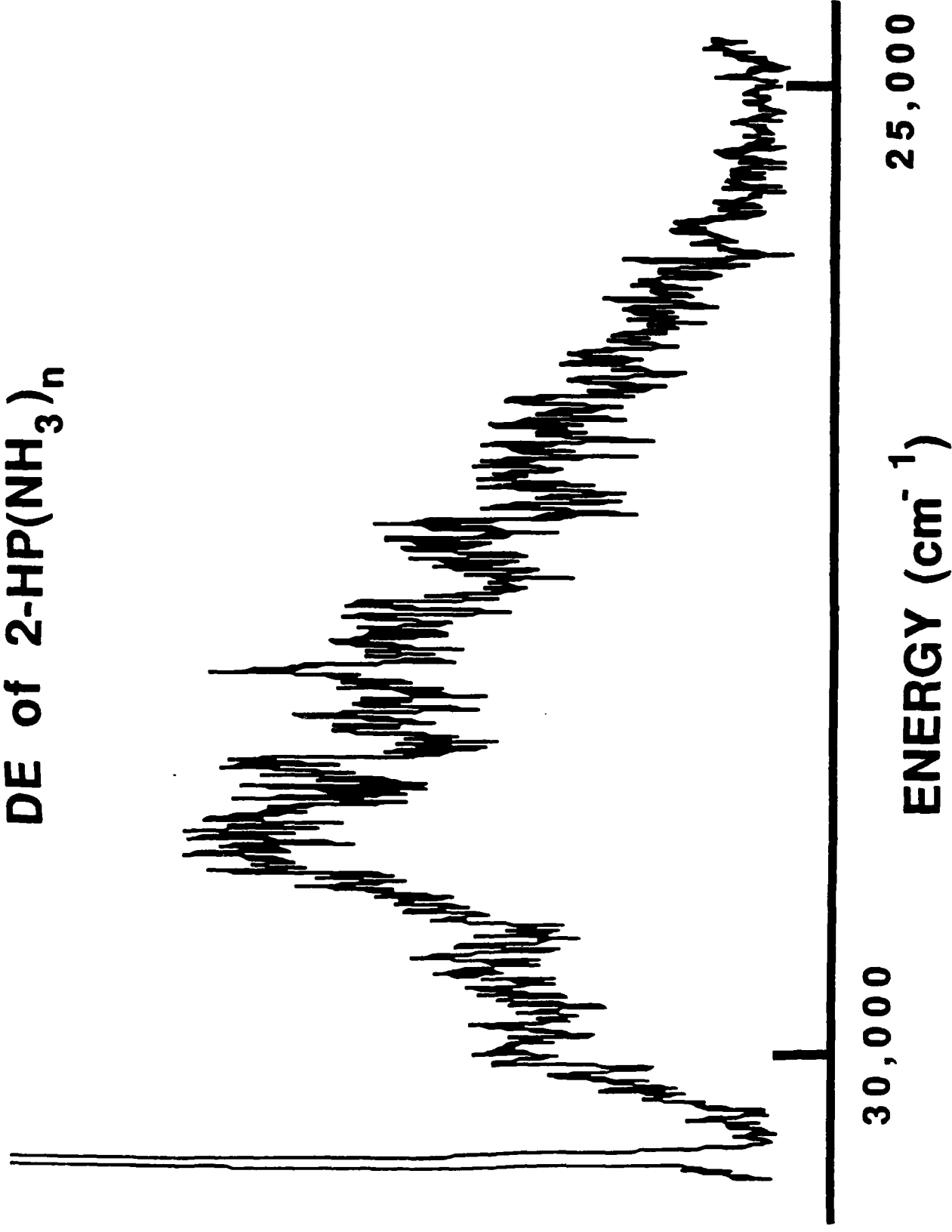


Figure 8

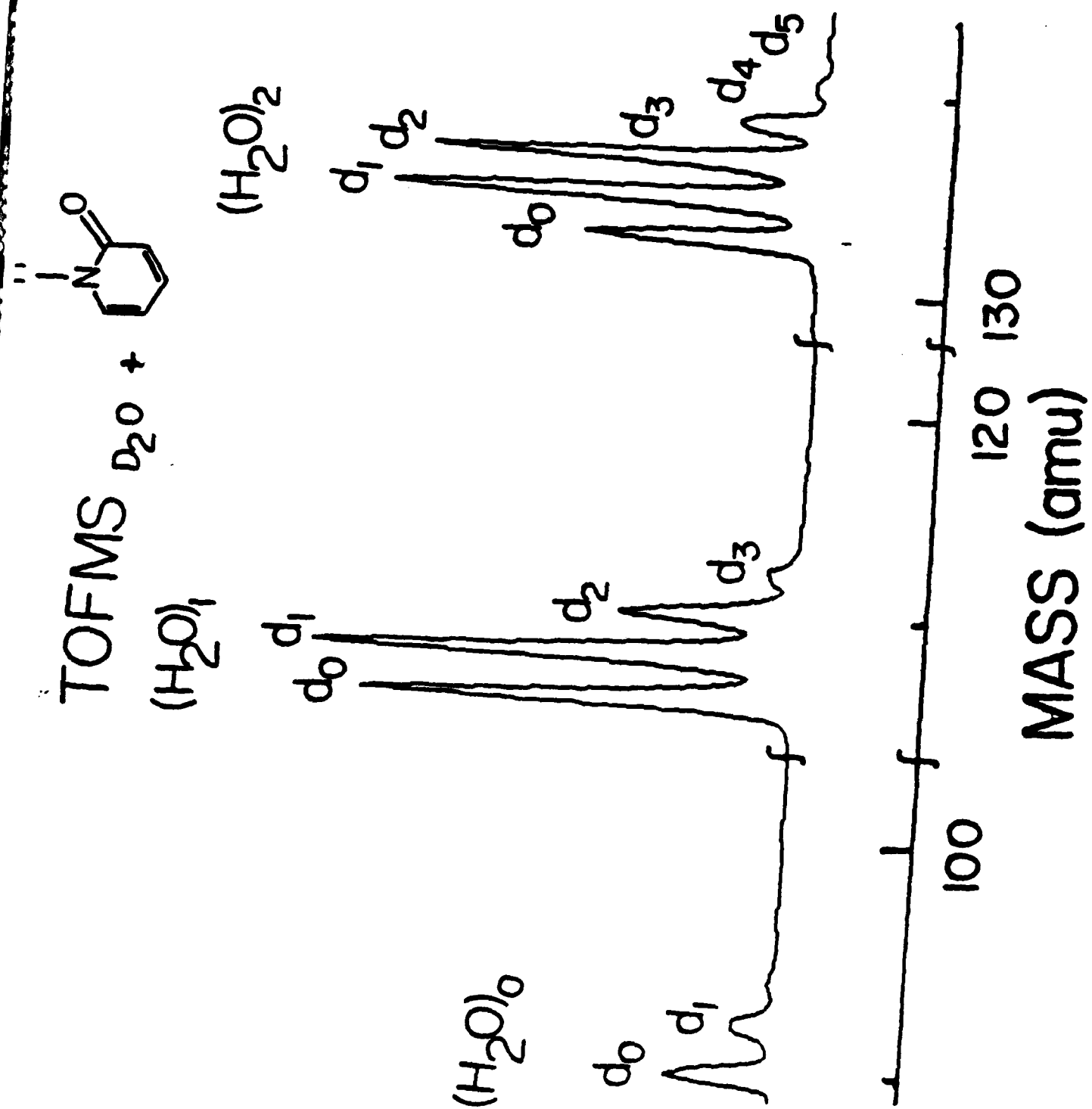


Figure 9

TOFMS of 2-HP Lactam/ H_2O d_n

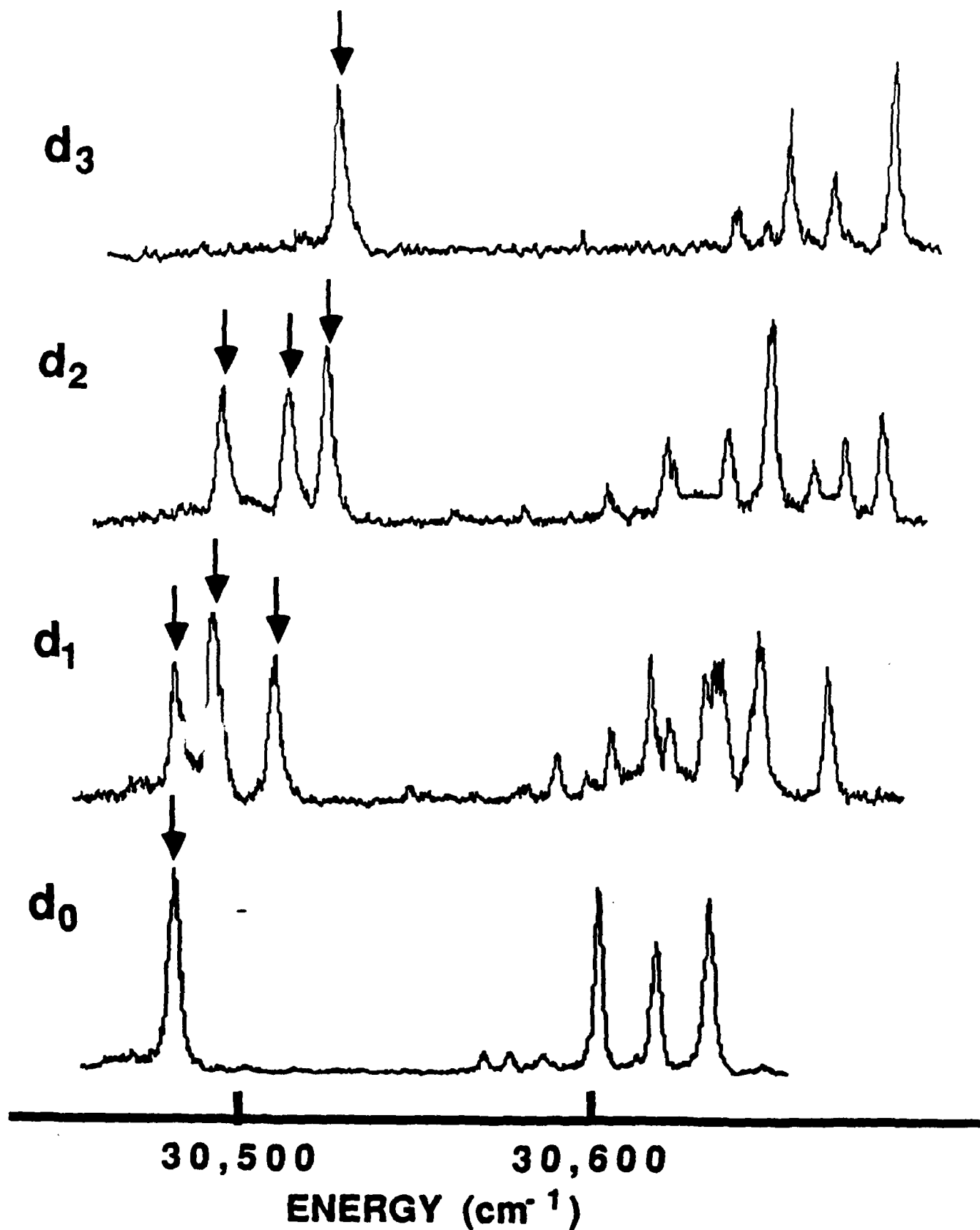


Figure 10

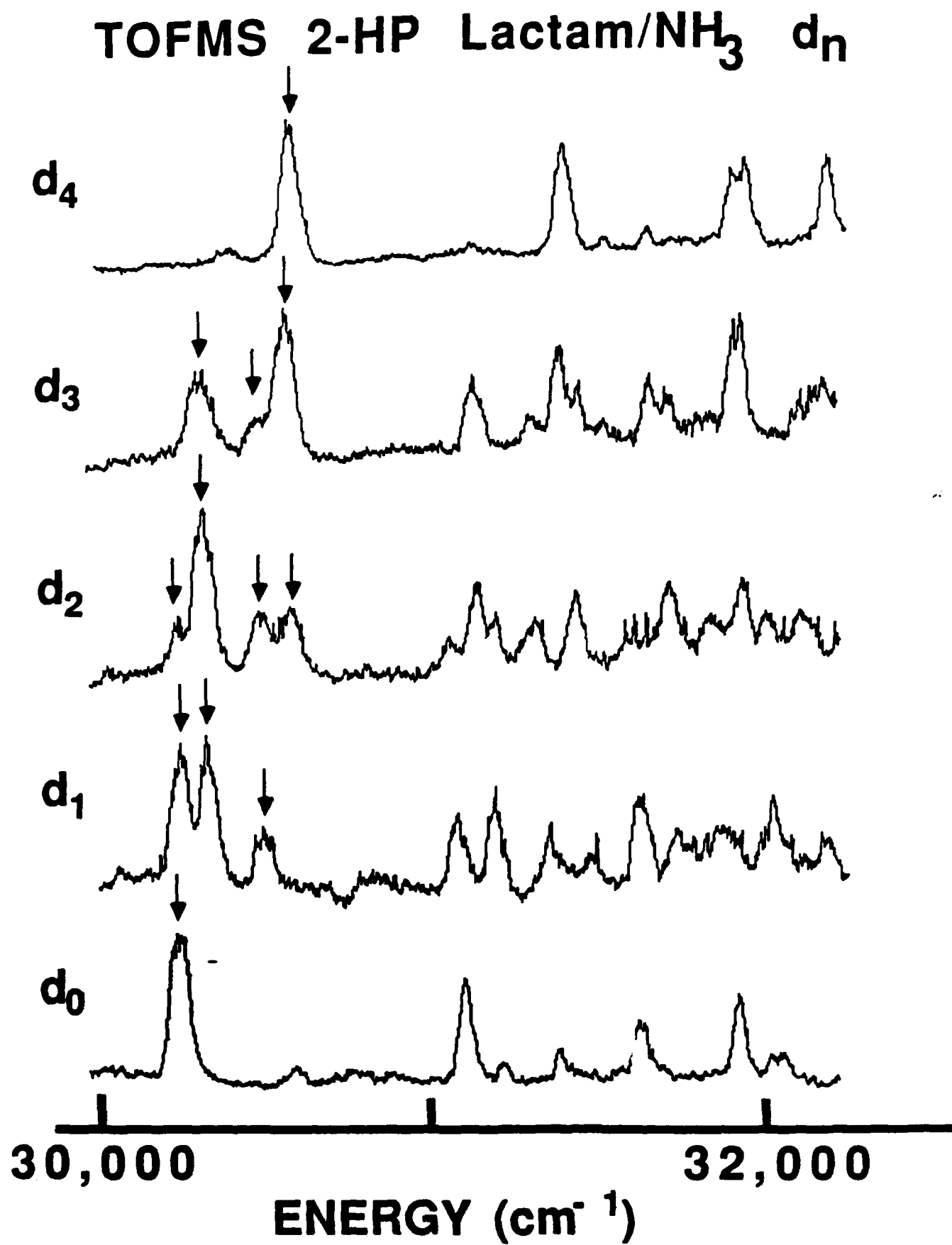


Figure 11

Table I

**Measured Spectroscopic and Thermodynamic Parameters for
Tautomerization of 2-HP in Ground and $\pi\pi^*$ States**

(All values in cm^{-1})

Cluster Stoichiometry	BE(S_0) ^a	Solvent Shift	BE($\pi\pi^*$)	Energy of Tautomerization Lactim $\rightarrow$ Lactam	
				$\Delta E(S_0)$	$\Delta E(\pi\pi^*)$
Bare				150 ^b	-6051
Lactim(H ₂ O) ₁	2418 (2900) ^c	-668	3086		
Lactam(H ₂ O) ₁	3321 (3100) ^c	538 ^d	2783	-750 (-168) ^c	-5748
Lactim(H ₂ O) ₂	4687	-921	5608		
Lactam(H ₂ O) ₂	6885	793 ^d	6102	-2048 (-1580) ^c	-6545
Lactim(NH ₃) ₁		-941			
Lactam(NH ₃) ₁		78 ^d			
Lactam(NH ₃) ₂		248 ^d			
Solution (H ₂ O)				-1000 ^e	

a. Binding energies (BE) are those obtained for cyclic cluster structures. See text.

b. Ref. 14

c. Ref. 19

d. Lactam solvent shifts are relative to peak B in Fig. 3.

e. Ref. 16

Table I

**Measured Spectroscopic and Thermodynamic Parameters for
Tautomerization of 2-HP in Ground and $\pi\pi^*$ States**

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d. Lactam solvent shifts are relative to peak B in Fig. 3.

e. Ref. 16

Table II

Peak Possitions in Spectra of 2-hydroxypyridine (2-HP)

Spacings from origin (in cm^{-1})

$S_1 \leftarrow S_1$			$S_0 \leftarrow S_0$		
Lactim	Lactam ^a		Lactim	Lactam ^a	
d_0	d_1	d_0	d_1	A	B
(36,136)	(36,140)	(29,832)	(29,935)	(29,869)	(29,967)
200	198	348	71	122	120
293	293	568	144	155	144
378			289	321	289
385	385				
400	399				
404					
500					
510	509				
525	525				
542					
				423	447
				560	536
				617	598
				627	739
				841	809
				991	848
				1040	981
				1113	1071
				1176	1195
				1186	1226
				1231	1252
				1254	1272
				1297	1352
				1398	1532
				1459	1714
				1469	1765
				1548	1897
				1590	1970
				1623	1993
				1684	2072

a. A and B refer to the origins in Fig. 3.

Table III

2-HP Clusters: TOFMS Peak Positions with Respect to Appropriate Origins (in cm^{-1})

Lactim				Lactam			
Energy	Assignment	Energy	Assignment	Energy	Assignment	Energy	Assignment
(H₂O)₁		(NH₃)₁		(H₂O)₁		(NH₃)₁	
(35,468)	(0,0)	(35,195)	(0,0)	(30,473)	(0,0)	(30,013)	(0,0)
127		155		90	ν_a	87	ν_a
135		198		99	ν_b	98	ν_b
169		211		108	ν_c	116	ν_c
186		235		124	ν_d	141	ν_d
228		261		144	ν_e	170	$2\nu_a$
268		294		158	ν_f	227	$\nu_a + \nu_d$
298		366		174	ν_g	252	$3\nu_a$
320		401		239	$2\nu_d$	267	ν_e
327		410		258	$\nu_d + \nu_e$	286	$2\nu_c$
		420		271	$2\nu_e$		
(H₂O)₂		494		276	$\nu_d + \nu_f$	(NH₃)₂	
		516		294	$\nu_e + \nu_f$		
(35,215)	(0,0)	519		308	$2\nu_f$	(30,183)	(0,0)
21	ν_a	534		549	ν_g	60	ν_a
28	ν_b	562		580	ν_h	115	ν_b
41	$2\nu_a$	568				152	ν_c
48	$\nu_b + \nu_a$	707		(H₂O)₂		172	ν_d
55	ν_c	721				269	ν_e
62	$3\nu_a$	774		(30,728)	(0,0)		
68	$\nu_b + 2\nu_a$	815		56	ν_a		
76	$\nu_c + \nu_a$			64	ν_b		
82	$4\nu_a$			109	$2\nu_a$		
89	$\nu_b + 3\nu_a$			151	ν_c		
97	$\nu_c + 2\nu_a$			162	ν_d		
102	$5\nu_a$			201	$\nu_c + \nu_a$		
108	$\nu_b + 4\nu_a$			211	$\nu_d + \nu_a$		
117	$\nu_c + 3\nu_a$			225	$\nu_d + \nu_b$		
122	$6\nu_a$			252	$\nu_c + 2\nu_a$		
128	$\nu_b + 5\nu_a$			262	$\nu_d + 2\nu_a$		
157	ν_d			304	$2\nu_c$		
166	ν_e			321	ν_b		
169	ν_f			343	ν_f		
177	$\nu_b + \nu_a$						
189	$\nu_b + \nu_a$						
197	$\nu_d + 2\nu_a$						
206	$\nu_e + 2\nu_a$						
209	$\nu_b + 2\nu_a$						

Table IV

Locations of Origins of Deuterated Monosolvates of Lactam

(relative to d_0 origins in Fig. 6)(all values in cm^{-1})

H ₂ O				NH ₃			
d_0	-			-			
d_1	0	12	27	0	8	25	
d_2		8	26	0	7	24	34
d_3			36		7	24	32
d_4							34

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