The infrared spectra of uracil, thymine, and adenine in the gas phase

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Received 14 December 1996; in final form 28 January 1997

Abstract

The infrared spectra of gas-phase uracil, thymine, and adenine have been recorded from 100 to 3700 cm$^{-1}$ at a resolution of 1 cm$^{-1}$. The vibrational band positions and qualitative band intensities are reported and compared to published matrix data as well as to theoretical calculations. Our work suggests that gas-phase emission spectroscopy is a sensitive technique for recording spectra of organic and biological molecules. © 1997 Elsevier Science B.V.

1. Introduction

Spectroscopic investigations of the nucleic acid (NA) bases contained in non-interacting environments may help clarify the role of these molecules in biological systems. The spectra of the isolated bases, for example, may serve as reference data for the interpretation of results obtained in more complex surroundings. Indeed, gas-phase infrared studies of one class of biological molecules, the metalloporphyrins, have indicated that it may be possible to distinguish between thermal and solvent effects on the optical spectra of these molecules [1,2].

The spectroscopy of the isolated NA bases also may be used to probe the molecular underpinning of point mutations. It been proposed [3,4] that mutations occur when minor tautomers of the NA bases form non-standard base pairs; if left uncorrected, the mispairs may lead to changes in the genetic code. Whether the NA bases tautomerize to minor forms can be studied by analyzing the spectra of the isolated monomers.

Two techniques that approximate isolated conditions are matrix and gas-phase spectroscopy. Although matrix techniques yield spectra that are extremely well-resolved, the vibrational bands can exhibit splittings or shifts, arising from differences in the local environment and in the type of matrix, respectively. Gas-phase spectroscopy, in turn, is hampered by the low vapor pressures and the propensity toward decomposition exhibited by the NA bases. It is clear that results from both gas-phase and matrix approaches help to elucidate the spectral properties of the NA bases.

In this Letter, we present survey spectra of uracil, thymine, and adenine in the infrared. The spectra extend from 100 to 3700 cm$^{-1}$, a region that includes most of the fundamental modes of vibration for the NA bases. We compare the gas-phase results with published experimental and theoretical studies.

Previous investigations in the infrared region include both gas-phase and matrix-phase work. The absorption spectra of gas-phase uracil, methylated uracils, and methylated adenines have been reported in the C=O and NH stretching regions [5]. Recently,
Viant et al. reported an analysis of a rotationally resolved spectrum of the (ν6 C2=O,C4) stretch in uracil; the spectrum was recorded by exciting the molecules with an infrared diode laser in a supersonic jet expansion [6]. The infrared spectra of uracil [7–13] and deuterated uracil [10], thymine [7,11–15], and adenine [16–19] have also been reported in rare gas matrices.

As for many polyatomic molecules, the thorough assignment of NA infrared spectra requires an interplay between theoretical predictions and experimental results. Some recent theoretical treatments of the infrared spectrum of uracil include calculations at the Hartree-Fock level using a 6-31G** basis set [12,20] as well as calculations based on density functional methods [21]. For thymine, similar predictions of the vibrational spectra have been carried out at the SCF level using 6-31G** [12] and 6-31G(d) [15] basis sets. More current work on adenine includes Hartree-Fock calculations with a 6-31G(d,p) basis set [17,18] and a density functional investigation [19].

2. Experiment

Uracil, thymine, and adenine were heated in a tube furnace in separate experiments. Approximately 30 g of each compound were placed in the central portion of a stainless steel tube lined with pyrex. The stainless steel tube was sealed with KRS-5 (above 350 cm⁻¹) or polyethylene (below 400 cm⁻¹) windows at both ends, and then evacuated. Next, 10–15 Torr of argon were introduced into the tube; a buffer gas such as argon was necessary to prevent deposition of the compound on the windows.

The central region of the tube was contained in a commercial furnace (CM Rapid-Temp). The temperature of the furnace was raised at a rate of 10°C per minute. Spectra of the NA bases were recorded from 200 to 325°C in both emission and absorption. The blackbody source in the absorption measurements, a globar, was placed at one end of the tube. For both the emission and absorption measurements, the infrared radiation was directed with a mirror from the other end of the tube through an external port of a Fourier transform spectrometer (Bruker IFS 120 HR). The regions between the tube and the port as well as between the tube and the globar were purged with dry N₂ in order to minimize atmospheric contamination from CO₂ and H₂O.

In the spectrometer, the beam of infrared radiation was divided by a Ge coated KBr beamsplitter (400–4800 cm⁻¹) or a 3.5 μm Mylar beamsplitter (100–720 cm⁻¹). Liquid-nitrogen cooled In : Sb (1850–9000 cm⁻¹) and MCT (800–1850 cm⁻¹) detectors as well as liquid helium-cooled Si : B (300–1500 cm⁻¹) and bolometer (below 350 cm⁻¹) detectors were used to measure the infrared radiation. Each interferogram, corresponding to two hundred co-added scans, was collected at a resolution of 1 cm⁻¹; the Fourier transform was carried out by the Bruker Opus software. The final spectrum was obtained by taking the ratio of the raw spectrum to the background spectrum that was recorded without a sample in the tube. In order to check for decomposition products, mass spectra of the sample were recorded before and after each run.

3. Results and discussion

The spectra of the three NA bases were recorded as a function of temperature. For each compound, the vibrational bands began to appear at temperatures above 200°C. Although we recorded spectra in both emission...
and in absorption, we report the emission results because the technique yielded a superior signal-to-noise ratio for most modes, especially in the wavenumber region below 1000 cm\(^{-1}\). We found similar results in the infrared spectra of polycyclic aromatic compounds [22].

The infrared spectra, illustrated in Figs. 2–5, were measured at 325°C for uracil and adenine, and at 300°C for thymine. Mass spectra of uracil, thymine, and adenine recorded before and after each run confirmed that no appreciable decomposition occurred during the runs. We were unsuccessful in our attempts to record the gas-phase spectra of cytosine and guanine, the two other major NA bases, because the compounds have low vapor pressures and decompose readily when heated.

The gas-phase band positions and qualitative intensities are summarized in Tables 1–3. The error in the reported gas-phase values is approximately ±2 cm\(^{-1}\). For comparison, we have also included matrix and theoretical values that have appeared in published reports.
Table 1
Uracil. Comparison of the gas-phase, matrix, and theoretical results. Band positions are in units of cm\(^{-1}\). For the theoretical results, the absolute intensities follow in parentheses, in units of km/mol.

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Abbreviations: ν, stretch; β, bend; γ, wag; R, ring; sh, shoulder; vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

*Density functional, local density approximation;

*Hartree–Fock, 6-31G** basis.

The calculated intensities, which follow the theoretical wavenumbers in parentheses, are in units of km/mol. The assignments of some modes differ among the quoted theoretical work; to remain consistent, we list the mode descriptions of Ref. [12] for uracil and thymine and Ref. [19] for adenine. For simplicity, the descriptions include only the dominant mode contributions.

A one-to-one comparison of our results with the previous matrix and theoretical results is not always possible because some of the gas-phase bands contain two or more vibrational modes. To observe most of the vibrational modes, it is necessary to heat the molecules to about 300°C. At such elevated temperatures, rotational broadening causes some of the vibrational modes to overlap. In addition, the gas-phase spectra almost certainly contain combination and overtone transitions of the lower-wavenumber vibrational modes. One example is the band observed at 576 cm⁻¹ in the adenine spectrum, which is not predicted to be a fundamental mode [19].

We did not observe any evidence of the tautomerization of uracil or thymine to the enol form or of adenine to the imino form, findings that agree with previous infrared matrix experiments. If the enol tautomer were present in either uracil and thymine, an OH stretch would be expected above 3500 cm⁻¹. The imino form of adenine would expect to show a band near 3320 cm⁻¹; such a band was not observed, although it could be obscured by the strong NH stretching modes in the region. Our experiments, of course, do not preclude the existence of minor tautomers: they
Table 2
Thymine. Comparison of the gas-phase, matrix, and theoretical results. Band positions are in units of cm\(^{-1}\). For the theoretical results, the absolute intensities follow in parentheses, in units of km/mol

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Abbreviations: ν, stretch; β, bend; γ, wag; R, ring; Me, in methyl; sh, shoulder; vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

a Hartree–Fock, 6-31G** basis.

may be present in concentrations below the detection threshold (on the order of 1%).

Where a direct comparison is possible, the agreement between the gas-phase and matrix-phase band positions is within 10 cm⁻¹. In addition, the theoretical calculations predict the vibrational band positions to a reasonable accuracy. Both the Hartree–Fock and density functional methods yield comparable results for uracil and adenine, although one approach may lead to better results for a specific vibrational mode.

As illustrated in Fig. 5, the gas-phase spectrum of adenine exhibits three strong modes at 162, 204, and 270 cm⁻¹ and a weak mode at 244 cm⁻¹. The band positions are in good agreement with the density functional calculation, which predicts modes at 162, 205, 244, and 269 cm⁻¹ [19]. The qualitative intensities of the gas-phase modes, however, do not match the predicted intensities quite so well. Of the four modes, the one at 244 cm⁻¹ should be the strongest, with a predicted absolute intensity of 177 km/mol. Instead, the mode at 244 cm⁻¹ is extremely weak in the gas-phase spectrum. Furthermore, the calculation predicts the mode at 161 cm⁻¹ to be very weak, but it is observed to have a moderate intensity.

The wavenumber region below 1000 cm⁻¹, which includes most of the wag and torsion modes, may serve as a convenient fingerprint region for the NA bases. As can be expected, the spectra of uracil and thymine are very similar above because their structures differ only by a methyl group bonded to a ring carbon. The spectra below 1000 cm⁻¹, however, contain a few modes that make the spectra distinguishable, as seen in Fig. 4. It can also be noted that adenine has several clearly defined modes in the same region. Moreover, the vibrational modes are well-separated in the lower wavenumber region and the overlap of the various modes is minimal compared to the mid-infrared (MCT detector) region.

The spectra of the isolated bases may help guide the interpretation of results obtained in interacting environments, such as in solvents or in molecular clusters [23]. Selected vibrational bands could be moni-
Table 3
Adenine. Comparison of the gas-phase, matrix, and theoretical results. Band positions are in units of cm$^{-1}$. For the theoretical results, the absolute intensities follow in parentheses, in units of km/mol.

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Abbreviations: ν, stretch; β, bend; γ, wag; R, six-membered in ring; r, five-membered ring; sh, shoulder; vs, very strong; s, in strong; m, medium; w, weak; vw, very weak.
a Hartree–Fock, 6-31G(d,p) basis.
b Density functional, local density approximation.

tored for changes in position and intensity as indicators of the formation of intermolecular bonds. In the uracil and thymine spectra, the bands that are associated with the various motions of the CO groups could prove to be useful marker bands. For instance, the relative intensities of the CO bands in the spectrum of thymine oligomers dissolved in D₂O are affected when base pairing with adenine occurs [24]. In the adenine spectrum, it is probable that the bands associated with the NH₂ modes may be sensitive to the formation of intermolecular bonds.

The experiments reported here have led to the infrared spectra of uracil, thymine, and adenine over the wavenumber region that contains the fundamental modes of vibration of these molecules. Although the low vapor pressures and ease of decomposition present obstacles to gas-phase work, it is possible to obtain spectra by heating the molecules and recording the infrared emission. The vibrational bands of the isolated molecules may be used as marker bands for studies carried out in interacting environments. In particular, the lower frequency bands, corresponding to the ring torsions and functional group wags, may be suitable for identifying the NA bases in more complex systems.
Acknowledgements

We thank the National Sciences and Engineering Research Council of Canada (NSERC) for the support of this research. The authors would like to thank Dr. H. Hunziker for bringing some useful references to their attention.

References

[23] J.B. Paul and R.J. Saykally, private communication. They have been studying the formation of water-NA base clusters in the gas-phase using laser diode spectroscopy.