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Infrared Laser Spectroscopy of Uracil and Thymine in Helium Nanodroplets: Vibrational Transition Moment Angle Study

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Vibrational spectra are reported in the N−H stretching region for uracil and thymine monomers in helium nanodroplets. Each monomer shows only a single isomer, the global minimum, in agreement with previous experimental and theoretical studies. The assignment of the infrared vibrational bands in the spectra is aided by the measurement of the corresponding vibrational transition moment angles (VTMAs) and ab initio frequency calculations. The ambiguity in the VTMA assignment of the N3H band for the uracil monomer is explained by the presence of dimer bands, which are overlapped with the monomer band.

Introduction

Uracil and its methylated molecule, thymine (5-methyluracil), are the simplest of the naturally occurring nucleic acid bases (NABs) of RNA and DNA, respectively, and as such represent benchmark systems for both experimental and theoretical studies. In the present study, we focus our attention on isolated molecules, such that direct comparisons can be made between theory and experiment. The theoretical literature on uracil and thymine monomers is in agreement that the lowest energy tautomer of each is the diketo form shown in Figure 1, and that it is well separated from the higher energy tautomers.[1−5] The next lowest energy enol tautomer, U(T)E32, lies approximately 40 kJ/mol above the global minimum on the potential energy surface. As a result, experiments carried out at the moderate temperatures needed to evaporate uracil and thymine are expected to show only the diketo tautomers, UK and TK, respectively. This is confirmed by rotationally resolved microwave[6−8] and infrared laser[9] studies of jet cooled uracil and/or thymine, which show only the diketo form.

In a recent paper,[10] we reported infrared laser spectroscopy of uracil-water (UW) binary complexes formed in helium nanodroplets. The high-resolution obtained in those spectra enabled us to identify the four lowest energy isomers predicted by ab initio calculations. The assignment of the observed spectra was based on both the vibrational frequencies of the free and bonded OH and NH stretches of the four UW isomers and their associated vibrational transition moment angles (VTMAs). However, the difficulty in assigning the free N1H and N3H bands of the UW isomers remained due to their small shifts from the strong monomer bands. In this paper, we report a complete study of uracil and thymine monomers in which we focus on their free N1H and N3H stretches (see Figure 1) using VTMAs to alleviate the previously reported problems.

Nucleic acid bases (NABs) are known to be difficult to investigate by electronic spectroscopy owing to the rapid nonradiative deactivation of the S_1 state, which makes the associated spectra broad with low quantum yields for fluorescence.[11−19] In the present study, we use infrared laser spectroscopy to obtain vibrational spectra of the diketo tautomers of uracil and thymine, in the N−H stretching region of the spectrum. The molecules are solvated in helium nanodroplets, which provide the cooling necessary to obtain high-resolution spectra. Pendular-state spectroscopy[20−23] is used to orient the molecules in a strong electric field, allowing for the measurement of VTMAs, explained in detail below.

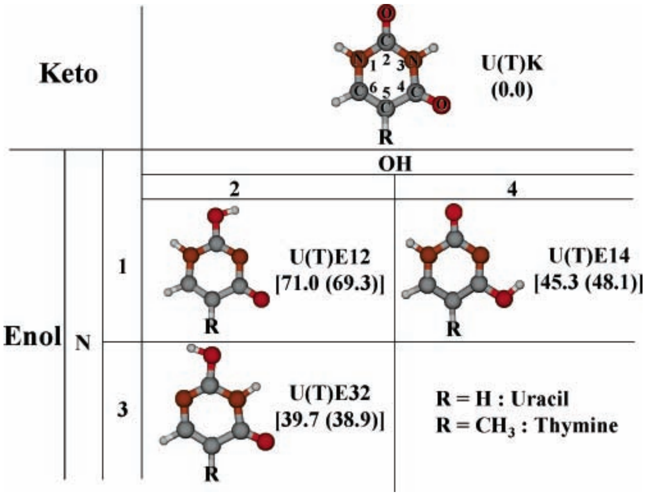

Figure 1. The ab initio structures and relative energies (MP2/aug-cc-pVDZ level) of the various tautomers of uracil (U) and thymine (T). Keto and enol forms are classified by their functional groups, namely C═O (keto) and O−H (enol), in the pyrimidine base. In addition, the naming scheme is followed by U or T for uracil or thymine, respectively, and K or E for keto or enol forms, respectively. Next, the following numbers identify the nitrogen position (1 or 3) to which the hydrogen is attached and similarly for the carbon position (2 or 4) to which the O−H is attached. The values in the brackets give the energies relative to U(T)K in kJ/mol with a harmonic zero-point energy correction. Uracil and thymine differ by their substituents, R = H and CH_3, respectively.

Experimental Method

The apparatus used in the present study has been described in detail elsewhere.[24] Helium nanodroplets are formed by expanding helium gas (99.9999%) through a 5 μm diameter orifice. The spectra were recorded using a source pressure of 55 atm with the nozzle being maintained at 20 K by a closed

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cycle refrigerator. Under these conditions droplets are produced with a mean size of approximately 3000 helium atoms. Uracil and thymine are added to the droplets as they pass through an oven maintained at approximately 160 and 170 °C, respectively, corresponding to vapor pressures between 10^{-6} and 10^{-5} Torr (Aldrich, 98% purity). The pick-up process is governed by Poisson statistics, allowing us to control the average number of molecules captured by the droplets.[25] To remove water from the solid uracil/thymine samples, they were held in the oven overnight at 110 °C.

The N−H stretching vibrations of uracil/thymine were excited using a periodically poled lithium niobate-optical parametric oscillator (PPLN-OPO) (LINOS Photonics). Several external etalons and a wavemeter were used to calibrate the spectra. A multipass cell[24] was used to reflect the laser across the droplet beam approximately 20 times to increase the excitation efficiency.[26,27] Two electrodes were positioned on either side of the laser interaction region so that an 80 kV/cm DC electric field could be applied. The IR excited molecules undergo rapid vibrational relaxation to the helium, resulting in the evaporation of several hundred helium atoms. A bolometer detector[28] was used to monitor the resulting depletion of the droplet beam. The spectra reported here were recorded by amplitude modulating the laser and using phase sensitive detection methods.

Previous studies[29−33] have shown that the electric dipole moment of a polar molecule can be oriented in a large DC electric field. In the present study, we make use of this method to measure vibrational transition moment angles (VTMAs)[10,26,34−37] for both uracil and thymine. VTMAs are defined as the angles between the permanent dipole moment and the transition moment vectors for the various vibrational modes of the molecule. The VTMAs are experimentally determined by measuring the band intensities for the various vibrational modes, as a function of the laser polarization direction relative to the DC electric field. For a vibrational mode with its transition moment parallel to the permanent dipole moment, parallel polarization of the laser will result in a significant increase in the band intensity compared to the zero-field case, and perpendicular laser polarization will result in a decrease in intensity. A quantitative description of this effect requires that the orientation distribution for the permanent dipole moment be known. This distribution depends upon the magnitude of the dipole moment, the applied electric field, the rotational constants, and temperature of the molecule in question. The methods for calculating these distributions have been discussed in detail previously by Kong et al.[38−41] For the systems discussed herein, the experimental spectra are broadened to a Lorentzian line shape. Although this means that the rotational constants cannot be directly determined from the experimental spectra, it also means that the overall orientation distribution is less sensitive to the rotational constants. In this case we use the ab initio rotational constants, divided by a factor of 3 to account for the effects of the helium,[26,42] to determine the orientation distribution needed to calculate the VTMAs. This approach works rather well given that the rotational temperature of the droplets, and hence the rotational temperature of the molecules, are well-known, namely 0.37 K.[43,44] A detailed discussion of how the experimental VTMAs are extracted from the integrated areas of the zero-field, parallel, and perpendicular polarization spectra is given elsewhere.[33−37,45]

Ab initio Caculations

Although both the uracil and thymine have been the subjects of numerous previous ab initio calculations, none of these have reported permanent dipole or transition dipole directions needed for comparison with the experimental VTMAs. For this reason, we carried out extensive ab initio calculations for the various tautomers of uracil and thymine, using Gaussian 03.[46] Unless otherwise specified, the calculations were performed using second-order Møller-Plesset perturbation theory (MP2) with an aug-cc-pVDZ basis set. Figure 1 shows the four lowest tautomers of uracil and thymine, whose relative energies are listed in kJ/mol for the equilibrium geometries with a harmonic zero point energy correction.

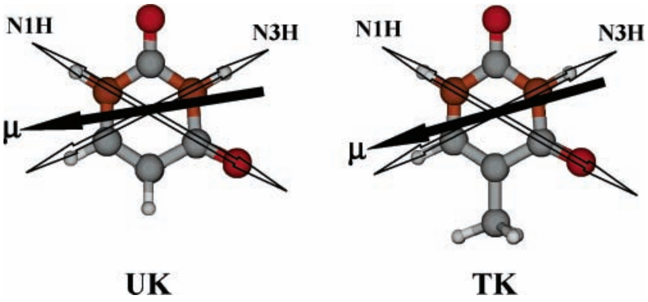

Figure 2. The lowest energy tautomer of uracil (UK) and thymine (TK), showing the corresponding directions of the permanent electric dipole moments (solid arrow) and the vibrational transition moments (empty double ended arrows) for the various vibrational modes. The magnitudes of these moments are given in Table 1.

Figure 2 shows the lowest energy diketo form of uracil and thymine monomer onto which are superimposed vectors representing the directions of the permanent electric dipole moments (solid arrow) and the vibrational transition moments (empty double ended arrows).

Results and Discussion

We begin this discussion by considering the spectra, Figure 3, of the uracil (a) and thymine (b) monomer in the region of the N−H stretching vibrations. In light of the published experimental[6−9] and theoretical[1−5] work on this system, we expect to see only a single tautomer, namely the diketo form. As shown in Figure 1, the diketo tautomers of uracil/thymine possess two N−H vibrational modes, referred to hereafter as N1H and N3H. The upper panel in Figure 3(a),(b) shows an experimental spectrum of uracil and thymine monomer, respectively, in helium droplets that spans both the N1H and N3H stretching vibration regions. The other four panels show the ab initio spectra (all scaled by a factor of 0.958458 and 0.95877 with an aug-cc-pVDZ basis set to give good agreement between theory and experiment for the free N1H stretches) for the four lowest energy tautomers of uracil and thymine, respectively. The fact that the expected free OH stretch mode in the 3550−3650 cm^{-1} region of the enol forms is clearly missing in the survey scans of Figure 3, leads us to believe that only the global minimum tautomers, UK and TK, are present in the helium nanodroplets for uracil and thymine.

As shown in the survey scans in Figure 3, the spectra of uracil and thymine are very similar to each other both experimentally and theoretically, which means that the spectral difference due to the methylation to the uracil is not significant. The two main peaks in both spectra, Figure 3(a),(b), are easily assigned by comparison with the scaled ab initio calculations to be the N1H and N3H vibrations of the monomer (UK and TK). A detailed discussion of these peaks is given below. The weaker bands in the spectra are assigned to the uracil/thymine dimer or higher clusters, given that they grow in at higher oven temperatures, indicating that they require the pick-up of more than one uracil/

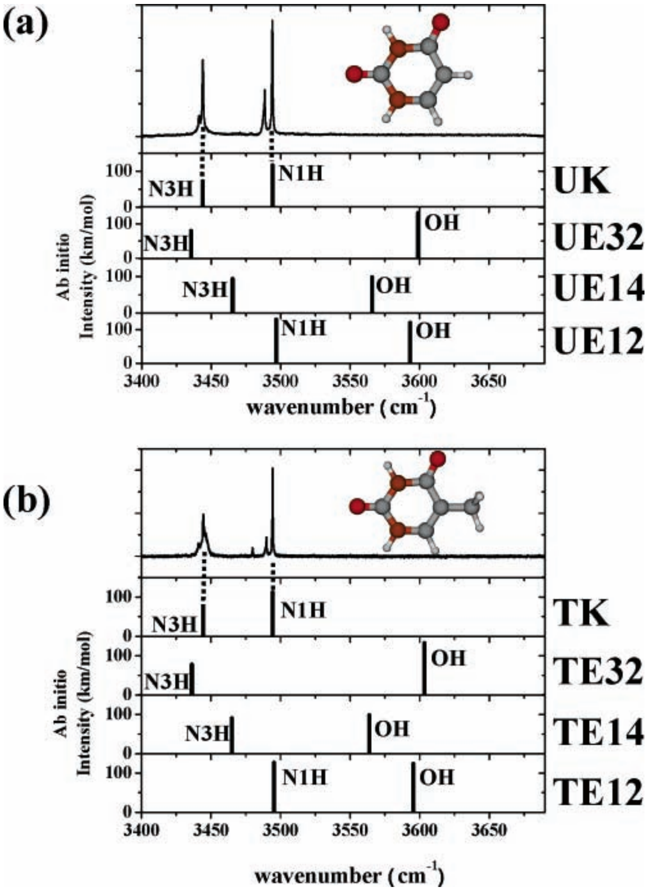

Figure 3. A survey spectrum of (a) uracil and (b) thymine isolated in helium droplets. The ab initio vibrational spectra for the four lowest energy tautomers of uracil and thymine are shown in separate panels below the experimental spectrum. The vertical bars in the bottom panels summarize the ab initio frequencies and intensities for the N1H, N3H, and OH stretch modes of the various tautomers. The harmonic ab initio calculations were all scaled by a factor of 0.958458 and 0.95877 to obtain the best overall agreement between theory and experiment, particularly for the free N1H stretch of the UK and TK tautomer, respectively. The dotted lines are meant as a guide to assign the bands associated with calculated frequencies of the N1H and N3H bands of uracil and thymine.

thymine molecule. However, the discussion of these bands is beyond the scope of the present study.

We now proceed to consider the VTMA assignment of the N1H stretch mode of uracil. Figure 4 shows the three different laser polarization spectra of uracil in the N1H region corresponding to (a) a pendular spectrum with parallel polarization, (b) a zero-field spectrum, and (c) a pendular spectrum with perpendicular polarization (electric field strength being 80 kV/cm), all plotted on the same absolute intensity scale. The peaks labeled with * and # are due to uracil dimer and trimer, respectively, a conclusion based on the oven temperature dependence of the integrated band areas (see detailed discussion in Supporting Information). Using the methods discussed elsewhere,[10,26,34−37] we made use of the integrated areas under the N1H mode in Figure 4 to determine experimental VTMAs for the monomer, yielding 43°. The result is in excellent agreement with the result of ab initio calculations (MP2/aug-cc-pVDZ) for the diketo tautomer, which gave 43° (see Table 1). Although there are no real surprises here as the calculated frequency of N1H of the diketo form also agrees with the experimental value, these results do provide another example in which the experimental and ab initio VTMAs are in quantitative agreement, as they were in the uracil−water complexes.[10]

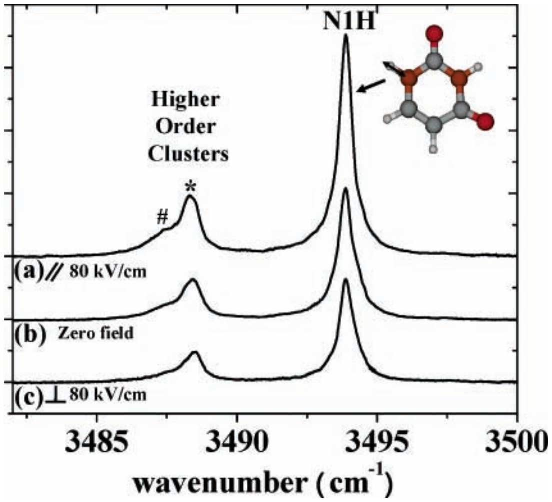

Figure 4. An expanded view of the N1H stretching region of the UK spectrum. Spectra (a), (b), and (c) correspond to parallel polarization, zero-field, and perpendicular polarization, respectively. The two bands marked with an “*” and a “#” are due to the uracil dimer and trimer, respectively.

We now turn our attention to the N3H mode, which appears at 3444 cm^{-1}. According to the ab initio frequency calculations shown in Figure 3(a), we expect to observe an N3H mode at about 50 cm^{-1} to the red of the N1H band of uracil. Figure 5 shows the electric field dependence of the N3H mode of uracil discussed above from which the VTMA is determined to be 24°. In this case, the agreement with the ab initio VTMA of 15° is poor. Although this band is very close to being a parallel band (below 15°) for which the experimental VTMA gives larger errors (normal experimental error being within ± 5°),[26,36] this error is outside the experimental uncertainty that we have come to expect, leading us to consider other explanations for the differences. Because we are confident in the assignment of this band, we are forced to consider other mechanisms that might affect this comparison. One possibility is that there are other bands that overlap with the N3H band, which would affect the corresponding experimental VTMA value. Another possibility is that the local environment of N3H, positioning between the two C═O functional groups, is different from that of N1H, which may cause an intramolecular interaction, yielding a geometric distortion. However, the interaction is negligible and the geometry of uracil is known to be very planar from both theoretical[1−5] and experimental[6−8] studies. The planar structure thus leaves contributions from other bands as the best explanation for the problem in reconciling the experimental and theoretical VTMAs.

To test these ideas we compare the N3H bands of uracil and thymine in Figure 6. Fortunately, we were able to observe the frequency separation of the N3H band from the thymine dimer bands. The bands in Figure 6(b) marked with an “*” are due to higher order clusters. As shown in the Supporting Information and Table 1, the experimental VTMA of both N1H (52°) and N3H (13°) modes of the methylated uracil, thymine (5-methyluracil), is in excellent agreement with the result of ab initio calculations (MP2/aug-cc-pVDZ), which gave 52° and 8°, respectively. The fact that the experimental VTMA of the N3H band of thymine is in good agreement with ab initio value, leads us to believe that the discrepancy in the VTMA of the N3H of uracil comes from the disturbance of the experimental VTMA

TABLE 1: A Summary of the Experimental and Calculated Vibrational Frequencies and VTMAs for the Various Isomers of Uracil and Thymine

tautomer	harm freq (cm−1)	scaled freq (cm−1)[a]	exp freq (cm−1)	IR intensity (km/mol)	assignment	ab initio VTMAs (degree)	exp VTMAs (degree)	dipole moment (Debye)	relative energy (kJ/mol)[b]
UK								4.38	0
	3645.4	3493.9	3493.9	116.5	N1H	43	43		
	3593.1	3443.8	3443.9	72.2	N3H	15	24		
UE32								3.02	40.8
	3755.0	3599.0		131.9	OH	3			
	3584.3	3435.4		80.0	N3H	79			
UE14								4.84	44.8
	3720.3	3565.8		98.1	OH	41			
	3615.5	3465.3		94.2	N1H	85			
UE12								6.46	72.2
	3749.1	3593.3		121.0	OH	66			
	3648.3	3496.8		130.3	N1H	11			
TK	[c]							4.34	0
	3644.5	3494.3	3494.2	112.3	N1H	51	52		
	3592.6	3444.5	3444.5	70.9	N3H	8	13		
TE32								2.54	38.9
	3758.2	3603.3		132.8	OH	10			
	3584.0	3436.2		78.1	N3H	74			
TE14								5.27	48.1
	3716.9	3563.6		97.8	OH	45			
	3613.9	3464.9		90.3	N1H	90			
TE12								6.09	69.3
	3750.1	3595.4		123.6	OH	63			
	3645.5	3495.2		126.4	N1H	14			

[a] The ab initio calculations were performed at the MP2/aug-cc-pVDZ level and the scaled frequencies were obtained by multiplying the harmonic frequencies by a factor of 0.958458. [b] The energy was obtained with zero-point energy correction. [c] The ab initio calculations were performed at the MP2/aug-cc-pVDZ level and the scaled frequencies were obtained by multiplying the harmonic frequencies by a factor of 0.95877.

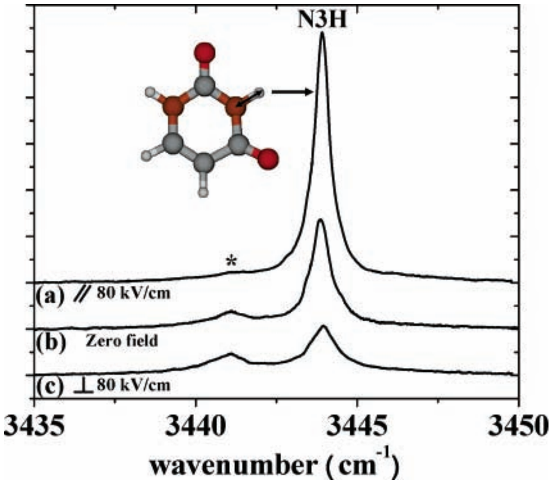

Figure 5. An expanded view of the N3H stretching region of the UK spectrum. Spectra (a), (b), and (c) correspond to parallel polarization, zero-field, and perpendicular polarization, respectively. The band marked with an "*" is due to the uracil dimer.

by the overlapping uracil dimer bands. This is somewhat supported by the fact that the spectra (particularly those shown in Figure 5(b),(c)) are not symmetrical, which might indicate that there are overlapping bands in the uracil case. After correction for the dimer contributions (i.e., excluding the integrated area of the dimer), the VTMA of the N3H band is estimated to be 17 ± 7°, which is close to the ab initio value. It shows that this band is close to parallel as suggested by the ab initio value (15°). Thus the problem in reconciling the experimental and theoretical VTMAs appears to be the heterogeneous peak broadening due to the presence of dimer bands in the vicinity of the monomer band.

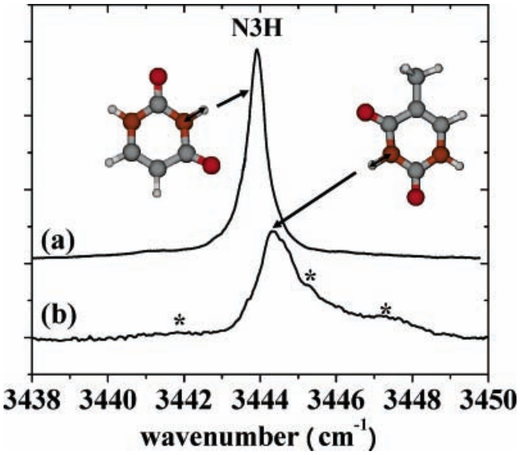

Figure 6. A comparison of the N3H stretching region of the uracil (a) and thymine (b) spectrum. Spectra (a) and (b) correspond to parallel polarization of uracil and thymine, respectively. The bands marked with an "*" are due to the thymine dimers.

Conclusions and Future Work

In this paper, we have presented the high-resolution infrared laser spectra of uracil and thymine monomers isolated in helium nanodroplets in the 3400−3700 cm^{-1} region. When combined with results from ab initio calculations, we obtain only the global minimum tautomer (diketo form) of the uracil and thymine. By orienting the target molecules in the laboratory frame of reference with a strong DC electric field, we measured the VTMAs of the uracil and thymine monomers. The calculated frequencies are very well matched with the observed frequencies, and the VTMA assignments provide additional and unambiguous assignment for the uracil and thymine molecules. Furthermore, using high-resolution and ultra cold matrix (He nanodroplet) spectroscopic techniques in the uracil/thymine system, we were able to resolve the ambiguity in the VTMA assignment of the N3H vibrational band of uracil for the first time.

Indeed, this may help assign the spectra of uracil dimers, which we are currently analyzing.[47] Now that we have well-characterized spectra of uracil and thymine monomer, the challenge for the future is the study of the dimers of the given systems, which would be more biologically important systems. The formation of hydrogen bonds between pairs of NABs is fundamental to the structure and dynamics of DNA and RNA and is the subject of continued intensive study. Although the Watson−Crick base pairs are justifiably often the center of such attention, NAB dimers also can provide important information concerning such hydrogen bonding. For example, N−H−O−C hydrogen bonds are of fundamental importance and are amenable to study in the simplest of these systems, namely the uracil and thymine dimers.[47] Nevertheless, other isomers on this system (i.e., T-shaped and stacked, the latter being primarily stabilized by induction and dispersion forces) are also of importance in the dimer studies, especially when a free energy contribution gets larger at elevated temperatures.

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Supporting Information Available: Figure of the oven temperature dependence of the intensities of the three bands shown in Figure 4. Figures of the N1H and N3H stretching region of the thymine (TK) spectrum upon different polarization scans. This material is available free of charge via the Internet at http://pubs.acs.org.

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