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

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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 condi-

tions 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 (ν_6 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 or-

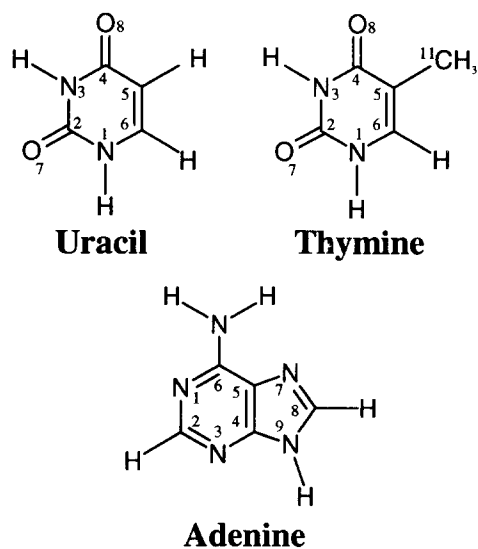


Fig. 1. Uracil, thymine, and adenine. The atom numbering follows Refs. [12,20] for uracil, Ref. [12] for thymine, and Ref. [19] for adenine.

der 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

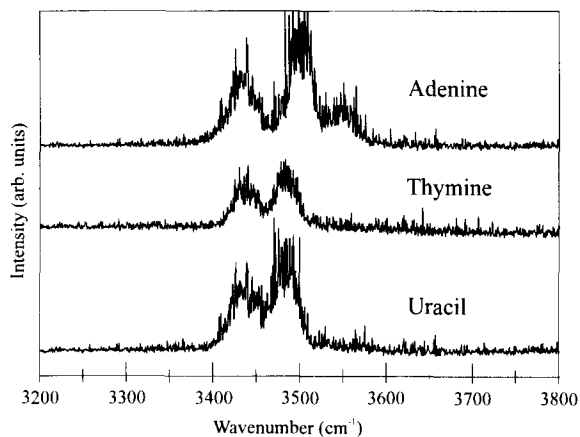


Fig. 2. The infrared spectra of gas-phase uracil, thymine, and adenine measured with an InSb detector. The temperature was 325°C for uracil and adenine and 300°C for thymine.

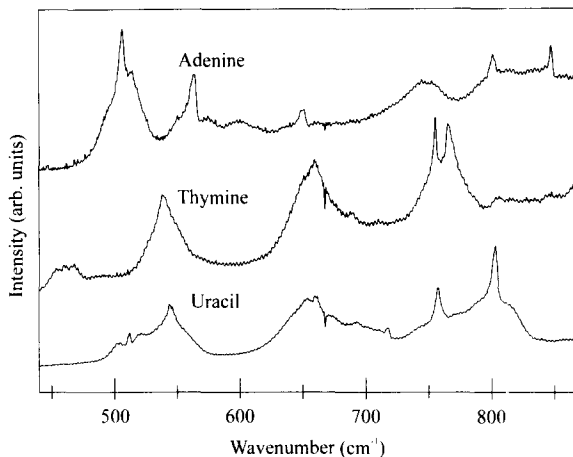


Fig. 4. The infrared spectra of gas-phase uracil, thymine, and adenine obtained with a Si : B detector. The temperature was 325°C for uracil and adenine and 300°C for thymine.

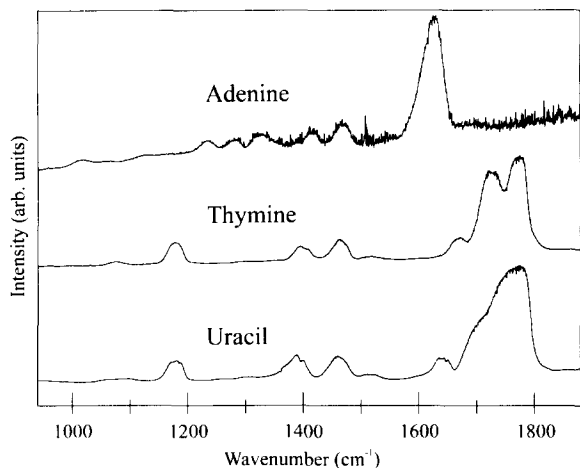


Fig. 3. The infrared spectra of gas-phase uracil, thymine, and adenine obtained with an MCT detector. The temperature was 325°C for uracil and adenine and 300°C for thymine.

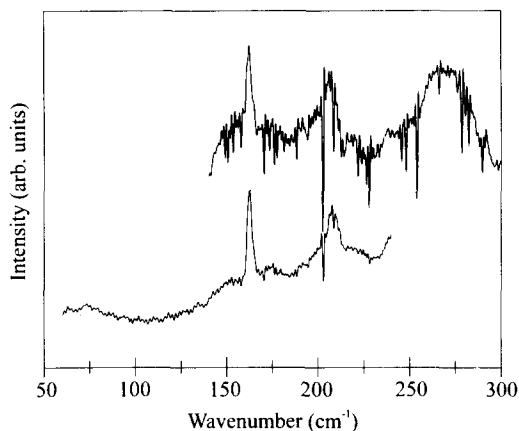


Fig. 5. The infrared spectra of gas-phase adenine obtained with a bolometer detector. The temperature was 325°C.

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 con-

firmed 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 $\pm 2 \text{ cm}^{-1}$. For comparison, we have also included matrix and theoretical values that have appeared in published reports.

Table I

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

Gas	Matrix		Theory		Approximate mode description Refs. [12,20]
	Ref. [13]	Ref. [12]	Ref. [21] ^a	Refs. [12,20] ^b	
3484s	3484.3	3485 3480 3474	3582(138)	3511(134)	νN1H
	3479				
	3472.8				
3436s	3434.5	3435	3539(74)	3477(99)	νN3H
3124m			3227(6)	3087(1)	νC5H
			3184(0)	3054(4)	νC6H
1897m					
	1791.5	1792			
	1774.3	1775			
	1770.2	1771			
1756vs	1763.7	1764			
	1762.8				
	1761.4				
	1757.5	1758	1813(705)	1811(459)	νC2O , νC4O
	1741	1742			
	1733.2	1733			
	1731.3				
	1730.3	1730			
	1728.2				
	1717.3	1719			
	1706.4	1706	1768(669)	1795(1218)	νC4O , νC2O
	1705.3				
1703(sh)vs	1703.5				
	1698.4	1699			
		1687			
		1681			
1641s	1644	1644	1678(30)	1662(126)	νC5C6
		1609			
1515m	1517	1517			
	1474.2				
	1471.9	1472			
	1467.6		1521(107)	1482(147)	βN1H , νC6N1
	1465.0	1466			
1461s	1458.5	1459			
		1425			
		1422			
1400s	1399.6	1399	1424(81)	1401(82)	βN3H , νC2N3
	1396.7		1405(17)	1399(103)	βN3H , νN3C4
1387s	1388.7	1389	1357(1.4)	1377(17)	βC6H , βC5H
	1386.3				
1371(sh)m		1380			
1356(sh)m	1359.3	1359			
	1313.3	1314			
	1306.2	1307			
	1302.8	1303			
	1217.4	1217	1260(14)	1212(17)	νN3C4 , βC5H
1187s	1185	1192			
	1184.4	1185	1179(69)	1175(115)	βC6H , βN1H
1172s	1183.5	1176			

Table 1 — continued

Gas	Matrix		Theory		Approximate mode description Refs. [12,20]
	Ref. [13]	Ref. [12]	Ref. [21] ^a	Refs. [12,20] ^b	
1082m	1102.4	1102			
	1075.5	1076			
		1069	1083(8)	1057(20)	ν C6N1, β C5H
	1068.7	1065			
990(sh)w	987.5	987	994(6)	998(0.06)	γ C6H
972(sh)w	981.5	982	960(6)	969(7)	γ ring
952w	958.3	958	926(1)	947(6)	ν ring
		944			
802w	804	804	786(66)	814(103)	γ C5H, γ C4O
		792			
757w	756.5	757	778(2)	776(105)	γ C2O
	759.2	759	747(37)	746(4)	ν ring
717vw	717.4	717	697(22)	723(5)	γ C4O, γ C5H
692vw	662.1	662	663(67)	658(98)	γ N3H
660w	659.5				
	657.3				
	559	559	580(32)	548(5)	β ring, β CO
	556	555			
545w	551.2	550	545(5)	530(74)	γ N1H
		545			
512w	536.4	536	529(2)	533(7)	β CO, β ring
	516.5	516	505(19)	505(24)	β ring
		514			
395w		393	388(20)	387(32)	ring deform, γ C4O
374vw		391	376(22)	383(31)	β C4O, β C2O
			160(0)	162(1)	ring deform
			137(2)	151(1)	ring deform

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

^a Density functional, local density approximation;

^b 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

Gas	Matrix		Theory Ref. [12] ^a	Approximate mode description Ref. [12]
	Ref. [11]	Ref. [12]		
3484s	3480	3480	3513(131)	νN1H
3437s	3434	3434	3477(99)	νN3H
3076m	2992		3049(6)	νC6H
2984	2971		2943(23)	νMe
2941	2940		2937(19)	νMe
	2855		2876(31)	νMe
1772vs	1768	1769		
		1759		
		1752	1805(720)	νC2O
		1747		
		1742		
		1731		
		1725		
1725vs	1712	1713	1784(949)	νC4O
		1701		
	1684	1683	1693(87)	νC5C6
1668s		1668		
1518m		1510		
	1472	1472	1485(163)	βN1H
1463s	1455	1467		
		1455	1461(1)	βMe
	1451	1451		
	1437	1437	1440(5)	βMe
	1433	1433		
		1423		
		1419		
		1414		
1409s	1405	1406	1412(134)	$\nu\text{C2N3}, \beta\text{N1H}$
1393s	1388	1389	1404(15)	βMe
		1395	1396(10)	βN3H
		1367		
	1357	1357	1360(6)	βC6H
		1346		
		1315		
		1308		
		1297		
	1221	1221	1214(11)	$\beta\text{C6H}, \nu\text{C2N3}$
		1208		
	1198	1198		
		1190		
1178s	1183	1184	1166(154)	$\nu\text{C5C11}, \nu\text{C6N1}$
		1143		
	1140	1139		
		1096		
1078m	1087	1087	1128(28)	νC6N1
1031vw		1046	1056(0.4)	βMe
	1005	1005	1002(3)	βMe

Table 2—continued

Gas	Matrix		Theory	Approximate mode description Ref. [12]
	Ref. [11]	Ref. [12]	Ref. [12] ^a	
963vw	959	959	948(8)	ν N1C2
931vw	936	936		
885w	890	890	934(17)	γ C6H
804vw		800	785(7)	β R1
		785		
767w	764	764	778(146)	γ C2O
755w	754	754	764(1)	γ C4O, γ C2O
		726	705(4)	ν C4C5
689vw	662	662	658(92)	γ N3H
658w	659	660		
			593(2)	β C2O, β C4O
541w	545	540	536(7)	β R3, β R2
	541	545	522(89)	γ N1H
462vw		455	446(23)	β R2
		394	387(24)	R1, R2, R3 deform
		391	385(31)	β C2O, β C4O
			291(0.2)	γ C5C11
		280	267(3)	β C5C11
			152(0.3)	Me deform
			148(0.5)	Me deform
			106(0.03)	R2 deform

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^2/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

Gas	Matrix Ref. [19]	Theory		Approximate mode description Ref. [19]	
		Ref. [17] ^a	Ref. [19] ^b		
3552m	3565	3601	3676(53)	νNH_2 antisym	
	3557				
	3555				
	3552				
	3506				
3501s	3503	3530	3589(80)	$\nu\text{N}_9\text{H}$	
	3502				
	3498				
	3494				
	3489				
3434s	3448	3471	3540(90)	$\nu\text{NH}_2\text{sym}$	
	3441				
	3438				
3061m	3057	3082	3195(1)	$\nu\text{C}_8\text{H}$	
1903w	3041	3026	3115(30)	$\nu\text{C}_2\text{H}$	
	1910				
	1693				
	1659				
	1651				
	1645				
	1639	1635	1641(597)	βNH_2 sciss $\nu\text{C}_6\text{N}_{10}$, $\nu\text{C}_5\text{C}_6$	
	1633				
	1626				
	1625vs	1618			
1612		1639	1617(108)	$\nu\text{N}_3\text{C}_4$	
1599					
		1602	1584(7)	βNH_2 sciss	
1482		1549	1502(15)	$\nu\text{N}_7\text{C}_8$	
1468s		1474	1485	1487(57)	$\nu\text{C}_6\text{N}_1$, $\beta\text{C}_2\text{H}$
		1421			
1415s		1419	1419	1416(18)	$\nu\text{C}_4\text{C}_5$, $\nu\text{C}_4\text{N}_9$
		1389	1404	1400(11)	$\beta\text{N}_9\text{H}$, $\beta\text{C}_2\text{H}$
		1358			
1346(sh)m	1345		1350(38)	$\nu\text{N}_9\text{C}_8$	
	1334				
1326s	1328	1346	1342(30)	$\nu\text{N}_1\text{C}_2$	
		1330			
1280s	1290	1269	1317(67)	$\nu\text{C}_2\text{N}_3$	
	1246	1228	1250(30)	$\beta\text{C}_8\text{H}$	
	1240				
1234s	1229	1213	1228(11)	βNH_2 rock, $\nu\text{C}_5\text{N}_7$	
	1133				
1126w	1127	1120	1129(20)	$\nu\text{C}_4\text{N}_9$	
	1078				
1065(sh)w	1061		1065(17)	$\nu\text{C}_8\text{N}_9$	
1053(sh)w		1050			
	1032				

Table 3 — continued

Gas	Matrix Ref. [19]	Theory		Approximate mode description Ref. [19]
		Ref. [17] ^a	Ref. [19] ^b	
1018m	1017			
	1005	996	1000(5)	β NH ₂ rock
957vw	958	1009	953(2)	γ C2H
926vw	927	922	925(15)	β r4
	887	882	882(13)	β R1
	869			
847w	848	904	831(4)	γ C8H
801w	802	809	793(14)	R1 deform
748w				
	717	702	713(3)	ν N3C4
	698			
	687			
	678			
		694	672(3)	γ C6N10
650vw	655	652	658(6)	r4 deform, r5 deform
600vw	610	601	607(1)	r5 deform
	591			
576vw	583			
563w	566			
		557	568(64)	R1, R2 deform, γ N9H
		515	528(13)	twist NH ₂
		517	521(8)	R3 deform
515w	513	500	514(61)	γ N9H
506m	503	505	504(5)	twist NH ₂
497(sh)vw				
		298	298(0.5)	R3 deform
270m	276	271	269(22)	β C6N10
244vw	242		244(177)	inv NH ₂
	214		205(90)	Rr torsion
208m		215		
162m		168	162(2)	R2 deform
		93		

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 in-

frared 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.

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