Ab Initio Study of the Vibrational Spectra of N9–H and N7–H Adenine and 9-Methyladenine

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Abstract: The structures and vibrational spectra of adenine in two tautomeric forms (N9–H and N7–H) and 9-methyladenine have been calculated at the Hartree–Fock level with a 4-21G basis set and are in good agreement with experimental structural data. The ab initio normal modes have been used to interpret experimental vibrational data for adenine and 9-methyladenine isolated in an argon matrix, in the crystalline solid and in solution. Experimental band assignments of the spectra in the low-temperature matrix and in the polycrystalline state have been analyzed and several reassignments have been proposed. Overall the agreement between the experimental argon matrix and calculated results is very good; for the scaled ab initio frequencies the deviation from experiment is 3% for the entire frequency range. The 4-21G geometries and force constants for adenine and 9-methyladenine have been used to calculate the vibrational spectra of N-deuterated derivatives of the studied systems. These results have proved to be helpful in analyzing experimental band assignments in spectra of deuterated adenine derivatives and in verifying the assignments for the undeuterated molecules.

1. Introduction

The biological importance of the nucleic acid bases is widely recognized. Numerous experimental and theoretical studies of the structure and vibrations of these molecules have been made.[1-21] However, for adenine in particular, a full understanding of the internal motions is not yet available. Adenine and its derivatives are particularly interesting nucleic acid compounds because of their multiple roles, including that of nucleic acid building blocks, reaction catalysts, and energy-storing molecules.[22]

Vibrational data for adenine and its derivatives include IR low-temperature argon matrix spectra of adenine and 9-methyladenine,[9] IR and Raman spectra of polycrystalline adenine[11,23] and 9-methyladenine,[12] and Raman spectra of adenine and adenosine 5′-monophosphate (AMP) in solution.[14,15,18] Low-temperature rare gas matrix isolation spectroscopy yields relatively sharp and well-defined bands for monomeric molecules with minimal influence of intermolecular interactions. Thus, in the absence of gas-phase data, low-temperature matrix isolation spectroscopy provides particularly suitable information for comparison with quantum mechanical and force field results. It may also serve as a reference for the analysis of molecular spectra in solution and in crystals and for the study of intermolecular solute–solute and solute–solvent interactions.

Ab initio calculations have proven to be of assistance in the interpretation of vibrational spectra of complex molecules. Such calculations have been recently reported for uracil,[2,3,24] cytosine,[4,8] and guanine.[19] Here we report the results of calculations of the vibrational spectra of adenine and its derivatives at the 4-21G level with the GAUSSIAN 82 program. The 4-21G basis set has been used previously to calculate the vibrational frequencies of benzene[25,26] and uracil[2,3] and yielded a deviation of the theoretical frequencies from the experimental values of about 10%. Analyses of ab initio calculations have shown that the size of the basis set used and the level of the correlation correction affects the calculated vibrational frequencies.[26] The 4-21G basis set employed in this work is a compromise between the size of the systems studied and the desired accuracy of the results. There exist a number of semi-empirical calculations for adenine and related compounds,[27-30] although no vibrational studies were performed.

Geometry optimization and frequency calculations have been made for three systems: the N9–H and N7–H tautomers of adenine, and 9-methyladenine (Figure 1). Both N9–H and N7–H tautomeric forms of adenine have been included in the analysis of the spectrum of adenine in the argon matrix[9] to test for the

presence of the rare N7–H tautomer. The compound 9-methyladenine is a model for adenine in adenosine and its derivatives.

As a test of the accuracy of 4-21G assignments, the vibrational spectra of deuterated derivatives of adenine and 9-methyladenine have been calculated by using the optimized geometries and force constants of the undeuterated parent molecule. These results prove to be useful in the assignments of matrix or vapor-phase experiments on isotopic derivatives of adenine. They are also used in

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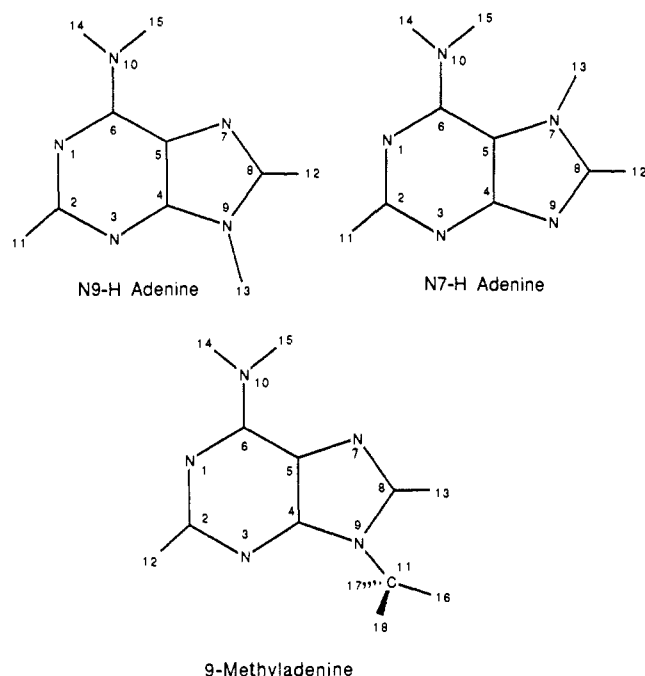
N9-H Adenine

N7-H Adenine

9-Methyladenine

Figure 1. Atom numbering in N_9-H and N_7-H tautomers of adenine and 9-methyladenine.

a more qualitative way to confirm band assignments from other phases and to correct misassignments.

The method used is outlined in section 2 below. Section 3 presents the results and discusses their significance. The conclusions are given in section 4.

2. Methods

The calculations were carried out at the Hartree–Fock level with the Pople split-valence shell 4-21G basis set.[31] Geometry optimization was performed with the GAUSSIAN 82 program[32] with no constraint on the planarity of the molecules. In previous studies molecules with amino groups have been found to be slightly nonplanar.[27] For the two adenine tautomers considered in this work a planar geometry was found to be the most stable at the 4-21G level. In 9-methyladenine the optimized geometry was also practically planar, with negligible deviations from nonplanarity (less than 0.001 Å for atoms other than the methyl hydrogens). The calculated geometric parameters are listed in Table I, together with average results from a series of crystallographic structures for adenine and its derivatives.[33]

The second derivative matrices for the Cartesian displacements were obtained by numerical differentiation of the analytical gradient at the equilibrium geometry. The Cartesian matrices were transformed to internal coordinates with the aid of the program MOLVIB,[34] which was also used to assign normal modes. The potential energy distribution matrix PED[35] was calculated as follows:

$$PED_{ij} = L_{ij}^T L_{ij}^{-1}$$

where L is the transformation matrix between the internal (symmetry) coordinates and normal coordinates; L^T and L^{-1} denote the transpose and the inverse of L, respectively.

The nonredundant internal coordinates used in this work are given in Tables II and III. The internal coordinates for the imidazole ring have been found from a redundancy analysis.[36,37] For the pyrimidine ring, internal coordinates given by Pulay et al.[25] for benzene are used. The out-of-plane ring deformation about the central C_4–C_5 bond (Figure 1) is described by coordinate 39 in Table II.

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Table I. 4-21G Optimized Structures of N_9-H Adenine, N_7-H Adenine, and 9-Methyladenine

coordinate[a]	N_9-H adenine	N_7-H adenine	9-methyl-adenine	adenine crystal	
				mean value[b]	SD[c]
Bond Lengths, Å					
N_1–C_2	1.3381	1.3450	1.3386	1.338	0.012
C_2–N_3	1.3256	1.3157	1.3251	1.332	0.014
N_3–C_4	1.3352	1.3389	1.3359	1.342	0.009
C_4–C_5	1.3817	1.3881	1.3818	1.382	0.010
C_5–C_6	1.3964	1.3978	1.3964	1.409	0.005
N_1–C_6	1.3364	1.3252	1.3365	1.349	0.011
C_5–N_7	1.3991	1.3901	1.3975	1.385	0.010
N_7–C_8	1.2933	1.3732	1.2950	1.312	0.007
C_8–N_9	1.3900	1.2978	1.3881	1.367	0.016
C_4–N_9	1.3688	1.3925	1.3660	1.376	0.009
C_6–N_{10}	1.3408	1.3556	1.3414	1.337	0.015
N_9–C_{11}			1.4596		
C_2–H_{11}	1.0678	1.0673	1.0679		
$(C_2$–$H_{12})^d$					
C_8–H_{12}	1.0637	1.0644	1.0645		
$(C_8$–$H_{13})^d$					
N_7–H_{13}		0.9936			
N_9–H_{13}	0.9949				
N_{10}–H_{14}	0.9957	0.9963	0.9956		
N_{10}–H_{15}	0.9957	0.9929	0.9957		
C_{11}–H_{16}			1.0804		
C_{11}–H_{17}			1.0806		
C_{11}–H_{18}			1.0806		
Bond Angles, deg					
C_6–N_1–C_2	119.77	120.12	119.78	118.8	0.8
N_1–C_2–N_3	126.62	126.08	126.59	129.0	0.6
C_2–N_3–C_4	113.27	114.84	113.23	110.8	0.6
N_3–C_4–C_5	125.14	122.92	125.26	126.9	0.8
C_4–C_5–C_6	117.26	118.57	117.16	116.9	0.6
N_1–C_6–C_5	117.93	117.47	117.97	117.6	0.6
C_4–C_5–N_7	110.13	105.71	109.85	110.7	0.5
C_5–N_7–C_8	105.25	106.01	104.97	103.9	0.7
N_7–C_8–N_9	112.28	113.12	112.87	113.8	0.7
C_4–N_9–C_8	106.85	105.68	106.16	105.9	0.5
N_3–C_4–N_9	129.37	127.60	128.60	127.4	0.6
C_6–C_5–N_7	132.60	135.71	132.99	132.3	0.7
N_1–C_6–N_{10}	119.35	118.08	119.31	119.0	0.8
C_5–C_6–N_{10}	122.72	124.45	122.73	123.4	1.0
C_4–N_9–C_{11}			125.66		
C_8–N_9–C_{11}			128.18		
N_1–C_2–H_{11}	116.31	116.16	116.27		
$(N_1$–C_2–$H_{12})^d$					
N_3–C_2–H_{11}	117.07	117.76	117.15		
$(N_3$–C_2–$H_{12})^d$					
N_7–C_8–H_{12}	125.85	121.71	125.80		
$(N_7$–C_8–$H_{13})^d$					
N_9–C_8–H_{12}	121.87	125.18	121.33		
$(N_9$–C_8–$H_{13})^d$					
C_5–N_7–H_{13}		128.04			
C_8–N_7–H_{13}		125.95			
C_4–H_9–H_{13}	125.54				
C_8–N_9–H_{13}	127.62				
C_6–N_{10}–H_{14}	118.93	117.55	118.94		
C_6–N_{10}–H_{15}	120.74	123.29	120.72		
H_{14}–N_{10}–H_{15}	120.33	119.16	120.35		
N_9–C_{11}–H_{16}			108.83		
N_9–C_{11}–H_{17}			110.06		
N_9–C_{11}–H_{18}			110.06		
H_{16}–C_{11}–H_{17}			109.49		
H_{16}–C_{11}–H_{18}			109.49		
H_{17}–C_{11}–H_{18}			108.91		
Dihedral Angles, deg					
C_4–N_9–C_{11}–H_{16}			180.0		
C_4–N_9–C_{11}–H_{17}			60.0		
C_4–N_9–C_{11}–H_{18}			-60.0		

[a] Atom numbering as in Figure 1. [b] Average value from 21 crystal structures of adenine and its derivatives from ref 33. [c] SD, standard deviation of distribution. [d] In 9-methyladenine the atom numbering is slightly different from that in adenine (see Figure 1). Consequently the adenine coordinates listed in this table corresponding to 9-methyladenine are given in parentheses. They are C_2–H_{12}, C_8–H_{13}, N_1–C_2–H_{12}, N_3–C_2–H_{12}, N_7–C_8–H_{13}, and N_9–C_8–H_{13}.

The evaluation of the vibrational frequencies of adenine and methyladenine at the 4-21G level required 39 and 48 h, respectively, on a

Table II. Vibrational Coordinates for N_9-H and N_7-H Adenine

no.[a]	definition[b]	N^c	description	symbol
1	N_{10}-H_{14}	1.0	$N_{10}H_{14}$ str	$\nu(NH_2)$
2	N_{10}-H_{15}	1.0	$N_{10}H_{15}$ str	$\nu(NH_2)$
3[d]	N_9-H_{13}	1.0	N_9H str	$\nu(N_9H)$
4	C_2-H_{11}	1.0	C_2H str	$\nu(C_2H)$
5	C_8-H_{12}	1.0	C_8H str	$\nu(C_8H)$
6	C_6-N_{10}	1.0	C_6N_{10} str	$\nu(C_6N_{10})$
7	C_5-C_6	1.0	C_5C_6 str	$\nu(C_5C_6)$
8	C_4-C_5	1.0	C_4C_5 str	$\nu(C_5C_6)$
9	N_3-C_4	1.0	N_3C_4 str	$\nu(N_3C_4)$
10	C_2-N_3	1.0	C_2N_3 str	$\nu(C_2N_3)$
11	N_1-C_2	1.0	N_1C_2 str	$\nu(N_1C_2)$
12	N_1-C_6	1.0	N_1C_6 str	$\nu(N_1C_6)$
13	C_5-N_7	1.0	C_5N_7 str	$\nu(C_5N_7)$
14	N_7-C_8	1.0	N_7C_8 str	$\nu(N_7C_8)$
15	C_8-N_9	1.0	C_8N_9 str	$\nu(C_8N_9)$
16	C_4-N_9	1.0	C_4N_9 str	$\nu(C_4N_9)$
17	$(N_1$-C_2-$H_{11}) - (N_3$-C_2-$H_{11})$	$2.0^{-1/2}$	C_2H bend	$\beta(C_2H)$
18	$(N_9$-C_8-$H_{12}) - (N_7$-C_8-$H_{12})$	$2.0^{-1/2}$	C_8H bend	$\beta(C_8H)$
19[e]	$(C_4$-N_9-$H_{13}) - (C_8$-N_9-$H_{13})$	$2.0^{-1/2}$	N_9H bend	$\beta(N_9H)$
20	$(C_5$-C_6-$N_{10}) - (N_1$-C_6-$N_{10})$	$2.0^{-1/2}$	C_6H_{10} bend	$\beta(C_6N_{10})$
21	$2(H_{14}$-N_{10}-$H_{15}) - (C_6$-N_{10}-$H_{14}) - (C_6$-N_{10}-$H_{15})$	$6.0^{-1/2}$	NH_2 sciss	$\delta(NH_2)$
22	$(C_6$-N_{10}-$H_{14}) - (C_6$-N_{10}-$H_{15})$	$2.0^{-1/2}$	NH_2 rock	$r(NH_2)$
23	$(N_1$-C_6-$C_5) - (C_6$-C_5-$C_4) + (C_5$-C_4-$N_3) - (C_4$-N_3-$C_2) + (N_3$-C_2-$N_1) - (C_2$-N_1-$C_6)$	$6.0^{-1/2}$	6-membered ring def I	$\delta(r_1)$
24	$2(N_1$-C_6-$C_5) - (C_6$-C_5-$C_4) - (C_5$-C_4-$N_3) + 2(C_4$-N_3-$C_2) - (N_3$-C_2-$N_1) - (C_2$-N_1-$C_6)$	$12.0^{-1/2}$	6-membered ring def II	$\delta(r_2)$
25	$(C_6$-C_5-$C_4) - (C_5$-C_4-$N_3) + (N_3$-C_2-$N_1) - (C_2$-N_1-$C_6)$	2.0^{-1}	6-membered ring def III	$\delta(r_3)$
26	$(-5^{1/2} + 1)(C_4$-C_5-$N_7) + (5^{1/2} + 1)(C_5$-N_7-$C_8) - 4(N_7$-C_8-$N_9) + (5^{1/2} + 1)(C_8$-N_9-$C_4) - (5^{1/2} - 1)(N_9$-C_4-$C_5)$	$40.0^{-1/2}$	5-membered ring def I	$\delta(r_4)$
27	$-(C_4$-C_5-$N_7) + 2(2c^2$-$1)(C_5$-N_7-$C_8) - 2(2c^2$-$1)(C_8$-N_9-$C_4) + (N_9$-C_4-$C_5)$	M^f	5-membered ring def II	$\delta(r_5)$
28[g]	angle between C_2-H_{11} bond and N_1-N_3-C_2 plane		C_2H wag	$\gamma(C_2H)$
29[g]	angle between C_8-H_{12} bond and N_7-N_9-C_8 plane		C_8H wag	$\gamma(C_8H)$
30[g,h]	angle between N_9-H_{13} bond and C_4-C_8-N_9 plane		N_9H wag	$\gamma(N_9H)$
31[g]	angle between C_6-N_{10} bond and N_1-C_5-C_6 plane		C_6N_{10} wag	$\gamma(C_6N_{10})$
32	$(N_1$-C_6-N_{10}-$H_{14}) - (C_5$-C_6-N_{10}-$H_{15})$	$2.0^{-1/2}$	NH_2 tors	$t(NH_2)$
33	$(N_1$-C_6-N_{10}-$H_{14}) + (C_5$-C_6-N_{10}-$H_{15})$	$2.0^{-1/2}$	NH_2 wag	$w(NH_2)$
34	$(N_1$-C_6-C_5-$C_4) - (C_6$-C_5-C_4-$N_3) + (C_5$-C_4-N_3-$C_2) - (C_4$-N_3-C_2-$N_1) + (N_3$-C_2-N_1-$C_6) - (C_2$-N_1-C_6-$C_5)$	$6.0^{-1/2}$	oopl 6-membered ring def I	$\chi(r_1)$
35	$-(N_1$-C_6-C_5-$C_4) + (C_5$-C_4-N_3-$C_2) - (C_4$-N_3-C_2-$N_1) + (C_2$-N_1-C_6-$C_5)$	2.0^{-1}	oopl 6-membered ring def II	$\chi(r_2)$
36	$-(N_1$-C_6-C_5-$C_4) + 2(C_6$-C_5-C_4-$N_3) - (C_5$-C_4-N_3-$C_2) - (C_4$-N_3-C_2-$N_1) + 2(N_3$-C_2-N_1-$C_6) - (C_2$-N_1-C_6-$C_5)$	$12.0^{-1/2}$	oopl 6-membered ring def III	$\chi(r_3)$
37	$4(N_9$-C_4-C_5-$N_7) - (5^{1/2} + 1)(C_4$-C_5-N_7-$C_8) + (5^{1/2} - 1)(C_5$-N_7-C_8-$N_9) + (5^{1/2} - 1)(N_7$-C_8-N_9-$C_4) - (5^{1/2} + 1)(C_8$-N_9-C_4-$C_5)$	$40.0^{-1/2}$	oopl 5-membered ring def I	$\chi(r_4)$
38	$2(2c^2 - 1)(C_4$-C_5-N_7-$C_8) - (C_5$-N_7-C_8-$N_9) + (N_7$-C_8-N_9-$C_4) - 2(2c^2 - 1)(C_2$$_8$-$N_9$-$C_4$-$C_5)$	M^f	oopl 5-membered ring def II	$\chi(r_5)$
39	$(N_3$-C_4-C_5-$N_7) - (N_9$-C_4-C_5-$C_6)$	$2.0^{1/2}$	oopl butterfly ring def	$\chi(r_6)$

[a] 1–27, in-plane vibrations; 28–39, out-of-plane vibrations. [b] Atom numbering as in Figure 1. [c] N is the normalizing factor. [d] N_7-H_{13}, N_7H str, and $\nu(N_7H)$ for N_7-H adenine. [e] $(C_8$-N_7-$H_{13}) - (C_5$-N_7-$H_{13})$, N_7H bend, and $\beta(N_7H)$ for N_7-H adenine. [f] $M = [10 + 32c^2(c^2 - 1)]^{-1/2}$; $c = [5 + (9 - 4(5^{1/2}))^{1/2}]/8 = \cos^2(\pi/5)$. [g] The out-of-plane coordinate is defined according to ref 36. [h] Angle between N_7-H_{13} bond and C_5-C_8-N_7 plane, N_7H wag, and $\gamma(N_7H)$ for N_7 adenine.

CRAY X-MP; most of the time was used for numerical evaluation of the second derivatives.

The vibrational spectra of N-deuterated adenine and N-deuterated 9-methyladenine were obtained by the Wilson GF method.[36] The 4-21G optimized geometry and force constant matrix of the parent molecule were used, with the assumption that they are not affected by isotopic substitution.[36]

Different scaling factors would be needed to correct the systematic overestimation of diagonal force constants obtained from Hartree–Fock calculations and the more complex pattern of the off-diagonal terms. A range of scaling factors has been used previously for different internal coordinates in benzene,[25] pyridine,[39,40] uracil,[2,3,24] pyrrole,[41] maleimide,[42] and imidazole.[43] Accumulation of ab initio calculation results and experimental gas-phase and matrix data for different pyrimidine and purine bases should lead to a more systematic adjustment of scaling factors and test the transferability of these factors among related mo-

lecular fragments. The calculated frequencies of all normal modes were all scaled by a factor of 0.91, which brings the calculated and experimental frequencies of the reliably assigned $\nu(NH_2)$ and $\nu(N_9H)$ [or $\nu(N_7H)$] vibrations in the argon matrix spectrum into close agreement. With the single scaling factor used here, the overall deviation between scaled calculated frequencies and the experimental values from the argon matrix is less than 3%. The root mean square (rms) deviation of the scaled calculated frequencies from the experimental values is less than 2% for in-plane modes, and 5% for out-of-plane modes; only a few bands assigned to out-of-plane deformations are observed experimentally, however.

Ab initio 4-21G force constants for N_9-H and N_7-H adenine and 9-methyladenine will be given elsewhere.[38]

3. Results and Discussion

3.1. Equilibrium Geometries, Dipole Moments, and Tautomerization Energy.
The 4-21G minimized geometry for N_9-H and N_7-H tautomers of adenine and 9-methyladenine are presented in Table I, together with crystallographic data for adenine.[33] The calculated bond lengths and bond angles agree very well with the crystallographic structures of neutral adenine derivatives.

The 4-21G dipole moments are 2.37, 7.52, and 2.57 D for N_9-H adenine, N_7-H adenine, and 9-methyladenine, respectively. Experimental dipole moments are not available for adenine tautomers; the calculated values may however be compared with the

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Vibrational Spectra of Adenine and 9-Methyladenine

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Table III. Vibrational Coordinates for 9-Methyladenine

no.[a]	definition[b]	N^c	description	symbol
1–2	same as 1–2 for adenine			
3	C_2–H_{12}	1.0	C_2H str	$\nu(C_2H)$
4	C_8–H_{13}	1.0	C_8H str	$\nu(C_8H)$
5	same as 6 for adenine			
6	N_9–C_{11}	1.0	N_9C_{11} str	$\nu(C_9H_{11})$
7–16	same as 7–16 for adenine			
17	$(N_1$–C_2–$H_{12}) - (N_3$–C_2–$H_{12})$	$2.0^{-1/2}$	C_2H bend	$\beta(C_2H)$
18	$(N_9$–C_8–$H_{13}) - (N_7$–C_8–$H_{13})$	$2.0^{-1/2}$	C_8H bend	$\beta(C_8H)$
19	same as 20 for adenine			
20	$(C_4$–N_9–$C_{11}) - (C_8$–N_9–$C_{11})$	$2.0^{-1/2}$	N_9C_{11} bend	$\beta(N_9C_{11})$
21–27	same as 21–27 for adenine			
28	$(C_{11}$–$H_{16}) + (C_{11}$–$H_{17}) + (C_{11}$–$H_{18})$	$3.0^{-1/2}$	CH_3 str	$\nu(CH_3)$ A'
29	$2(C_{11}$–$H_{16}) - (C_{11}$–$H_{17}) - (C_{11}$–$H_{18})$	$6.0^{-1/2}$	CH_3 str	$\nu(CH_3)$ A'
30	$(H_{16}$–C_{11}–$H_{17}) + (H_{16}$–C_{11}–$H_{18}) + (H_{17}$–C_{11}–$H_{18}) - $ $(N_9$–C_{11}–$H_{16}) - (N_9$–C_{11}–$H_{17}) - (N_9$–C_{11}–$H_{18})$	$6.0^{-1/2}$	CH_3 bend	$\delta(CH_3)$ A'
31	$2(H_{17}$–C_{11}–$H_{18}) - (H_{16}$–C_{11}–$H_{17}) - (H_{16}$–C_{11}–$H_{18})$	$6.0^{-1/2}$	CH_3 bend	$\delta(CH_3)$ A'
32	$2(N_9$–C_{11}–$H_{16}) - (N_9$–C_{11}–$H_{17}) - (N_9$–C_{11}–$H_{18})$	$6.0^{-1/2}$	CH_3 bend	$\delta(CH_3)$ A'
33	$(C_{11}$–$H_{18}) - (C_{11}$–$H_{17})$	$2.0^{-1/2}$	CH_3 str	$\nu(CH_3)$ A''
34	$(H_{16}$–C_{11}–$H_{18}) - (H_{16}$–C_{11}–$H_{17})$	$2.0^{-1/2}$	CH_3 bend	$\delta(CH_3)$ A''
35	$(N_9$–C_{11}–$H_{18}) - (N_9$–C_{11}–$H_{17})$	$2.0^{-1/2}$	CH_3 bend	$\delta(CH_3)$ A''
36[d]	angle between C_2–H_{12} bond and N_1–N_3–C_2 plane		C_2H wag	$\gamma(C_2H)$
37[d]	angle between C_8–H_{13} bond and N_7–N_9–C_8 plane		C_8H wag	$\gamma(C_8H)$
38	same as 31 for adenine			
39[d]	angle between N_9–C_{11} bond and C_4–C_8–N_9 plane		N_9C_{11} wag	$\gamma(N_9C_{11})$
40–47	same as 32–39 for adenine			
48	$(C_8$–N_9–C_{11}–$H_{16}) + (C_8$–N_9–C_{11}–$H_{17}) + (C_8$–N_9–C_{11}–$H_{18})$	$3.0^{-1/2}$	CH_3 tors	$t(CH_3)$

[a] 1–27, in-plane vibrations; 28–35, stretching and deformation motions of the methyl group; 36–48, out-of-plane vibrations. [b] Atom numbering as in Figure 1. [c] N is the normalizing factor. [d] The out-of-plane coordinate is defined according to ref 36.

experimental dipole moments of purine (2.92 D in ethyl acetate) and hypoxanthine (3.16 D in acetic acid).[44] The calculated dipole moment of 9-methyladenine may be compared with the dipole moment of 9-*n*-butyladenine (3.0 D in CCl_4).[45] The large difference between the dipole moments of the two tautomers arises from the change in the component parallel to the C_4–C_5 bond. The atomic populations other than at N_7, N_9, and the tautomeric hydrogen are essentially the same; in the N_9–H tautomer, they are N_7 (−0.66), N_9 (−0.57), H_{13} (0.39) and in the N_7–H tautomer, N_7 (−1.0), N_9 (−0.64), H_{13} (0.37). There is a resulting shift in the center of charge along the C_4–C_5 bond direction corresponding to a change in the contributions from the three atoms to the dipole moment.

The N_9–H tautomer was found to be favored by $\Delta E_0 = \Delta E^{SCF} + \Delta E_0^{vib} = 10.6$ kcal mol^{-1} over the N_7–H tautomer at the 4-21G level after correcting for zero-point vibrations. The energy difference between the two tautomers calculated at the 6-31G* for geometries optimized at the 3-21G level is 9.8 kcal mol^{-1}.[10] A value of 6 kcal mol^{-1} has been previously calculated by using the MNDO method.[27] The energy difference between the N_7–H and N_9–H tautomers calculated here suggests that the N_7–H tautomer is unlikely to be observed in the gas phase or low-temperature matrices by IR spectroscopy. However, in the low-temperature argon matrix,[9] the experimental spectrum appears to be a superposition of vibrations of both tautomers (see section 3.2). From a comparison of the calculated dipole moment for the N_9–H and N_7–H tautomers it is expected that the relative tautomeric populations in various media will depend on the polarity of the solvent; i.e., the population of the N_7–H tautomer is expected to increase with the polarity of the medium. Experimental estimates of the population of the N_7–H tautomer range from 15% in DMSO at 37 °C from chemical shifts in the carbon NMR spectrum of adenine[46] to 22% in water at 20 °C from T-jump relaxation measurements;[47] these values would correspond to a free energy difference of 1.1 and 0.7 kcal mol^{-1}, respectively.

3.2. Vibrational Spectra. 3.2.1. Adenine. The calculated vibrational spectra of N_9–H and N_7–H tautomers of adenine are

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presented in Table IV together with the argon matrix spectrum of adenine[9] and the Raman spectrum of polycrystalline adenine.[11] In the 3600–1000-cm^{-1} region, all but ν(CH) vibrations in the argon matrix and ν(NH_2) and ν(NH) vibrations in the crystal are observed in the experimental spectra. Below 1000 cm^{-1} most in-plane vibrations are observed in both the low-temperature matrix and crystal spectra. Only three lines corresponding to calculated $\delta(r)$ and $\beta(C_6N_{10})$ modes were missing from the experimental spectrum. For only one calculated frequency assigned to $\delta(r)$ deformations no appropriate band is observed in the crystal spectrum. For out-of-plane vibrations only 5 of the expected 12 modes for each tautomer are observed in the Ar matrix spectrum; 6 bands in the crystal spectrum have been assigned to out-of-plane modes.

3600–3000-cm^{-1} Range. In this region bands connected with the stretching vibrations ν(NH) and ν(CH) appear. The frequencies calculated at 3922 and 3910 cm^{-1} corresponding to stretching vibrations of the NH_2 group in the N_7–H and N_9–H tautomers, respectively, were scaled to 3566 and 3555 cm^{-1}. The scaling factor (see section 2) was chosen to obtain close agreement between the calculated and experimental frequencies of the reliably assigned ν(NH_2) and ν(NH) vibrations. The experimental bands at 3564 and 3556 cm^{-1} in the Ar matrix spectrum are assigned to antisymmetric –NH_2 stretching vibrations in the N_7–H and N_9–H tautomers, respectively. The experimental assignment[9] was based on a comparison of the spectrum of adenine in the Ar matrix with spectra of N-deuterated adenine derivatives, with spectra of molecules containing similar molecular fragments (pyrimidine and imidazole), and on empirical force field calculations. The bands at 3447 and 3440 cm^{-1} in the Ar matrix spectrum are assigned to symmetric stretching vibrations of the amino group. The calculated frequency difference between the N_9–H and N_7–H tautomers is 9–11 cm^{-1}, in accord with the 7–8-cm^{-1} band splitting observed experimentally.

NH stretching (scaled) frequencies have been calculated at 3511 and 3502 cm^{-1} for the N_7–H and N_9–H tautomers, respectively. The calculated frequencies are close to the experimental bands at 3497 and 3488 cm^{-1} in the Ar matrix spectrum. The calculated frequency difference of 9 cm^{-1} between the N_9–H and N_7–H tautomers is in agreement with the 8-cm^{-1} band splitting in the experimental spectrum.

The calculated (scaled) lines at 3153, 3147, 3105, and 3101 cm^{-1} corresponding to C_8–H and C_2–H stretching modes are not observed in the IR spectrum due to their low intensity. The

Table IV. Vibrational Frequencies in Adenine (in cm^{-1}) (Contribution in %)

N$_9$–H adenine			N$_7$–H adenine			adenine in Ar matrix		polycrystalline adenine (Raman)	
calc	scaled[a]	descrptn[b]	calc	scaled[a]	descrptn[b]	exp	descrptn	exp	descrptn
			3922	3566	ν(N$_{10}$H$_{14}$) (38) ν(N$_{10}$H$_{15}$) (62)	3564	ν(NH$_2$)as		
3910	3555	ν(N$_{10}$H$_{14}$) (50) ν(N$_{10}$H$_{15}$) (50)				3556	ν(NH$_2$)as		
			3861	3511	ν(N$_7$H) (99)	3497	ν(NH)		
3851	3502	ν(N$_9$H)(100)				3488	ν(NH)		
			3790	3446	ν(N$_{10}$H$_{14}$) (62) ν(N$_{10}$H$_{15}$) (38)	3447	ν(NH$_2$)s		
3780	3437	ν(N$_{10}$H$_{14}$) (49) ν(N$_{10}$H$_{15}$) (50)				3440	ν(NH$_2$)s		
3468	3153	ν(C$_8$H) (99)						3125	ν(C$_8$H)
			3461	3147	ν(C$_8$H) (99)				
			3415	3105	ν(C$_2$H) (99)				
3410	3101	ν(C$_2$H) (99)						3038	ν(C$_2$H)
			1811	1646	δ(NH$_2$) (95)	1644	δ(NH$_2$)as		
1804	1640	δ(NH$_2$) (91)				1637	δ(NH$_2$)as	1675	δ(NH$_2$)
						1632	ν(r) + δ(NH$_2$)s		
			1761	1602	ν(C$_2$N$_3$) (11) ν(C$_5$C$_6$) (33)				
1753	1594	ν(N$_3$C$_4$) (12) ν(C$_5$C$_6$) (30)						1612	ν(r) + δ(r)
						1618	ν(r) + δ(NH$_2$)s		
1738	1580	ν(N$_3$C$_4$) (11) ν(C$_4$C$_5$) (26)				1612	ν(r) + β(NH)	1597	ν(r) + δ(r)
			1706	1551	ν(N$_3$C$_4$) (23) ν(C$_4$C$_5$) (20) ν(N$_1$C$_6$) (18)	1598	ν(r)		
1639	1490	ν(N$_7$C$_8$) (44) β(C$_8$H) (19)	1641	1492	ν(C$_8$N$_9$) (34) β(C$_8$H) (16) β(N$_7$H) (20)	1481	ν(r) + β(CH)	1510	ν(r)
								1482	ν(r) + β(N$_9$H)
1624	1477	ν(C$_2$N$_3$) (10) ν(N$_1$C$_6$) (20) ν(C$_6$N$_{10}$) (18) β(C$_2$H) (29)	1622	1475	ν(N$_1$C$_6$) (11) ν(C$_6$N$_{10}$) (10) β(C$_2$H) (44)	1473 sh	ν(r) + β(CH)	1462	ν(r) + β(C$_2$H)
						1472	ν(r) + β(CH)		
1552	1411	ν(C$_4$C$_5$) (17) β(C$_2$H) (27) β(N$_9$H) (13) δ(r$_1$) (10)				1421	ν(r) + β(CH)	1418	ν(r) + β(N$_9$H)
						1418	ν(r) + β(CH)		
			1526	1388	ν(N$_7$C$_8$) (14) ν(C$_8$N$_9$) (11) β(C$_8$H) (13) β(N$_7$H) (43)	1388	ν(r)		
1519	1381	ν(N$_7$C$_8$) (14) ν(C$_4$N$_9$) (18) β(C$_2$H) (12) β(N$_9$H) (23)				1345		1370	ν(r) + β(N$_9$H) + β(C$_2$H)
			1494	1358	ν(C$_4$C$_5$) (30) ν(C$_6$N$_{10}$) (14) β(C$_2$H) (25)	1343			
			1468	1335	ν(C$_2$N$_3$) (17) ν(C$_5$N$_7$) (11) ν(C$_8$N$_9$) (15) β(C$_8$H) (18) δ(r$_1$) (15)	1333			
1463	1330	ν(N$_1$C$_2$) (12) ν(C$_6$N$_{10}$) (13) β(C$_2$H) (17) β(C$_8$H) (12) β(N$_9$H) (13)				1328	ν(r)	1331	ν(r)
			1442	1311	ν(N$_1$C$_2$) (11) ν(N$_3$C$_4$) (12) ν(C$_4$N$_9$) (14) β(C$_2$H) (18)	1325	ν(r)		
1429	1299	ν(N$_1$C$_2$) (21) ν(C$_4$C$_5$) (11) ν(C$_5$N$_7$) (11) β(C$_8$H) (21)				1288	ν(CH) + ν(r)	1307	β(C$_2$H) + ν(r)
1394	1267	ν(C$_2$N$_3$) (38) β(C$_8$H) (25)	1394	1267	ν(N$_1$C$_2$) (15) ν(C$_2$N$_3$) (14) ν(C$_8$N$_9$) (19) β(C$_8$H) (28)	1246 sh	β(CH)	1248	β(C$_8$H) + ν(r)
			1345	1223	ν(C$_2$N$_3$) (17) ν(N$_1$C$_6$) (11) ν(C$_5$N$_7$) (18) r(NH$_2$) (28)	1239	ν(C–NH$_2$)		
1332	1211	ν(C$_5$N$_7$) (22) r(NH$_2$) (34)				1227	β(NH) + β(CH)	1235	δ(NH$_2$) + ν(r)

Table IV (Continued)

N9–H adenine			N7–H adenine			adenine in Ar matrix		polycrystalline adenine (Raman)	
calc	scaled[a]	descrptn[b]	calc	scaled[a]	descrptn[b]	exp	descrptn	exp	descrptn
1309	1190	$\nu(N_1C_2)$ (27) $\nu(C_2N_3)$ (13)	1274	1158	$\nu(N_1C_2)$ (30) $\nu(N_3C_4)$ (12) $\nu(C_5N_7)$ (12)	1126	$\beta(CH) + \delta(r)$	1164	$\nu(r) + \beta(C_8H) + \beta(N_9H)$
1210	1101	$\nu(N_3C_4)$ (11) $\nu(C_5N_7)$ (15) $\nu(C_4N_9)$ (11) $\delta(r_5)$ (11)	1179	1072	$\nu(C_4N_9)$ (21) $\delta(r_1)$ (11) $\delta(r_5)$ (11)	1061	$\beta(CH)$	1126	$\nu(r) + \nu(C_6N_{10})$
			1170	1064	$\nu(N_7C_8)$ (68) $\beta(N_7H)$ (16)	1017	$\nu(r) + \delta(r)$		
1134	1031	$\gamma(C_2H)$ (100)							
1132	1029	$\nu(C_8N_9)$ (72) $\beta(N_9H)$ (18)						1023	$\delta(NH_2) + \nu(r)$
			1128	1026	$\gamma(C_2H)$ (100)				
1084	986	$\nu(N_1C_6)$ (35) $r(NH_2)$ (32)	1077	979	$\nu(N_1C_6)$ (31) $\nu(C_6N_{10})$ (10) $r(NH_2)$ (34)			940	$\delta(r) + \nu(r)$
			1066	968	$\gamma(C_8H)$ (96)				
			1033	939	$\nu(C_4C_5)$ (17) $\delta(r_4)$ (70)	958	$\delta(r)$		
1032	938	$\gamma(C_8H)$ (83)				918	$\gamma(CH)$	848	$\gamma(C_8H)$
1025	932	$\delta(r_4)$(67)						898	$\delta(r) + \nu(r)$
989	899	$\gamma(C_8H)$ (20) $\gamma(C_6N_{10})$ (15) $\chi(r_1)$ (41) $\chi(r_4)$ (20)	986	897	$\gamma(C_6H_{10})$ (14) $\chi(r_1)$ (50) $\chi(r_4)$ (26)	888	$\gamma(CH)$	870	$\gamma(NH)$
965	877	$\nu(C_5N_7)$ (10) $\delta(r_1)$ (41) $\delta(r_3)$ (19)				849	$\delta(r)$		
			954	868	$\nu(C_4N_9)$ (11) $\delta(r_1)$ (36) $\delta(r_3)$ (19)	802	$\delta(r)$		
833	758	$\gamma(N_9H)$ (10) $\gamma(C_6N_{10})$ (36) $\chi(r_4)$ (14) $\chi(r_6)$ (15)						797	$\gamma(C_2H)$
			820	745	$\gamma(C_6N_{10})$ (42) $\chi(r_4)$ (12) $\chi(r_5)$ (15) $\chi(r_6)$ (15)				
761	692	$\nu(N_3C_4)$ (25) $\nu(C_5N_7)$ (14) $\delta(r_5)$ (12)	765	696	$\nu(N_3C_4)$ (29) $\nu(C_5N_7)$ (11) $\delta(r_3)$ (12) $\delta(r_5)$ (15)	655	$\delta(r)$	722	$\nu(r) + \nu(C_6N_{10})$
757	688	$\gamma(N_9H)$ (22) $\chi(r_4)$ (14) $\chi(r_5)$ (46)						680	
721	655	$\gamma(N_9H)$ (68) $\chi(r_5)$ (25)						650 (IR)	$w(NH_2)$
			718	653	$\chi(r_3)$ (12) $\chi(r_4)$ (15) $\chi(r_5)$ (62)				
671	610	$\nu(C_5C_6)$ (26) $\delta(r_3)$ (23) $\delta(r_5)$ (26)				612	$\delta(r)$	620	$\nu(r) + \beta(C_6N_{10})$
			661	601	$\chi(r_1)$ (28) $\chi(r_2)$ (16) $\chi(r_3)$ (17) $\chi(r_5)$ (19)				
			660	600	$\nu(C_5C_6)$ (26) $\delta(r_3)$ (21) $\delta(r_5)$ (22)				
640	582	$\chi(r_1)$ (29) $\chi(r_2)$ (14) $\chi(r_3)$ (25) $\chi(r_4)$ (12) $\chi(r_5)$ (17)							
			622	565	$\gamma(N_7H)$ (92)	592	$w(NH_2)$		
584	531	$t(NH_2)$ (31) $w(NH_2)$ (58)				582	$w(NH_2)$		
581	529	$\delta(r_2)$ (71)	580	528	$\delta(r_2)$ (69)			558	$\delta(r) + \beta(C_6N_{10})$
577	525	$t(NH_2)$ (52) $w(NH_2)$ (40)				566	$w(NH_2)$		
			562	511	$\nu(C_4N_9)$ (10) $\beta(C_6N_{10})$ (27) $\delta(r_3)$ (22)				
			559	508	$t(NH_2)$ (41) $w(NH_2)$ (44)	512	$\gamma(NH)$		

Table IV (Continued)

N₉-H adenine			N₇-H adenine			adenine in Ar matrix		polycrystalline adenine (Raman)	
calc	scaled[a]	descrptn[b]	calc	scaled[a]	descrptn[b]	exp	descrptn	exp	descrptn
557	506	$\nu(C_4N_9)$ (12) $\beta(C_6N_{10})$ (27) $\delta(r_3)$ (23)						535	$\delta(r) + \beta(C_6N_{10})$
354	322	$\chi(r_2)$ (15) $\chi(r_3)$ (41) $\chi(r_4)$ (23) $\chi(r_6)$ (11)	362	329	$t(NH_2)$ (15) $\chi(r_3)$ (30) $\chi(r_4)$ (18) $\chi(r_6)$ (17)			315	
			341	310	$t(NH_2)$ (26) $w(NH_2)$ (37) $\chi(r_2)$ (18)				
			312	284	$\beta(C_6N_{10})$ (52) $\delta(r_3)$ (14) $\delta(r_5)$ (10)				
291	265	$\beta(C_6N_{10})$ (51) $\delta(r_3)$ (15) $\delta(r_5)$ (10)						330	$\beta(C_6N_{10}) + \delta(r)$
253	230	$\chi(r_2)$ (15) $\chi(r_6)$ (68)	248	225	$\chi(r_2)$ (10) $\chi(r_6)$ (61)			240	
203	185	$\gamma(C_6N_{10})$ (17) $\chi(r_1)$ (15) $\chi(r_2)$ (48) $\chi(r_3)$ (14)							
			184	167	$\gamma(C_6N_{10})$ (12) $\chi(r_1)$ (12) $\chi(r_2)$ (45) $\chi(r_3)$ (14) $\chi(r_4)$ (10)				

[a] The scaling factor is 0.91. [b] Contributions greater than 10% are given.

calculated frequency splitting for ν(CH) modes in the N₇-H and N₉-H tautomers is 4–6 cm⁻¹. The weak bands at 3125 and 3038 cm⁻¹ in the Raman spectrum may be assigned to C₈-H and C₂-H stretching vibrations of the N₉-H adenine tautomer. The calculated frequencies for C₈-H and C₂-H stretching modes in adenine are also in accord with the presence of a band at 3126 cm⁻¹ in the Ar spectrum of imidazole, and at 3020 cm⁻¹ in the spectrum of pyrimidine.[9]

The 4-21G assignments for the 3600–3000-cm⁻¹ frequency range are in agreement with those from earlier empirical force field calculations.[9,11,16] The rms deviation of the scaled 4-21G frequencies from the experimental values is 0.2%.

2000–1630-cm⁻¹ Range. The bands at 1644 and 1637 cm⁻¹ in the Ar spectrum are assigned to the scissoring mode of the NH₂ group in the N₇-H and N₉-H tautomers, respectively. The calculated 6-cm⁻¹ frequency difference for the two tautomers is in accord with the experimental band splitting of 7 cm⁻¹.

The band at 1675 cm⁻¹ in the Raman spectrum may be assigned to the $\delta(NH_2)$ mode in the N₉-H tautomer. The large difference between the calculated and observed frequencies may be the result of intermolecular interactions in the crystal; NH₂ vibrations have been shown to be particularly sensitive to the environment.[4,48]

The 4-21G assignments in the 2000–1630-cm⁻¹ frequency range are in agreement with earlier experimental assignments.[9,11,16]

1630–1250-cm⁻¹ Range. Ring stretching vibrations [$\nu(r)$] of both the pyrimidine and imidazole rings, with contributions from the stretching mode $\nu(C_6N_{10})$ in the amino group, deformation modes $\beta(C_8H)$ and $\beta(C_2H)$, and bending modes $\beta(NH)$ are predicted in this region. The difference between frequencies calculated for the N₉-H and N₇-H tautomers in this region is 0–29 cm⁻¹; it is interesting to note that the frequency splitting calculated for pyrimidine ring stretching modes (8–29 cm⁻¹) is larger than that calculated for stretching vibrations of the imidazole ring (2–7 cm⁻¹).

Our calculations suggest the assignment of the bands at 1618 cm⁻¹ in the Ar spectrum and at 1612 cm⁻¹ in the Raman spectrum to pyrimidine ring stretching modes. Contrary to the experimental assignment of the band in the Ar matrix spectrum, no contribution

from NH₂ bending deformations is calculated. Our assignment of this band to $\nu(r)$ vibrations is supported by the frequencies obtained for adenine-d_3 and the experimental spectrum of adenine-d_3 (see section 3.2.4) in this region, in which a band at 1610 cm⁻¹ is found. We do not find that ring bending modes contribute to the 1612-cm⁻¹ Raman band, as suggested by Majoube[11] on the basis of empirical force field calculations.

The bands at 1598 and 1597 cm⁻¹ in the Ar and Raman spectra, respectively, may be assigned to $\nu(r)$ vibrations of the pyrimidine ring. Here again no contributions from ring bending modes to the 1597-cm⁻¹ Raman band are obtained at the 4-21G level. The band at 1481 cm⁻¹ in the Ar spectrum and the band at 1482 cm⁻¹ in the Raman spectrum are predicted to be associated with $\nu(r)$ modes of the imidazole ring, with a contribution from the $\beta(C_8H)$ mode; in the case of the N₇-H tautomer a small contribution from the N₇-H bending deformation is also found. The $\beta(N_9H)$ bending mode in the N₉-H tautomer is predicted to contribute to lower frequency vibrations. The assignment of these two bands to $\nu(r)$ vibrations of the five-membered ring is supported by the presence of a band at 1480 cm⁻¹ in the Ar spectrum of imidazole.[9]

The band at 1472 cm⁻¹ in the Ar spectrum and the band at 1462 cm⁻¹ in the Raman spectrum correspond to C₂H bending deformations, with a contribution from $\nu(r)$ modes of the pyrimidine ring and $\nu(C_6N_{10})$ in the amino group. The calculated contributions to normal modes in the 1420–1350-cm⁻¹ range are different for the N₉-H and N₇-H tautomers. Our calculations suggest the assignment of the band at 1418 cm⁻¹ in the Raman spectrum to $\beta(C_2H)$ and $\nu(r)$ modes of the six-membered ring, and not to $\nu(C_6N_{10})$, as proposed by Majoube;[11] our assignment is supported by the presence of a band at 1400 cm⁻¹ in the Ar spectrum of pyrimidine. We propose to assign the band at 1388 cm⁻¹ in the Ar spectrum to $\beta(NH)$ deformations, and not to ring stretching modes.[9] The unassigned bands at 1345 and 1343 cm⁻¹ in the Ar spectrum may correspond to $\nu(r)$ and $\beta(C_2H)$ deformations, with a contribution from $\beta(N_9H)$ in the N₉-H tautomer, for which the calculated (scaled) frequencies are 1381 and 1358 cm⁻¹.

The 4-21G frequencies calculated in this region of the spectrum are in agreement with experimental values. Several new assignments or reassignments of the experimental bands both in the argon matrix and in the crystal are proposed.

1250–1050-cm⁻¹ Range. The experimental bands in this region are predicted to correspond to rocking modes of the –NH₂ group,

(48) Szczęśniak, M.; Nowak, M. J.; Rostkowska, H.; Szczepaniak, K.; Person, W. B.; Shugar, D. *J. Am. Chem. Soc.* **1983**, *105*, 5969.

ring stretching deformations, and ring bending deformations. Lines calculated at 1223 and 1211 cm^{-1} corresponding to the r(NH$_2$) and ν(r) modes in the N$_7$-H and N$_9$-H tautomers, respectively, suggest the experimental bands at 1239 and 1227 cm^{-1} in the Ar spectrum be assigned to these modes, rather than ν-(C$_6$N$_{10}$) and β(NH), as proposed by Sheina et al.[9] on the basis of empirical force field calculations. The calculated frequency difference for the r(NH$_2$) mode in the N$_9$-H and N$_7$-H tautomers is 12 cm^{-1}, in agreement with the band splitting observed experimentally. The bands at 1126 and 1061 cm^{-1} in the Ar spectrum, and at 1164 and 1126 cm^{-1} in the Raman spectrum, are predicted to correspond to ring stretching modes, with contributions from ring bending modes for the lower frequency.

Reassignments of several bands in this region in the argon matrix spectrum are proposed on the basis of 4-21G calculations. The frequencies calculated here are in good agreement with experimental values. Overall, for frequencies calculated in the 3600-1050-cm^{-1} spectral region, the rms deviation from values in the Ar matrix spectrum is 1.5%.

1050-150-cm^{-1} Range. In this region vibrations associated with both in-plane and out-of-plane deformation modes are expected in the spectrum.

In-Plane Modes. The bands at 1017 cm^{-1} in the Ar spectrum and at 1023 cm^{-1} in the Raman spectrum are associated with stretching deformations of the five-membered ring, with contributions from N-H bending modes. The presence of a band at 1056 cm^{-1} in the Ar spectrum of imidazole supports this assignment, as opposed to the assignment of the band at 1023 cm^{-1} to the r(NH$_2$) mode by Majoube.[11]

Lines due to rocking deformations of the -NH$_2$ group, with contributions from ring stretching modes, are calculated at 986 and 979 cm^{-1} for the N$_9$-H and N$_7$-H tautomers, respectively. These modes may be associated with the band at 940 cm^{-1} in the Raman spectrum. This assignment seems to be in better accord with the IR spectrum of pyrimidine, in which no bands have been observed around 950 cm^{-1}, rather than the assignment to δ(r) modes of the six-membered ring suggested by Majoube.[11] It is not clear whether the band at 958 cm^{-1} in the Ar spectrum should be associated with the rocking mode of the amino group or bending deformations of the five-membered ring. There is no corresponding band in the spectrum of imidazole, which would point to the assignment of the band to r(NH$_2$) vibrations; on the other hand, a band is observed at 969 cm^{-1} in the spectrum of deuterated adenine, which suggests the line corresponds to δ(r) deformations.

The band at 898 cm^{-1} in the Raman spectrum is associated with ring bending deformations of the five-membered ring. This assignment is supported by the presence of a band at 900 cm^{-1} in the spectrum of imidazole. Below 900 cm^{-1} one vibration with dominant ν(r) character is predicted for each tautomer. The calculated frequencies at 696 and 692 cm^{-1} for the N$_7$-H and N$_9$-H tautomers, respectively, may be associated with the bands at 655 and 722 cm^{-1} in the Ar and Raman spectra, respectively. Three modes with dominant ring bending character are calculated below 900 cm^{-1}. The lines calculated at 877 and 868 cm^{-1} for the N$_9$-H and N$_7$-H tautomers, respectively, corresponding to bending deformations of the pyrimidine ring, may be associated with the band at 849 cm^{-1} in the Ar spectrum. The calculated frequencies for δ(r) deformation vibrations at 610 cm^{-1} (N$_9$-H tautomer) and 600 cm^{-1} (N$_7$-H tautomer) correspond to the bands at 612 and 620 cm^{-1} in the Ar and Raman spectra, respectively. The bands at 566 and 558 cm^{-1} in the Ar and Raman spectra, respectively, may be assigned to pyrimidine ring bending deformations for which the calculated frequency is 529 cm^{-1} for the N$_9$-H tautomer, and 528 cm^{-1} for the N$_7$-H tautomer. The calculated lowest frequency in-plane vibrations correspond to C-N bending deformations of the amino group; the bands at 535 and 330 cm^{-1} in the Raman spectrum may be associated with the β(C$_6$N$_{10}$) mode.

As was the case for frequencies above 1000 cm^{-1}, several new assignments or reassignments have been proposed in this region of the spectrum. The rms deviation of the scaled 4-21G frequencies for in-plane vibrations from experimental values in the

argon matrix spectrum below 1000 cm^{-1} is 5%, somewhat larger than for higher frequencies.

Out-of-Plane Modes. Not all predicted out-of-plane vibrational modes are observed in the experimental spectra. Frequencies associated with out-of-plane bending C$_2$-H deformations are predicted to occur at 1031 and 1026 cm^{-1}, and C$_8$-H wagging modes at 938 and 968 cm^{-1} in the N$_9$-H and N$_7$-H tautomers, respectively. These bands are not observed in the IR spectrum.

The band at 888 cm^{-1} in the Ar spectrum may be assigned to out-of-plane deformations of the pyrimidine and imidazole rings for which frequencies at 899 and 897 cm^{-1} for the N$_9$-H and N$_7$-H tautomers, respectively, have been calculated. The band at 870 cm^{-1} in the Raman spectrum may also be assigned to out-of-plane ring deformations in the N$_9$-H tautomer. On the basis of empirical force field calculations, Sheina et al.[9] assigned the band at 888 cm^{-1} to C-H wagging vibrations, while Majoube[11] and Letellier et al.[13] suggested the Raman band at 870 cm^{-1} is associated with N-H wagging modes.

Vibrations associated with out-of-plane C$_6$-N$_{10}$ bending deformations in the amino group and ring deformations are predicted around 750 cm^{-1} (758 cm^{-1} for N$_9$-H adenine and 745 cm^{-1} for N$_7$-H adenine). These bands are not observed in the IR spectrum. The Raman band at 797 cm^{-1} associated by Majoube[11] with γ(C$_2$H) vibrations, and by Letellier et al.[13] with χ(r) modes, is assigned here to γ(C$_6$N$_{10}$) and χ(r) deformations.

In the 700-500-cm^{-1} range out-of-plane ring deformation modes are predicted, as well as out-of-plane deformations of the -NH$_2$ group and out-of-plane N-H bending deformations. Five out-of-plane deformation vibrations are predicted for the N$_9$-H tautomer in the 700-500-cm^{-1} range: two ring deformation modes, one N-H wagging mode, and two out-of-plane deformation modes of the -NH$_2$ group. Four out-of-plane deformation modes are predicted for the N$_7$-H tautomer: two ring deformation modes, one N-H wagging mode, and one out-of-plane deformation mode of the -NH$_2$ group. For vibrations arising mainly from ring deformation modes the calculated frequency splitting between corresponding modes in the N$_9$-H and N$_7$-H tautomers is 19-35 cm^{-1}. Out-of-plane deformations of the imidazole ring in the N$_9$-H tautomer are predicted to give rise to a line at 688 cm^{-1}. The band at 680 cm^{-1} in the Raman spectrum may be tentatively assigned to this mode. The corresponding vibration in the N$_7$-H tautomer is predicted to lie at 653 cm^{-1}. A vibration corresponding mainly to out-of-plane deformation modes of the pyrimidine ring is predicted at 601 cm^{-1} for the N$_7$-H tautomer, and at 582 cm^{-1} for the N$_9$-H tautomer. The calculated frequency for the γ(N$_9$H) mode in the N$_9$-H tautomer is 655 cm^{-1} and lies 100 cm^{-1} higher than the corresponding γ(N$_7$H) mode in the N$_7$-H tautomer. This mode may be associated with the band at 650 cm^{-1} in the IR spectrum of polycrystalline adenine, assigned to wagging deformations of the amino group.[11]

Deformation modes of the -NH$_2$ group in N$_9$-H adenine are predicted to give rise to lines at 531 and 525 cm^{-1} with an equal contribution from torsional and wagging deformations. It is interesting to note that the corresponding wagging and torsion deformations of the amino group in the N$_7$-H tautomer are predicted to have significantly different frequencies: they are calculated at 508 and 310 cm^{-1}. The larger frequency difference calculated for the N$_7$-H tautomer may be the result of intramolecular interactions between the amino group in C$_6$ position and the N$_7$-H group. Out-of-plane deformation modes of the amino group, rather than γ(CH) as proposed by Sheina et al.,[9] may be associated with the bands at 582, 566, and 512 cm^{-1} in the Ar spectrum. Letellier et al.[13] associated the bands at 660 and 640 cm^{-1} in the IR spectrum of polycrystalline adenine[11] with wagging deformations of the amino group, and the band at 650 cm^{-1} with C$_8$H wagging deformations; this assignment is contradicted by the presence of identical bands in the spectrum of N- and C$_8$-deuterated adenine.[11]

The three remaining calculated frequencies below 350 cm^{-1} corresponding to out-of-plane ring deformation modes in each tautomer are associated with vibrations of the pyrimidine and imidazole rings, as well as butterfly-type deformation of the whole

Table V. Vibrational Frequencies in 9-Methyladenine (in cm⁻¹) (Contributions in %)

9-methyladenine			9-methyladenine in Ar matrix		polycrystalline 9-methyladenine (Raman)		AMP (Raman)	
calc	scaled^a	descriptn^b	exp	descrptn	exp	descrptn	exp	descrptn
3910	3556	$\nu(N_{10}H_{14})$ (51) $\nu(N_{10}H_{15})$ (49)	3557	$\nu(NH_2)$as	3355	$\nu(NH_2)$		
			3443	$\nu(NH_2)$s				
3780	3437	$\nu(N_{10}H_{14})$ (49) $\nu(N_{10}H_{15})$ (51)	3438		3280	$\nu(NH_2)$		
					3146			
3459	3145	$\nu(C_8H)$ (99)			3104			
3407	3098	$\nu(C_2H)$ (100)			3091	$\nu(NH_2) + \nu(C_8H) + \nu(C_2H)$		
					3031	$\nu(NH_2) + \nu(C_8H) + \nu(C_2H)$		
3301	3002	$\nu(CH_3)$ (100)			2986	$\nu(CH_3)$		
3291	2992	$\nu(CH_3)$ (100)			2956	$\nu(CH_3)$		
3223	2931	$\nu(CH_3)$ (100)			2917	$\nu(CH_3)$		
					2808			
			1644	$\delta(NH_2)$as				
1803	1639	$\delta(NH_2)$ (91)	1636		1680	$\delta(NH_2)$		
			1632					
			1628	$\nu(r) + \delta(NH_2)$s				
			1622					
1749	1590	$\nu(N_9C_{11})$(37)	1615	$\nu(r) + \delta(NH_2)$	1600	$\nu(r) + \delta(NH_2)$	1580	$\nu(r) + \delta(r)$
			1610		1580			
1725	1568	$\nu(C_4C_5)$ (23) $\nu(C_5C_6)$ (21)	1596	$\nu(r)$	1573	$\nu(r) + \delta(r)$		
1680	1528	$\delta(CH_3)$ (82)	1511		1526			
1662	1512	$\nu(C_5N_7)$ (14) $\beta(C_8H)$ (13) $\delta(CH_3)$ (25)	1483	$\nu(r) + \beta(CH)$	1517		1508	$\nu(r) + \beta(C_8H)$
1654	1504	$\delta(CH_3)$ (92)	1476	$\nu(r) + \beta(CH)$	1489	$\beta(CH) + \nu(r)$		
1621	1474	$\nu(C_6N_{10})$ (16) $\nu(N_1C_2)$ (15) $\beta(C_2H)$ (31) $\delta(CH_3)$ (17)	1467		1470	$\beta(CH) + \nu(r)$	1485	$\nu(r) + \beta(C_2H)$
1608	1463	$\nu(C_5N_7)$ (26) $\delta(CH_3)$ (46)	1449	$\delta(CH_3)$	1442	$\delta(CH_3)$as		
			1443					
			1435	$\delta(CH_3)$				
1555	1414	$\nu(C_5C_6)$ (13) $\nu(C_5N_7)$ (27) $\nu(C_8N_9)$ (19)	1425	$\nu(r) + \beta(CH)$	1414	$\delta(r)$	1422	$\nu(r) + \nu(C_6N_{10}) + \beta(C_8H)$
			1411	$\nu(r) + \beta(CH)$				
1499	1363	$\nu(C_6H_{10})$ (13) $\nu(C_8N_9)$ (11) $\beta(C_2H)$ (41)	1370	$\nu(r)$	1373	$\nu(r)$	1377	$\nu(r) + \delta(r)$
			1358	$\delta(CH_3)$				
			1344					
1450	1319	$\nu(C_2N_3)$ (11) $\nu(N_7C_8)$ (22) $\delta(CH_3)$ (14)	1328		1349	$\nu(r) + \beta(C_8H)$	1337	$\nu(r) + \beta(C_2H)$
			1325	$\nu(r)$	1343			
1431	1301	$\nu(C_5C_6)$ (12) $\nu(C_2N_3)$ (22) $\nu(N_1C_6)$ (10) $\beta(C_8H)$ (15)	1295	$\nu(CH) + \nu(r)$	1328	$\delta(r)$	1308	$\beta(C_2H) + \nu(r)$
					1308	$\nu(r) + \beta(CH)$		
1389	1263	$\nu(N_3C_4)$ (29) $\delta(C_8H)$ (34)	1254	$\beta(CH)$	1256	$\delta(r) + \nu(r) + \beta(C_2H)$		
1366	1242	r(NH$_2$) (14) $\delta(CH_3)$ (15)	1237	$\nu(N-CH_3)$			1251	r(NH$_2$) + $\nu(r)$ + $\nu(N-CH_3)$
1314	1195	$\nu(C_5C_6)$ (11) $\nu(N_3C_4)$ (23) $\nu(C_2N_3)$ (13) $\nu(N_1C_2)$ (10) $\beta(C_8H)$ (14) r(NH$_2$) (11)	1234	$\nu(C-NH_2)$	1230	$\beta(C_8H) + \nu(r)$	1218	$\beta(C_8H) + \nu(r)$
1294	1177	$\nu(C_4C_5)$ (13) $\nu(C_2N_3)$ (16) $\nu(N_1C_6)$ (25)			1195		1175	$\nu(r) + \nu(C_6N_{10})$
1271	1156	$\delta(CH_3)$ (90)						
1148	1043	$\nu(C_2N_3)$ (11) r(NH$_2$) (12) $\delta(r_1)$ (13)			1085	$\nu(r) + \nu(N-CH_3)$		
1133	1031	$\nu(N_7C_8)$ (31) $\delta(r_4)$ (25) $\delta(CH_3)$ (31)	1044	$\beta(CH)$	1047	$\delta(CH_3)$		
1133	1030	$\gamma(C_2H)$ (100)			950			
1071	974	$\nu(C_6N_{10})$ (12) $\nu(N_1C_2)$ (37) r(NH$_2$) (24)	944	$\nu(r) + \delta(r)$	1019	r(NH$_2$) + $\delta(CH_3)$		
1029	936	$\gamma(C_8H)$ (85)			905			
986	897	$\gamma(C_8H)$ (18) $\gamma(C_6N_{10})$ (16) $\chi(r_1)$ (42) $\chi(r_4)$ (21)	894	$\gamma(CH)$				

Table V (Continued)

9-methyladenine			9-methyladenine in Ar matrix		polycrystalline 9-methyladenine (Raman)		AMP (Raman)	
calc	scaled[a]	descriptn[b]	exp	descrptn	exp	descrptn	exp	descrptn
969	881	$\nu(N_1C_6)$ (11) $\delta(r_1)$ (35) $\delta(r_3)$ (15)	843	$\delta(r)$	841		912	$\delta(r) + \nu(r)$
829	754	$\gamma(C_6N_{10})$ (38) $\chi(r_5)$ (17) $\chi(r_6)$ (14)	800	$\delta(r)$	799	$\gamma(CH)$		
801	729	$\nu(N_7C_8)$ (10) $\nu(C_4N_9)$ (27) $\delta(r_3)$ (26) $\delta(r_4)$ (22)			744		727	$\delta(CH_3) + \nu(r)$
770	700	$\nu(C_4C_5)$ (26) $\nu(N_1C_6)$ (11)	681	$\delta(r)$	718	δr		
			645	$\delta(r)$				
751	683	$\chi(r_4)$ (11) $\chi(r_5)$ (70)						
644	585	$\chi(r_1)$ (31) $\chi(r_2)$ (15) $\chi(r_3)$ (24) $\chi(r_4)$ (10) $\chi(r_5)$ (13)						
624	568	$\nu(N_9C_{11})$ (16) $\delta(C_6N_{10})$ (17) $\delta(r_5)$ (31)			606	$\delta(r) + \delta(CH_3) + \beta(C_6N_{10})$	570	$\beta(C_6N_{10}) + \delta(r)$
582	529	$t(NH_2)$ (19) $w(NH_2)$ (73)	581	$w(NH_2)$	562			
581	529	$\nu(N_1C_2)$ (11) $\delta(r_2)$ (67)			542	$\delta(r)$	535	$\delta(r) + \nu(C_6N_{10})$
580	528	$\nu(C_8N_9)$ (11) $\nu(C_4N_9)$ (15) $\beta(N_9C_{11})$ (13) $\delta(r_3)$ (30)			530	$\delta(r)$		
573	522	$t(NH_2)$ (66) $w(NH_2)$ (25)	575	$w(NH_2)$				
360	327	$\gamma(N_9C_{11})$ (11) $\chi(r_2)$ (14) $\chi(r_3)$ (45) $\chi(r_4)$ (19)			355		385	$\beta(C_6N_{10}) + \delta(CH_3)$
335	305	$\beta(C_6N_{10})$ (46) $\beta(N_9C_{11})$ (29)			312		325	$\beta(C_6N_{10}) + \delta(CH_3) + \delta(r) + \nu(r)$
297	270	$\gamma(C_6N_{10})$ (12) $\gamma(N_9C_{11})$ (29) $\chi(r_6)$ (43)			245			
229	208	$\beta(C_6N_{10})$ (14) $\beta(N_9C_{11})$ (40) $\delta(r_3)$ (17)			205			
227	206	$\gamma(N_9C_{11})$ (14) $\chi(r_2)$ (57) $\chi(r_6)$ (22)						
					155			
131	119	$\gamma(N_9C_{11})$ (40) $\chi(r_3)$ (15) $\chi(r_4)$ (14)			130			
					113			
					90			
					64			
-79	<100	$t(CH_3)$ (100)			49			
					38			

[a] The scaling factor is 0.91. [b] Contributions greater than 10% are given.

molecule. These vibrations are not observed in the Ar spectrum. The band at 240 cm^{-1} in the Raman spectrum may be associated with the butterfly ring deformation mode in N_9-H adenine.

The calculated vibrational spectra of the N_9-H and N_7-H tautomeric forms of adenine presented here have enabled us to check band assignments in the experimental spectra of adenine in the argon matrix and in the crystal and to propose several new assignments. Comparison of the Raman spectrum of polycrystalline adenine[11] with the spectra calculated for the two tautomers examined in this work shows that only the N_9-H form is detected in the crystal, in agreement with X-ray data for single crystals of adenine.[33]

The interpretation of the spectrum of adenine in the low-temperature argon matrix is more complex. The energy difference between the two tautomers calculated here ($\Delta E_0 = \Delta E^{SCF} + \Delta E_0^{vib}$ = 10.6 kcal mol^{-1}) suggests that the N_7-H tautomer should not

be detected spectroscopically. On the other hand, as found above, the Ar matrix spectrum of adenine is best analyzed when the N_9-H and N_7-H tautomers are both included. The experimental Ar spectrum contains many bands that are close to frequencies calculated for the N_7-H tautomer in all parts of the spectrum. In the spectra of adenine in argon, neon, and nitrogen matrices measured by Nowak et al.[10] in the 3600–3400-cm^{-1} region corresponding to NH stretching vibrations, two bands assigned to $\nu(NH)$ are observed in the Ar and N_2 spectra (at 3498 and 3489 cm^{-1}, and 3486 and 3477 cm^{-1}, respectively), and only one band in the Ne spectrum (at 3503 cm^{-1}). Nowak et al.[10] argued that a change of environment from argon to neon should not affect the tautomeric distribution in adenine and that the band splitting in the Ar spectrum is a "matrix effect". However, the influence of the trapping medium on the tautomeric equilibrium and spectrum of adenine is not clear.[49] Although it might be expected

Table VI. Vibrational Frequencies in Adenine-d_3 (in cm^{-1}) (Contributions in %)

N9–D adenine-d_3 calc	scaled[a]	descrptn[b]	N7–D adenine-d_3 calc	scaled[a]	descrptn[b]	adenine-d_3 in Ar matrix exp	descrptn	polycrystalline adenine-d_3 (Raman) exp	descrptn
3468	3153	ν(C₈H) (99)						3120	ν(C₈H)
			3461	3147	ν(C₈H) (99)				
			3415	3105	ν(C₂H) (99)				
3410	3101	ν(C₂H) (99)							
						2679 sh			
			2905	2641	ν(N₁₀D₁₄) (42)	2672	ν(ND₂)as		
					ν(N₁₀D₁₅) (57)	2667	ν(ND₂)as		
2898	2635	ν(N₁₀D₁₄) (50)				2605	ν(ND)		
		ν(N₁₀D₁₅) (50)				2603 sh			
			2837	2580	ν(N₇D) (98)	2597	ν(ND)		
						2586 sh			
2830	2573	ν(N₉D) (100)				2548			
			2738	2489	ν(N₁₀D₁₄) (57)	2520			
					ν(N₁₀D₁₅) (42)	2505	ν(ND₂)s		
2729	2482	ν(N₁₀D₁₄) (49)				2502	ν(ND₂)s		
		ν(N₁₀D₁₅) (49)							
			1747	1588	ν(C₅C₆) (37) ν(C₂N₃) (13)	1619			
1743	1585	ν(C₅C₆) (39)				1610	ν(r)	1610	ν(r) + δ(r)
1723	1566	ν(C₄C₅) (18) ν(N₃C₄) (28) ν(N₁C₆) (12)						1568	ν(r) + δ(r)
			1706	1551	ν(C₄C₅) (18) ν(N₃C₄) (25) ν(N₁C₆) (18)				
1639	1490	ν(C₆N₁₀) (15) ν(N₇C₈) (30) δ(C₂H) (10) β(C₈H) (13)				1497	ν(r) + β(ND)	1514	ν(r) + ν(C₆N₁₀)
			1624	1476	ν(C₆N₁₀) (13) ν(C₈N₉) (12) β(C₂H) (34)	1485	ν(r) + β(CH)		
1618	1471	ν(C₆N₁₀) (10) ν(C₂N₃) (10) ν(N₁C₆) (13) ν(N₇C₈) (24) β(C₂H) (28)				1482	ν(r) + β(CH)	1466	ν(r) + β(C₂H)
			1612	1466	ν(N₁C₆) (11) ν(C₈N₉) (40) β(C₂H) (15) β(C₈H) (20)	1448 1444 1442 1438			
1544	1404	ν(C₆N₁₀) (13) ν(C₄C₅) (24) ν(C₄N₉) (10) β(C₂H) (21) δ(r₁) (11)				1416 1414	ν(r) + β(CH) ν(r) + β(CH)	1424	ν(r) + β(C₈H) + ν(C₆N₁₀)
			1505	1369	ν(C₆N₁₀) (24) ν(C₄C₅) (24) β(C₂H) (21)	1361	ν(r)		
1484	1349	ν(C₄N₉) (23) β(C₂H) (29)				1340		1372	ν(r) + δ(r)
			1471	1337	ν(C₂N₃) (26) ν(C₅N₇) (15) ν(C₈N₉) (10) β(C₈H) (12) δ(r₁) (11)	1325 1319 sh	ν(r) ν(r)		
1432	1302	ν(C₄C₅) (10) ν(C₂N₃) (13) ν(N₁C₂) (28)	1434	1304	ν(C₄C₅) (15) ν(N₃C₄) (10) ν(N₁C₂) (11) ν(C₄N₉) (17) β(C₂H) (13)	1310 sh		1333	ν(r) + β(C₂H)
			1428	1298	ν(N₇C₈) (20) β(C₈H) (32)				
1419	1290	ν(N₇C₈) (11) β(C₈H) (49)				1290	β(CH) + ν(r)	1305	δ(ND₂) + ν(r) + β(C₂H)
						1261	β(CH)		
			1356	1233	ν(N₁C₂) (14) ν(N₇C₈) (21) β(N₇D) (15)				
1337	1216	ν(C₂N₃) (25) ν(N₁C₂) (19) ν(C₈N₉) (19) β(N₉D) (11)						1250	δ(ND₂) + β(CH)
1317	1198	δ(ND₂) (58) δ(r₁) (10)	1317	1198	δ(ND₂) (71)			1230	β(C₈H) + ν(r)
			1288	1171	ν(C₂N₃) (22) ν(N₁C₂) (13) ν(N₁C₆) (23)	1186	ν(C–ND₂)		

Table VI (Continued)

N9–D adenine-d_3			N7–D adenine-d_3			adenine-d_3 in Ar matrix		polycrystalline adenine-d_3 (Raman)	
calc	scaled[a]	descrptn[b]	calc	scaled[a]	descrptn[b]	exp	descrptn	exp	descrptn
1285	1168	$\nu(N_3C_4)$ (12) $\nu(N_1C_2)$ (10) $\nu(N_1C_6)$ (10) $\nu(C_8N_9)$ (20) $\beta(N_9D)$ (10)						1178	$\gamma(r)$
1264	1149	$\nu(C_2N_3)$ (12) $\nu(N_1C_6)$ (13) $\nu(C_5N_7)$ (29) $r(ND_2)$ (11)						1100	$\delta(ND_2) + \nu(C_6N_{10})$
			1256	1142	$\nu(N_1C_2)$ (19) $\nu(C_5N_7)$ (19) $\nu(N_7C_8)$ (15) $\beta(C_8H)$ (11)	1099	$\beta(CH)$		
1181	1074	$\nu(C_6N_{10})$ (10) $\nu(N_3C_4)$ (10) $\nu(C_4N_9)$ (15) $\delta(ND_2)$ (10) $\delta(r_5)$ (17)						970	$\delta(r) + \nu(r) + \beta(N_9D)$
			1149	1044	$\nu(C_6N_{10})$ (13) $\nu(C_4N_9)$ (25) $\delta(r_5)$ (14)				
1134	1031	$\gamma(C_2H)$ (100)							
			1128	1025	$\gamma(C_2H)$ (100)				
			1065	968	$\gamma(C_8H)$ (96)				
			1039	945	$\nu(N_7C_8)$ (23) $\beta(N_7D)$ (11) $\delta(r_4)$ (44)	969	$\delta(r)$		
1032	938	$\gamma(C_8H)$ (84)							
1018	926	$\nu(C_4C_5)$ (10) $\nu(C_8N_9)$ (19) $\delta(r_1)$ (61)				958	$\beta(ND)$	933	$\beta(N_9D) + \nu(r)$
988	898	$\gamma(C_8H)$ (19) $\gamma(C_6N_{10})$ (16) $\chi(r_1)$ (42) $\chi(r_4)$ (21)	986	896	$\gamma(C_6N_{10})$ (14) $\chi(r_1)$ (50) $\chi(r_4)$ (26)	864	$\gamma(CH)$		
			975	887	$\beta(N_7D)$ (28) $\delta(r_1)$ (13) $\delta(r_4)$ (27)	858	$\gamma(CH)$		
973	884	$\nu(C_8N_9)$ (14) $\beta(N_9D)$ (24) $\delta(r_1)$ (25)						888	$\delta(r)$
949	863	$\beta(N_9D)$ (24) $r(ND_2)$ (13) $\delta(r_1)$ (10)				846	$\delta(r)$		
			933	848	$\beta(N_7D)$ (23) $\delta(r_1)$ (15) $\delta(r_3)$ (15)				
927	843	$\nu(N_1C_6)$ (19) $r(ND_2)$ (41)	925	841	$\nu(N_1C_2)$ (10) $\nu(N_1C_6)$ (19) $r(ND_2)$ (51)	794	$\delta(r)$	853	$\delta(ND_2) + \nu(r)$
828	753	$\gamma(C_6N_{10})$ (40) $\chi(r_4)$ (16) $\chi(r_6)$ (15)						798	$\gamma(C_2H)$
			818	743	$\gamma(C_6N_{10})$ (44) $\chi(r_4)$ (12) $\chi(r_5)$ (15) $\chi(r_6)$ (15)				
			754	686	$\nu(N_3C_4)$ (30) $\nu(C_5N_7)$ (10) $\delta(r_3)$ (13) $\delta(r_5)$ (21)				
749	681	$\chi(r_4)$ (12) $\chi(r_5)$ (70)						650	
747	679	$\nu(N_3C_4)$ (24) $\nu(C_5N_7)$ (12) $\delta(r_3)$ (16) $\delta(r_5)$ (18)						706	$\nu(r) + \nu(C_6N_{10})$
			716	651	$\chi(r_3)$ (13) $\chi(r_4)$ (16) $\chi(r_5)$ (60)				
			658	599	$\gamma(C_6N_{10})$ (10) $\chi(r_1)$ (28) $\chi(r_2)$ (18) $\chi(r_3)$ (18) $\chi(r_5)$ (21)				

Table VI (Continued)

N$_9$–D adenine-d_3			N$_7$–D adenine-d_3			adenine-d_3 in Ar matrix		polycrystalline adenine-d_3 (Raman)	
calc	scaled[a]	descrptn[b]	calc	scaled[a]	descrptn[b]	exp	descrptn	exp	descrptn
645	586	ν(C$_5$C$_6$) (30) δ(r$_3$) (19) δ(r$_5$) (18)						602	ν(r) + β(C$_6$N$_{10}$)
643	584	χ(r$_1$) (31) χ(r$_2$) (16) χ(r$_3$) (23) χ(r$_5$) (12)	640	582	ν(C$_5$C$_6$) (28) ν(C$_4$N$_9$) (13) δ(r$_3$) (24) δ(r$_5$) (14)				
571	520	δ(r$_2$) (70)						560	δ(r) + ν(r) + β(C$_6$N$_{10}$)
			569	517	ν(C$_6$N$_{10}$) (11) δ(r$_2$) (66)				
542	493	γ(N$_9$D) (89)						508	
			528	480	ν(C$_5$N$_7$) (10) β(C$_6$N$_{10}$) 20 r(ND$_2$) (12) δ(r$_3$) (19)				
521	474	ν(C$_4$N$_9$) (11) β(C$_6$N$_{10}$) (21) δ(r$_3$) (21)						525	δ(r) + ν(C$_6$N$_{10}$)
			475	432	γ(N$_7$D) (87)				
458	416	t(ND$_2$) (84)	428	389	t(ND$_2$) (47) w(ND$_2$) (36)	407	w(ND$_2$)	473 (IR)	w(ND$_2$)
419	381	w(ND$_2$) (95)							
345	314	γ(C$_6$N$_{10}$) (11) χ(r$_2$) (11) χ(r$_3$) (39) χ(r$_4$) (24) χ(r$_6$) (10)	342	311	γ(C$_6$N$_{10}$) (14) χ(r$_2$) (11) χ(r$_3$) (33) χ(r$_4$) (22) χ(r$_6$) (10)				
			284	258	t(ND$_2$) (23) w(ND$_2$) (29) χ(r$_2$) (25) χ(r$_6$) (20)				
			283	257	β(C$_6$N$_{10}$) (55) δ(r$_3$) (12)				
265	241	β(C$_6$N$_{10}$) (55) δ(r$_3$) (13)						302	β(C$_6$N$_{10}$) + δ(r)
246	224	χ(r$_2$) (20) χ(r$_6$) (64)						238	
			233	212	w(ND$_2$) (25) χ(r$_3$) (12) χ(r$_6$) (42)				
192	175	γ(C$_6$N$_{10}$) (20) χ(r$_1$) (15) χ(r$_2$) (43) χ(r$_3$) (15)							
			162	148	t(ND$_2$) (15) χ(r$_2$) (36) χ(r$_3$) (11)				

[a] The scaling factor is 0.91. [b] Contributions greater than 10% are given.

that in nitrogen matrices—in contrast to argon and neon—intermolecular interactions of the trapped system with N$_2$ molecules might influence the tautomeric equilibrium,[7,48] the spectra of adenine isolated in Ar and N$_2$ matrices are similar in the region corresponding to NH stretching vibrations and are different from the spectrum in the Ne matrix. It might also be argued that "matrix size effects" could occur; the smaller the particles of the trapping medium, the less effect they should have on the behavior of the trapped system. From the analysis of the ν(NH) region in adenine spectra in the three matrices used by Nowak et al.[10] it is evident that the influence of the trapping medium is not systematic and that the simple arguments presented above do not explain the observed spectra. The agreement between the 4-21G frequencies for the N$_9$–H and N$_7$–H tautomers with the bands in the argon matrix spectrum in the entire spectral range, as well as the correspondence between the calculated tautomeric frequency differences and the experimental band splittings, supports the existence of both tautomers in the low-temperature matrix. The calculated energy difference between the two tautomers suggests that only the N$_9$–H tautomer should be detected, although no free

energy data from the gas phase are available and the reliability of the ab initio energy calculations at the 4-21G level is not established. Further experimental and theoretical investigations are needed to elucidate this discrepancy.

The rms deviation of the frequencies observed in the Raman spectrum of polycrystalline adenine from the bands assigned to the N$_9$–H tautomer in the Ar matrix spectrum is 4% in the entire spectral range; it is 1% for frequencies higher than 1200 cm^{-1}. The influence of intermolecular interactions in the crystal on intramolecular vibrations cannot be readily analyzed from the comparison of the two spectra, as only 17 common bands out of the expected 39 lines for adenine are observed in both spectra; most of the bands assigned to the same normal modes in the two spectra occur above 1000 cm^{-1}. Intermolecular interactions in the crystal appear to be significant for bending modes of the amino group and ring bending modes. It is expected that intermolecular interactions will increase the frequencies of out-of-plane vibrations,[50] but a detailed analysis could not be performed, as only one band assigned to the same normal mode [γ(CH)] is observed in both spectra.

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3.2.2. 9-Methyladenine. The results obtained for 9-methyladenine (9-MA) are presented in Table V and compared with the Ar spectrum of 9-MA[9] and the Raman spectra of polycrystalline 9-MA[12] and 5'-AMP in H_2O.[14,15,51]

3600–3000-cm⁻¹ Range. In this region, $\nu(NH_2)$ and $\nu(CH)$ stretching modes are observed. The bands at 3557, 3443, and 3438 cm⁻¹ in the Ar matrix spectrum are assigned to antisymmetric and symmetric stretching vibrations of the –NH_2 group. The bands assigned to $\nu(NH_2)$ modes in the Raman spectrum of crystalline 9-MA are observed at 3355 and 3280 cm⁻¹, i.e., about 200 cm⁻¹ below the 4-21G and argon matrix frequencies; this frequency shift may be due to intermolecular interactions—both hydrogen bonds and/or planar associations with neighboring molecules. The calculated $\nu(C_2H)$, $\nu(C_8H)$, and $\nu(CH_3)$ stretching deformations are not observed in the Ar spectrum of 9-MA and Raman spectrum of AMP. The bands in the 3150–2800-cm⁻¹ region of the Raman spectrum of 9-MA are associated with these vibrations.

2000–1620-cm⁻¹ Range. The bands at 1628 and 1622 cm⁻¹ in the Ar spectrum and at 1680 cm⁻¹ in the Raman spectrum of 9-MA may be assigned to the scissoring mode of the NH_2 group.

1620–1150-cm⁻¹ Range. The experimental bands in this region are assigned to stretching ring deformations, and C–H and NH_2 bending vibrations. Our calculations suggest that the bands at 1615 and 1610 cm⁻¹ correspond to $\nu(r)$ modes, rather than r(NH_2) modes, as proposed by Sheina et al.;[9] our assignment is supported by the presence of similar bands in the experimental spectra of deuterated adenine and its 9-methyl derivative (see sections 3.2.4 and 3.2.5). The frequencies for rocking deformation modes of the –NH_2 group are calculated to lie below 1250 cm⁻¹. Savoie et al.[12] assigned the band at 1573 cm⁻¹ in the Raman spectrum of 9-MA to ring stretching and bending modes; the calculated normal mode at 1568 cm⁻¹ has no ring bending character. Ring bending deformations are predicted to contribute to vibrations below 1100 cm⁻¹. For bands below 1550 cm⁻¹ contributions from CH_3 bending modes are predicted. The unassigned bands at 1526 and 1517 cm⁻¹ in the Raman spectrum of 9-MA may be associated with bending modes of the methyl group. We assign the band at 1414 cm⁻¹ in the Raman spectrum of 9-MA to ring stretching modes, and not to ring bending deformations, as suggested by Savoie.[12] The calculated vibration at 1363 cm⁻¹ has a dominant $\beta(C_2H)$ character; this mode may correspond to the band at 1373 cm⁻¹ in the Raman spectrum of 9-MA, associated by Savoie et al.[12] with pyrimidine ring stretching deformations. The band at 1237 cm⁻¹ in the Ar spectrum has been assigned by Sheina et al.[9] to stretching deformations of the N_9–C_{11} bond; our results have this band correspond to r(NH_2) and $\beta(CH_3)$ modes, the $\nu(N_9C_{11})$ mode giving rise to a line at 1590 cm⁻¹ associated with the experimental bands at 1615 and 1610 cm⁻¹. The band at 1234 cm⁻¹ in the Ar spectrum is associated with stretching deformations of the pyrimidine ring, with contributions from $\beta(C_8H)$ and r(NH_2) modes. Sheina et al.[9] assign this band to C_6–N_{10} stretching vibrations in the amino group. The unassigned band at 1195 cm⁻¹ in the Raman spectrum of 9-MA is associated here with $\nu(r)$ modes.

1150–0-cm⁻¹ Range. In this region, the bands observed experimentally are associated with both in-plane and out-of-plane deformation modes. The assignments proposed here are in general agreement with those suggested by Sheina et al.[9] for the Ar spectrum of methyladenine and by Majoube[51] for the solution Raman spectrum of AMP.[14,15] The discrepancies between 4-21G normal modes and force field assignments are described below. Sheina et al.[9] have assigned the band at 894 cm⁻¹ in the matrix spectrum to CH wagging modes; in the 4-21G spectrum this band is associated with out-of-plane ring bending deformations. The unassigned bands at 950 and 905 cm⁻¹ in the Raman spectrum of 9-MA may correspond to $\gamma(CH)$ vibrations, calculated at 1030 and 936 cm⁻¹ for C_2H and C_8H, respectively. The band at 841 cm⁻¹ in the Raman spectrum of 9-MA has been assigned by Savoie et al.[12] to wagging CH modes; this band may correspond to either

in-plane or out-of-plane ring bending deformations. The band at 727 cm⁻¹ in the Raman spectrum of AMP has been associated by Majoube[51] with N_9–C_{11} bending deformations; here this band is assigned to ring breathing modes, in agreement with similar modes calculated for adenine (see Table IV) and force field assignments by Tsuboi et al.[16] for AMP. The unassigned band at 744 cm⁻¹ in the Raman spectrum of 9-MA may correspond to ring breathing deformations. The band at 681 cm⁻¹ in the Ar spectrum, assigned by Sheina et al.[9] to ring bending modes, may correspond to ring stretching vibrations. The band at 530 cm⁻¹ in the Raman spectrum of 9-MA, associated by Savoie et al.[12] with ring out-of-plane deformations, may be assigned to either in-plane ring bending modes (calculated at 528 cm⁻¹) or out-of-plane torsions of the –NH_2 group (522 cm⁻¹). The other out-of-plane vibration of the amino group, calculated at 529 cm⁻¹, may correspond to the unassigned band at 562 cm⁻¹.

The bands at 385 and 325 cm⁻¹ in the spectrum of AMP have been associated by Majoube[51] with $\beta(C_6N_{10})$ and $\beta(N_9R)$ modes; our calculations predict these modes to give rise to lines at 305 and 208 cm⁻¹. Bands at 355 and 312 cm⁻¹ are also observed in the Raman spectrum of 9-MA.[12] Kyogoku et al.[17] have shown that the band around 350 cm⁻¹ in the Raman spectrum of AMP is depolarized and thus corresponds to an out-of-plane vibration. In adenine only one $\beta(C_6N_{10})$ mode has been calculated at 265 cm⁻¹ and assigned to the band at 330 cm⁻¹ in the Raman spectrum. Thus, we propose the assignment of the bands at 312 and 325 cm⁻¹ in the Raman spectra of 9-MA and AMP, respectively, to β-(C_6N_{10}) and $\beta(N_9R)$ modes, and bands at 355 and 385 cm⁻¹ to out-of-plane skeletal modes (calculated at 327 cm⁻¹).

For the lowest frequency vibration in 9-MA, a negative eigenvalue was obtained with the molecular geometry shown in Table V during evaluation of the second energy derivatives in the 4-21G calculations. This normal mode corresponds to the torsion of the methyl group. The energy hypersurface along the coordinate describing the torsion of the methyl group has a rather wide and flat well in the vicinity of the minimum energy conformation: rotation of the methyl group about the N_9–C_{11} bond by 10° lowered the total energy by 5 cal mol⁻¹. It is expected that a minor change in the torsional coordinate would yield a real vibrational frequency without significantly affecting the energy of the system. Such an adjustment of the 4-21G geometry presented in Table I was not performed, as recalculating the spectrum of 9-methyladenine with a skewed methyl group would have affected only one vibrational mode and been very time-consuming. Harmonic force constants for the libration of methyl groups in different systems cover a broad range.[50,52,53] For 1-methyluracil, the frequency for twisting of the methyl group has been calculated at 75 cm⁻¹.[2] The –CH_3 torsional mode in 9-methyladenine is also expected below 100 cm⁻¹.

Overall, a good agreement between the 4-21G frequencies and the values observed in the argon matrix has been obtained for 9-methyladenine. The rms difference between the calculated and experimental frequencies is 3%.

3.2.3. Isotopic Spectra. As a test of the accuracy of assignments of experimental bands to vibrational modes in adenine and 9-MA the spectra of N-deuterated derivatives of adenine and 9-MA have been calculated with the 4-21G force constants. The geometry and force field obtained for the undeuterated systems were used in these calculations; the 4-21G force constants will be published elsewhere.[38] The results for adenine-d_3 are shown in Table VI, together with experimental Ar matrix and Raman spectra. Table VII presents the results for 9-MA-d_2, as well as the Ar matrix spectrum of 9-MA-d_2 and the Raman spectrum of AMP-d_2.

3.2.4. Adenine-d_3. The vibrational spectra calculated for N_9 and N_7 tautomers of N-deuterated adenine are compared with Ar matrix[9] and Raman[11] spectra in Table VI. The bands from 2672 to 2502 cm⁻¹ in the matrix spectrum are associated with antisymmetric and symmetric stretching deformations of the –ND_2

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Table VII. Vibrational Frequencies in 9-Methyladenine-d_2 (in cm^{-1}) (Contributions in %)

9-methyladenine-d_2			9-methyladenine-d_2 in Ar matrix		AMP-d_2 (Raman)	
calc	scaled[a]	descrptn[b]	exp	descrptn	exp	descrptn
			3567			
			3507			
			3497			
3459	3145	ν(C$_8$H) (100)			3120	ν(C$_8$H)
3407	3098	ν(C$_2$H) (100)			3053	ν(C$_2$H)
3301	3002	ν(CH$_3$) (100)				
3291	2992	ν(CH$_3$) (100)				
3223	2931	ν(CH$_3$) (100)				
			2670			
2898	2635	ν(N$_{10}$D$_{14}$) (50)	2591			
		ν(N$_{10}$D$_{15}$) (50)	2581			
			2535			
2729	2482	ν(N$_{10}$D$_{14}$) (49)	2511	ν(ND$_2$)s		
		ν(N$_{10}$D$_{15}$) (50)				
			1629			
1744	1585	ν(N$_9$C$_{11}$) (37)	1620	ν(r)	1624	ν(r) + δ(r)
		ν(C$_5$C$_6$) (10)	1615			
			1603			
1724	1568	ν(C$_5$C$_6$) (14)	1592	ν(r)	1577	ν(r) + δ(r)
		ν(N$_3$C$_4$) (26)				
		ν(N$_1$C$_2$) (10)				
		ν(C$_8$N$_9$) (10)				
1680	1528	δ(CH$_3$) (82)				
1662	1511	ν(C$_5$N$_7$) (12)	1497	ν(r) + β(CH)	1520	ν(r) + β(C$_8$H)
		β(C$_8$H) (12)				
		δ(CH$_3$) (21)				
1654	1504	δ(CH$_3$) (92)	1488	ν(r) + β(ND)		
1624	1477	ν(C$_6$N$_{10}$) (17)	1475		1485	ν(r) + β(C$_2$H)
		ν(N$_1$C$_2$) (14)				
		β(C$_2$H) (27)				
		δ(CH$_3$) (25)				
1608	1462	ν(C$_5$N$_7$) (27)	1446	δ(CH$_3$)		
		β(C$_2$H) (10)	1432	δ(CH$_3$)		
		δ(CH$_3$) (42)				
1556	1415	ν(C$_5$C$_6$) (14)	1416	ν(r) + β(CH)	1426	ν(r) + ν(C$_6$H$_{10}$) + β(C$_8$H)
		ν(C$_5$N$_7$) (25)	1410			
		ν(C$_8$N$_9$) (16)				
			1375	ν(r)		
1503	1367	ν(C$_6$N$_{10}$) (13)	1369		1383	ν(r) + δ(r)
		ν(C$_8$N$_9$) (14)				
		β(C$_2$H) (36)				
			1359	δ(CH$_3$)		
1456	1324	ν(C$_2$N$_3$) (12)	1342		1340	ν(r) + β(C$_2$H)
		ν(N$_7$C$_8$) (20)	1326	ν(r)		
		δ(CH$_3$) (14)				
			1312			
1424	1295	ν(C$_5$C$_6$) (14)	1293sh		1307	δ(ND$_2$) + β(C$_2$H)
		ν(C$_2$N$_3$) (18)	1290	β(CH) + ν(r)		
		ν(N$_1$C$_6$) (14)				
		β(C$_8$H) (22)				
1386	1261	ν(N$_3$C$_4$) (29)	1259	β(CH)		
		β(C$_8$H) (23)				
		δ(CH$_3$) (15)				
1348	1226	ν(C$_4$N$_9$) (14)	1235	β(ND) + β(CH)		
		β(C$_8$H) (16)				
1307	1189	δ(ND$_2$) (57)				
1301	1183	ν(C$_4$C$_5$) (13)	1194	ν(C–ND$_2$)	1183	ν(r) + ν(N–CH$_3$)
		ν(N$_3$C$_4$) (14)				
		ν(C$_2$N$_3$) (13)				
		ν(N$_1$C$_2$) (16)				
		δ(ND$_2$) (13)				
1271	1156	δ(CH$_3$) (90)				
1264	1149	ν(N$_3$C$_4$) (12)				
		ν(N$_1$C$_2$) (11)				
		ν(N$_1$C$_6$) (32)				
		r(ND$_2$) (10)				
1134	1031	ν(N$_7$C$_8$) (37)	1063	β(CH)		
		δ(r$_4$) (18)				
		δ(CH$_3$) (36)				
1133	1030	γ(C$_2$H) (100)				
1114	1013	ν(C$_6$N$_{10}$) (11)	957	δ(r)		
		δ(r$_1$) (10)				
		δ(r$_4$) (14)				
1029	936	γ(C$_8$H) (85)	937	γ(CH)		

Table VII (Continued)

9-methyladenine-d_2			9-methyladenine-d_2 in Ar matrix		AMP-d_2 (Raman)	
calc	scaled[a]	descrptn[b]	exp	descrptn	exp	descrptn
986	896	$\gamma(C_8H)$ (18) $\gamma(C_6N_{10})$ (16) $\chi(r_1)$ (42) $\chi(r_4)$ (21)	883	$\gamma(CH)$		
968	880	$\nu(N_1C_6)$ (11) $\delta(r_1)$ (34) $\delta(r_3)$ (14)	868	$\delta(r)$	910	$\delta(r) + \nu(r)$
932	847	$\nu(N_1C_2)$ (27) $r(ND_2)$ (52)				
			806	$\delta(r)$		
827	752	$\gamma(C_6N_{10})$ (41) $\chi(r_5)$ (16) $\chi(r_6)$ (15)				
801	728	$\nu(N_7C_8)$ (10) $\nu(C_4N_9)$ (27) $\delta(r_3)$ (26) $\delta(r_4)$ (21)			721	$\delta(CH_3)$
762	693	$\nu(C_4C_5)$ (27) $\nu(N_1C_6)$ (10) $\delta(r_4)$ (10) $\delta(r_5)$ (13)	664	$\delta(r)$		
748	680	$\chi(r_4)$ (12) $\chi(r_5)$ (71)				
643	585	$\chi(r_1)$ (30) $\chi(r_2)$ (16) $\chi(r_3)$ (23) $\chi(r_4)$ (10) $\chi(r_5)$ (15)				
591	537	$\nu(N_9C_{11})$ (21) $\nu(C_4N_9)$ (12) $\delta(r_5)$ (31)			560	$\beta(C_6N_{10}) + \delta(r)$
577	525	$\beta(N_9C_{11})$ (14) $\delta(r_2)$ (17) $\delta(r_3)$ (22)			530	$\delta(r)$
571	519	$\nu(N_1C_6)$ (13) $\delta(r_2)$ (54)				
455	414	$t(ND_2)$ (83)	412	$w(ND_2)$		
419	381	$w(ND_2)$ (93)				
356	323	$\gamma(N_9C_{11})$ (13) $\chi(r_2)$ (10) $\chi(r_3)$ (47) $\chi(r_4)$ (18)			385	$\beta(C_6N_{10}) + \delta(CH_3)$
314	286	$\beta(C_6N_{10})$ (40) $\beta(N_9C_{11})$ (36)			300	$\beta(C_6N_{10}) + \delta(CH_3) + \delta(r)$
289	263	$\gamma(C_6N_{10})$ (14) $\gamma(N_9C_{11})$ (27) $\chi(r_6)$ (41)				
223	203	$\gamma(N_9C_{11})$ (16) $\chi(r_2)$ (55) $\chi(r_6)$ (21)				
221	201	$\beta(C_6N_{10})$ (22) $\beta(N_9C_{11})$ (32) $\delta(r_3)$ (17)				
127	116	$\gamma(N_9C_{11})$ (37) $\chi(r_3)$ (15) $\chi(r_4)$ (14)				
	<100	$t(CH_3)$ (100)				

[a] The scaling factor is 0.91. [b] Contributions greater than 10% are given.

group and $\nu(ND)$ stretching vibrations. The calculated frequency splitting between the two tautomers is 6–7 cm^{-1} for these modes. The presence of bands at 1619 and 1610 cm^{-1} in the Ar spectrum, and at 1610 cm^{-1} in the Raman spectrum, confirms the assignment of the band at 1618 cm^{-1} in the matrix spectrum of adenine to pyrimidine ring stretching modes. The band at 1497 cm^{-1} in the Ar spectrum has been assigned by Sheina et al.[9] to $\beta(ND)$ bending deformations. Our calculations suggest the assignment of bands at 1497, 1485, and 1482 cm^{-1} to $\beta(CH)$ and $\nu(r)$ modes, in accord with the presence of similar bands in the spectrum of adenine. The calculated mode at 1404 cm^{-1} for the N_9–D tautomer suggests that the band at 1424 cm^{-1} in the Raman spectrum is associated with $\nu(r)$ and $\beta(C_2H)$ vibrations, rather than C_8H bending deformations as proposed by Majoube.[11] The bands at 1372 and 1333 cm^{-1} in the Raman spectrum may correspond to C_2H bending

vibrations and pyrimidine ring stretching deformations, respectively; the assignment made by Majoube[11] has these two modes in the inverse order. We also propose assigning the bands at 1305, 1250, and 1230 cm^{-1} in the Raman spectrum to $\beta(C_8H)$, $\nu(r)$, and $\delta(ND_2)$ modes, respectively. Majoube[11] has associated the first two bands with $\delta(ND_2)$ vibrations, and the third band with the $\beta(C_8H)$ mode. Our assignment is supported by the presence of corresponding bands at 1307 and 1248 cm^{-1} in the Raman spectrum of adenine. The band at 1186 cm^{-1} in the Ar spectrum may either correspond to $\delta(ND_2)$ or $\nu(r)$ deformations. Sheina et al.[9] assigned this band to $\nu(C_6N_{10})$ vibrations. Our calculations predict C_6–N_{10} stretching deformations to give rise to lines at 1404 and 1369 cm^{-1} in the N_9–D and N_7–D tautomers, respectively, in accord with bands observed in the spectra of adenine and its deuterated derivatives. The bands at 958 and 933 cm^{-1} in the

Ar and Raman spectra, respectively, have been assigned by Sheina et al.[9] and Majoube[11] to $\beta(ND)$ modes, while the Ar band at 846 cm^{-1} and the Raman band at 888 cm^{-1} have been associated with $\delta(r)$ modes. Our calculations assign these bands in the reverse order: the frequencies calculated at 945 and 926 cm^{-1} for the N_7-D and N_9-D tautomers, respectively, correspond to $\delta(r)$ modes; the lines calculated at 887 and 884 cm^{-1} are associated with $\beta(ND)$ and $\delta(r)$ modes. Our calculations suggest that the band at 794 cm^{-1} in the Ar spectrum be assigned to the $r(ND_2)$ mode, with contributions from $\nu(r)$ deformations, and not to $\delta(r)$ modes, as suggested by Sheina.[9] Lines at 898 and 896 cm^{-1} have been calculated for out-of-plane ring deformation modes for the N_9-D and N_7-D tautomers, respectively, close to the frequencies calculated for N_9-H and N_7-H adenine; we suggest the assignment of the bands at 864 and 858 cm^{-1} in the Ar spectrum to $\chi(r)$, and not $\gamma(CH)$ modes, as proposed by Sheina et al.[9] As was the case for N_9-H adenine, our calculations suggest the assignment of the band at 798 cm^{-1} in the Raman spectrum to $\gamma(C_6N_{10})$ and $\chi(r)$ deformations, and not to the $\gamma(C_2H)$ mode, as proposed by Majoube.[11] The unassigned bands at 650 and 508 cm^{-1} in the Raman spectrum may correspond to $\chi(r)$ and $\gamma(N_9D)$ modes, respectively. The band at 473 cm^{-1} in the IR spectrum of polycrystalline adenine-d_3 has been assigned by Majoube[11] to wagging deformations of the $-ND_2$ group; our calculations give lower frequencies for the out-of-plane vibrations of the amino group in the N_9-D tautomer: 416 and 381 cm^{-1} for the torsion and wagging modes, respectively. Our results suggest that the unassigned band at 238 cm^{-1} in the Raman spectrum may be associated with out-of-plane butterfly and ring bending deformations.

As was the case for the undeuterated species, in the crystal only the presence of the N_9-D tautomer is detected experimentally. The low-temperature argon matrix spectrum seems again to be best interpreted when the two tautomeric forms of adenine-d_3, N_9-D and N_7-D, are taken into account. The rms deviation of the scaled 4-21G frequencies from the experimental values is 2%, which supports the transferability of the force constants calculated for the undeuterated parent compounds to the deuterated derivatives.

3.2.5. 9-Methyladenine-d_2. The vibrational spectrum calculated for N-deuterated 9-methyladenine is presented in Table VII, together with the Ar matrix spectrum of 9-MA-d_2[9] and the Raman spectrum of 5'-AMP-d_2 in water.[14,15,51] Only the discrepancies between our calculations and the assignments proposed by Sheina et al.[9] for the Ar spectrum of deuterated 9-MA and by Majoube[51] for deuterated AMP will be discussed here. The band at 1307 cm^{-1} in the spectrum of AMP has been associated by Majoube[51] with bending modes of the $-ND_2$ and $-C_2H$ groups. Our assignment has this mode correspond to pyrimidine ring stretching deformations, with a contribution from the $\beta(C_8H)$ mode. The calculated frequency for the $\delta(ND_2)$ mode is 1189 cm^{-1}. The band at 1194 cm^{-1} in the Ar spectrum of 9-MA-d_2 is assigned here to ring stretching modes, and not $\nu(C_6N_{10})$ deformations, as proposed by Sheina et al.;[9] contributions from the $\nu(C_6N_{10})$ mode have been obtained here for higher frequency vibrations (1477 and 1367 cm^{-1}). The band at 721 cm^{-1} in the Raman spectrum of deuterated AMP may be associated with ring stretching and bending modes, similarly to the band at 727 cm^{-1} in the spectrum of undeuterated AMP; Majoube[51] has this band assigned to the stretching and bending modes of the $-N_9R$ group. As in the spectrum of the undeuterated compound, we propose to assign the band at 560 cm^{-1} in the spectrum of AMP-d_2 to ring bending deformations,

with contributions from $\nu(N_9C_{11})$ and $\nu(r)$ modes, and not to $\nu(C_6N_{10})$ vibrations, as suggested by Majoube.[51] The low-frequency in-plane vibrations due to $\beta(C_6N_{10})$ and $\beta(N_9C_{11})$ modes are calculated here at 286 and 201 cm^{-1}. As was the case for undeuterated AMP, we assign the band at 300 cm^{-1} in the Raman spectrum of AMP-d_2 to $\beta(C_6N_{10})$ and $\beta(N_9C_{11})$ in-plane deformations, and the band at 385 cm^{-1} to out-of-plane skeletal ring vibrations.

Overall a good agreement between the calculated and experimental spectra of 9-MA-d_2 has been obtained. The rms deviation of the scaled 4-21G frequencies from the values in the argon matrix spectrum is 2%, which again supports the transferability of the force constants calculated for the undeuterated compound to the deuterated derivative.

4. Conclusions

The structures of N_9-H and N_7-H tautomers of adenine and 9-methyladenine have been optimized and found to be planar in a 4-21G Hartree-Fock calculation. The structures are in good agreement with experimental results.

Ab initio 4-21G vibrational spectra of adenine, its 9-methyl derivative, and N-deuterated analogues made it possible to examine previously assigned fundamental modes and to propose a number of new assignments. Overall, the agreement between the experimental argon matrix and calculated results is very good; for the scaled ab initio frequencies the deviation from experiment is 3% for the entire frequency range. Although only the N_9-H tautomer is detected in spectra of polycrystalline adenine, the spectrum of adenine in the low-temperature argon matrix was found to be consistent with the superposition of spectra calculated for the N_9-H and N_7-H tautomers, which suggests that both species are present; this is in disagreement with expectations from the calculated energy difference (10.6 kcal mol^{-1} favoring the N_9-H form). However, it is possible that the results observed in the argon matrix spectrum are due to band splitting. Further studies are required to resolve this question.

The spectrum calculated for 9-methyladenine proved to be useful in analyzing the spectra of adenine, adenosine, and other more complex derivatives. The normal modes calculated for deuterated derivatives of adenine and 9-methyladenine have verified and confirmed band assignments for undeuterated molecules.

The 4-21G optimized geometries, charges, and force constants calculated for adenine and its derivatives will be used to develop a force field for nucleosides, nucleotides, and their polymers.[54]

(54) Wiórkiewicz-Kuczera, J.; Karplus, M., to be submitted for publication.