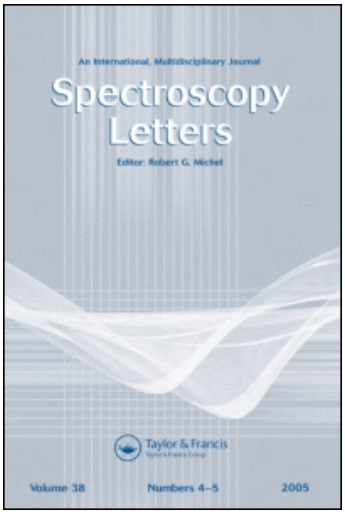

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Infrared and Raman Spectra of Solid Guanine Derivatives. 7-METHYLGUANINE, 9-METHYLGUANINE, 9-ETHYLGUANINE, 1,7-DIMETHYLGUANINE, and 1,9-DIMETHYLGUANINE.

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INFRARED AND RAMAN SPECTRA OF SOLID GUANINE DERIVATIVES.

7-METHYLGUANINE, 9-METHYLGUANINE, 9-ETHYLGUANINE, 1,7-DIMETHYLGUANINE, and 1,9-DIMETHYLGUANINE.

Key words: Guanine derivatives, Infrared and Raman Spectra.

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ABSTRACT

The infrared and Raman spectra of 7-methylguanine, 9-methylguanine, 9-ethylguanine, 1,7-dimethylguanine, and 1,9-dimethylguanine in the solid state have been reported and discussed. Hydrogen bonds in these solid guanine derivatives bring about strong perturbations which are discussed in terms of structural data given by X-ray diffraction methods. The spectra of guanine and 9-methylguanine are compared with the spectra of the monomers isolated in low-temperature matrices.

INTRODUCTION

The infrared spectra of some N-alkylated guanine derivatives have been investigated by matrix isolation technique [1-4] and ab initio calculations have been performed in order to make reliable assignments of absorption bands for all normal modes [4-5]. It must be pointed out however that to the best of our knowledge, the Raman and infrared spectra of N-alkylated guanine derivatives such as 7-methylguanine, 9-methylguanine, 9-ethylguanine, 1,7-dimethylguanine, and 1,9-dimethylguanine in the solid state have never been published. Nevertheless, the biological significance of N-alkylated guanine derivatives as mutagens and carcinogens agents have been reported [6-8] and earlier investigations [1] have suggested that N-alkylated derivatives of guanine like 9-methylguanine have biological properties related to the integrity of the genetic code.

In this paper which is a continuation of our vibrational studies of hydrogen bonding in solid guanine derivatives [9], the infrared and Raman spectra of 7-methylguanine, 9-methylguanine, 9-ethylguanine, 1,7-dimethylguanine, and 1,9-dimethylguanine are reported and discussed.

MATERIALS AND METHODS

The samples of 7-methylguanine, 9-methylguanine, 9-ethylguanine, 1,7-dimethylguanine, and 1,9-dimethylguanine have been kindly provided by Professor Nelson Leonard of the University of Illinois (for a description of the synthesis see ref 10).

The FT-infrared spectra of solid guanine derivatives were recorded in KBr pellets with the Nicolet model 740 FTIR spectrometer. The spectra were studied at a spectral resolution of 1 cm^{-1}. Spectra Calc (Galactic Industries Corp.) software has been used for deconvolution and integration of overlapping bands of multicomponent spectrum.

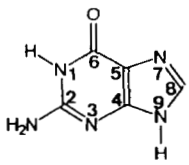
The Raman spectra of solid guanine derivatives were recorded with a resolution of 4 cm^{-1} on a Bruker FT Raman instrument (IFS Model 66) equipped with the FRA 106 Raman station.

RESULTS AND VIBRATIONAL ASSIGNMENTS

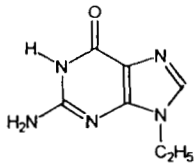
The infrared and Raman spectra of 7-methylguanine, 9-methylguanine, 9-ethylguanine, 1,7-dimethylguanine, and 1,9-dimethylguanine are shown in Figures 1, 2, 3, 4 and 5. Tables 1 and 2 list the wavenumbers of the observed infrared and Raman bands and their assignments.

9-Ethylguanine

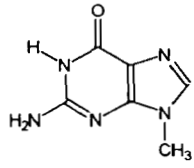
The spectra of guanine and 9-methylguanine in Ar or N_2 matrices have shown that in these low temperature inert materials, guanine and 9-methylguanine exist as mixtures of enol-amino and keto-amino tautomers [1-2]. The keto-amino tautomer is the only tautomeric form found in the



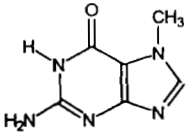
GUANINE



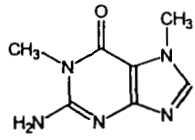
9-ETHYLGUANINE



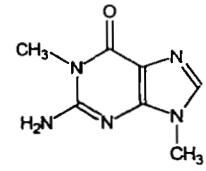
9-METHYLGUANINE



7-METHYLGUANINE



1,7-DIMETHYLGUANINE



1,9-DIMETHYLGUANINE

solid state. Like in the base pair guanine-cytosine, the O(6) atom, the N(1)H(1) and one of the N(2)H(2) groups of guanine are involved in hydrogen bond formation [11] but in the 9-ethylguanine crystal, the N(7) atom acts as a proton acceptor. Two molecules A and B are joined by hydrogen bonds, the distances between as follows [12]

$N(1)_A$ - $H(1)_A$ ... $N(7)_B$	2.846 Å
$N(2)_A$ - $H(2)_A$ ... $O(6)_B$	2.874 Å
$N(2)_A$ - $H(2)_A$ ... $N(3)_B$	3.272 Å
$N(1)_B$ - $H(1)_B$ ... $N(7)_A$	2.776 Å
$N(2)_B$ - $H(2)_B$ ... $O(6)_A$	2.844 Å
$N(2)_B$ - $H(2)_B$ ... $O(6)_A$	3.086 Å

The N(2)-H(2) groups are involved in NH...O hydrogen bonds characterized by distances of about 2.85 and 3.09 Å, one of the N(2)-H(2) group remaining essentially free. In 9-ethylguanine, the band at 3428 cm^{-1} is assigned to the $\nu_{as}(NH_2)$ vibration of this group and the bands at 3347 cm^{-1}

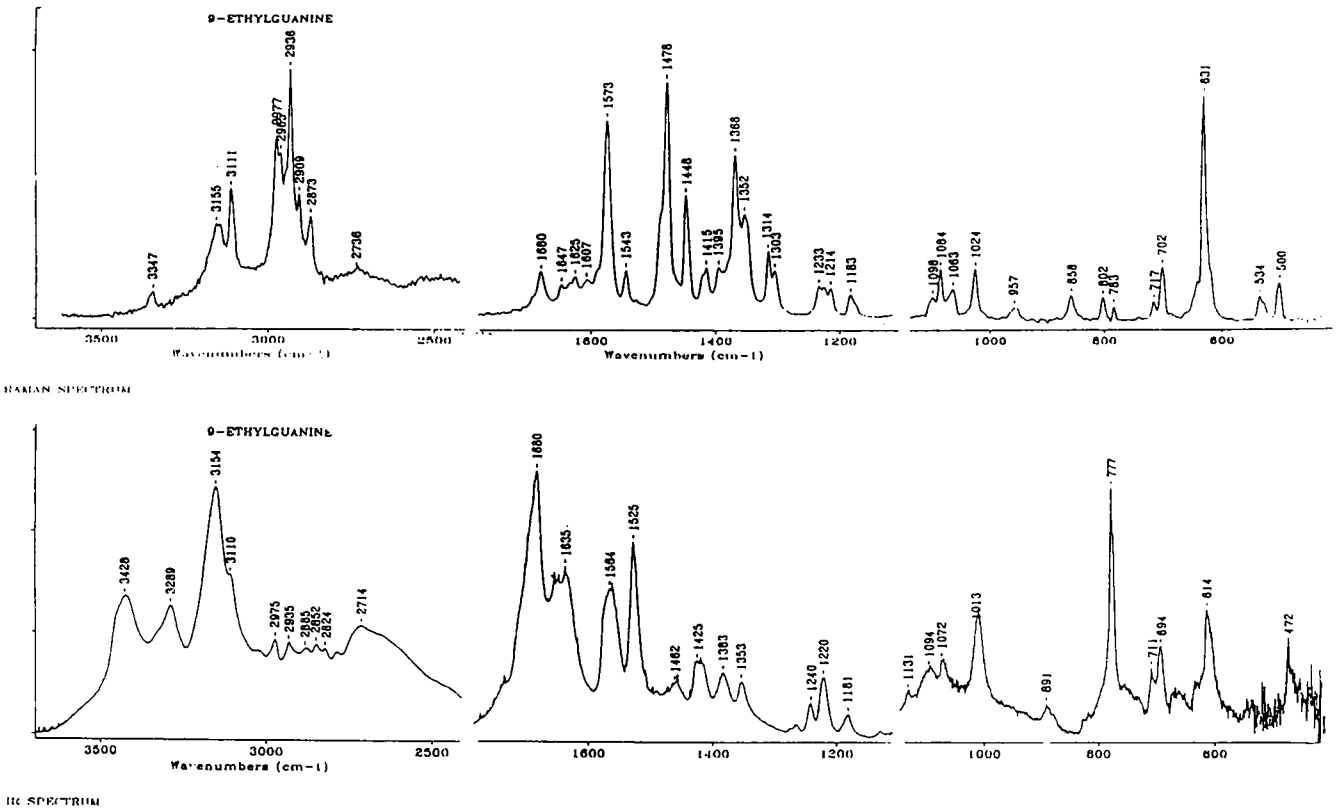


Fig 1 Infrared and Raman Spectra of 9-Ethylguanine

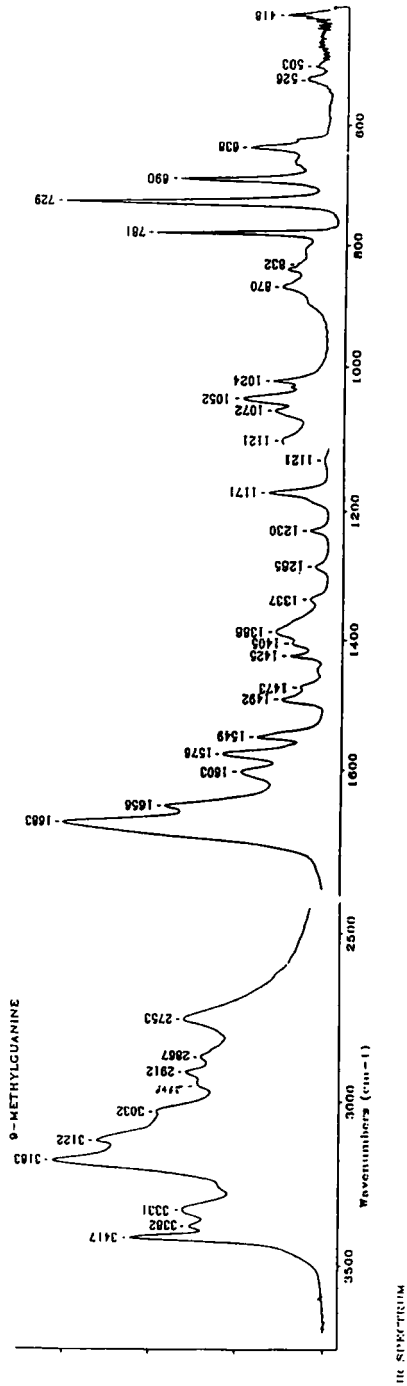


Fig 2 Infrared and Raman Spectra of 9- Methylguanine

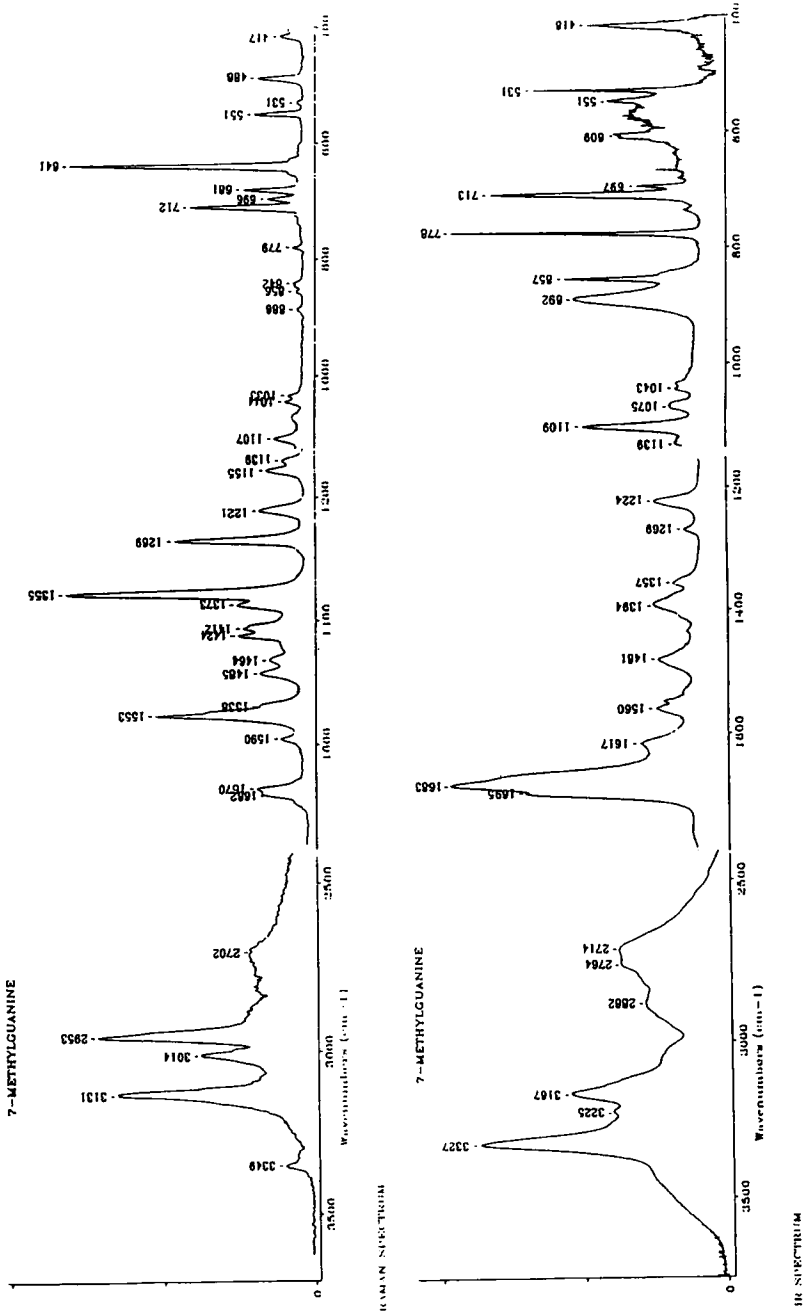


Fig 3 Infrared and Raman Spectra of 7 Methylguanine

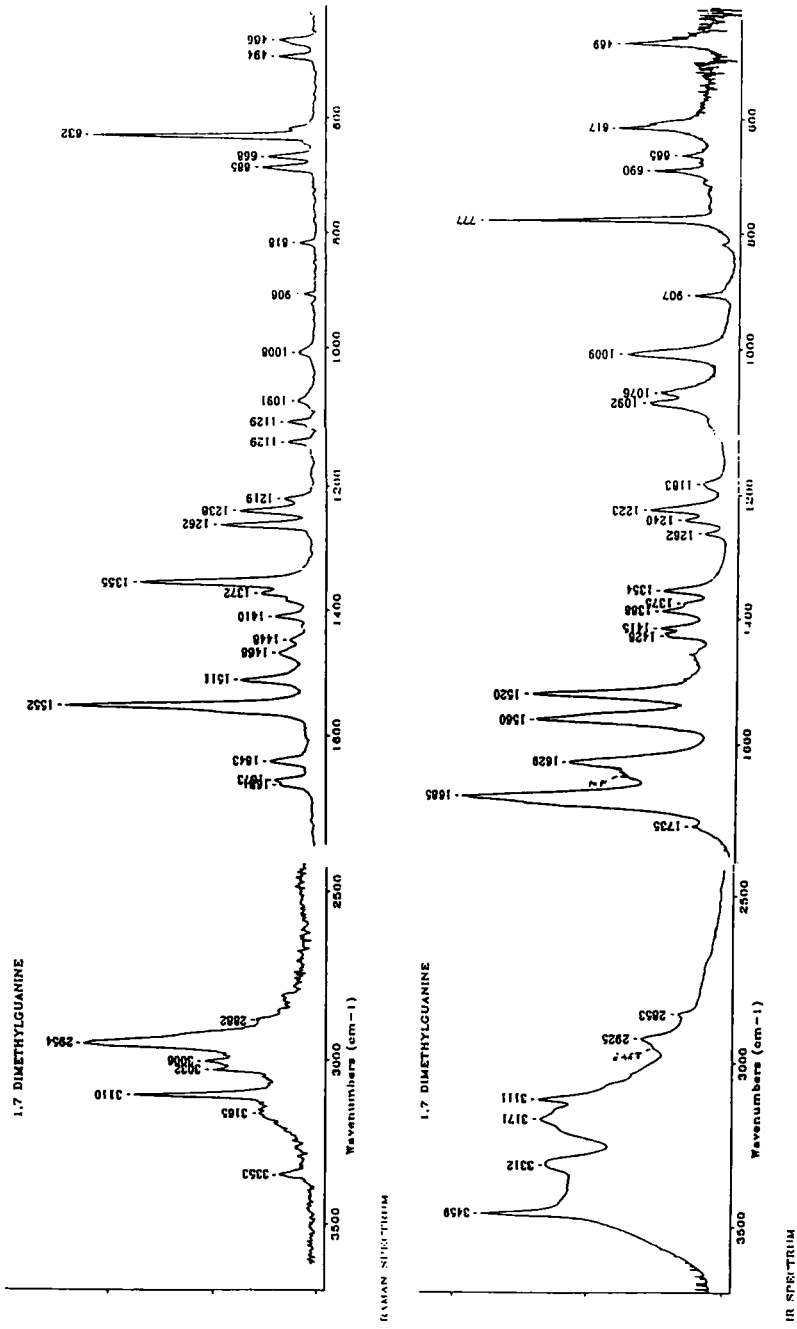


Fig 4 Infrared and Raman Spectra of 1-7 Dimethylguanine

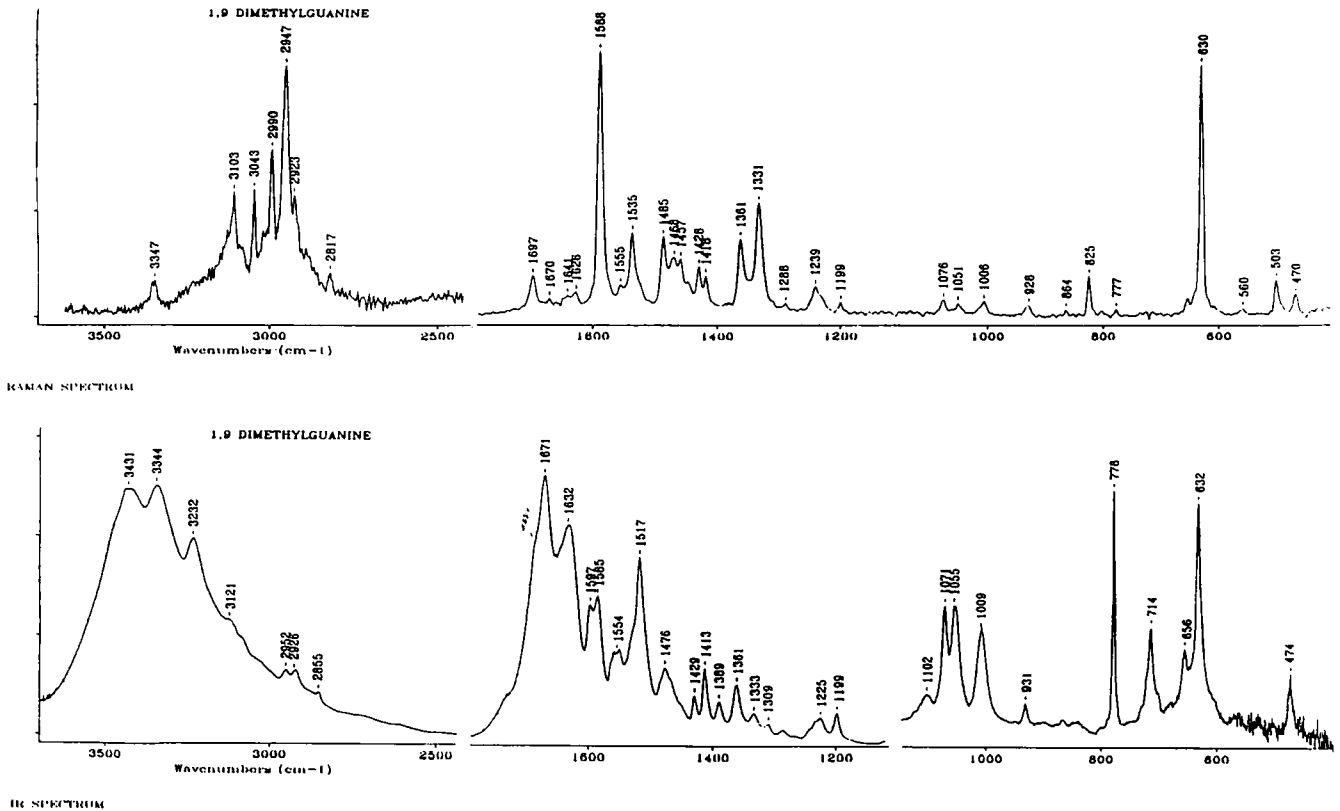


Fig 5 Infrared and Raman Spectra of 1-9 Dimethylguanine

Table 1. Infrared data (cm^{-1}) for 9-methylguanine isolated in N_2 [16] and in the polycrystalline state.

9-methylguanine in N_2 (keto form)	9-methylguanine Crystalline state		Assignment
3534	3417	s	$\nu_{as}(NH_2)$
	3382	m, br	
	3331	m, br	
3422	3183	vs	$\nu_s(NH_2)$
	3122	s	
3435	2753	vbr	ν(N1H1)
3000	3032	m	ν(C8H)
2962	2948	m	$\nu(CH_3)$
2927	2912	m	
2900	2867	w	
1738 b	1683	vs	ν(C=O)
1626	1653	s	$\delta(NH_2)$
1592	1603	m	
1587	1576	m	ν(R)
1564	1549	m	
1488	1492	m	ν(R), δ(C8H)
1465	1473	m	$\delta(CH_3)$
1436	1425	m	ν(R), $\delta(CH_3)$
1431	1405	m	
1413			
	1388	m, br	δ(NH)
1372			
1330	1337	m, br	ν(R)+δ(NH)
1314			
1295			ν(R) + δ(CH)
1276	1285	w	
1227	1230	w	ν(R), δ(CH)
	1171	m	
1192			ν(R), δ(CH)[a]
1183			
1083			ν(R), ν(C=O)
1060	1121	m	
1053	1072	m	ν(R)+r(NH_2)
1047	1052	m	
	1024	m	
723, 699, 672	870	m, br	γ(N1H1)
838	832	w	δ(R)
795	781	s	γ(R)
779	729	vs	
699	690	s	
662	665	w, br	γ(NH), γ(C=O)
635	638?	m	γ(C=O), δ(R)
625			
538	or 638	m	$\omega(NH_2)$
	526	m	γ(R)
	503	w	γ(R)

v = very, s = strong, m = medium, w = weak, br = broad, ν = stretching, δ = in-plane deformation, γ = out-of-plane deformation, r = rocking, ω = wagging, R = ring, a = coupled with the δ(CH) vibration; b = two components are observed probably due to Fermi resonance.

Table 2. Some relevant infrared and Raman data for polycrystalline 7-methylguanine, 1,7-dimethylguanine and 1,9-dimethylguanine.

7-methylguanine		1,7-dimethylguanine		1,9-dimethylguanine		Assignment
IR	Raman	IR	Raman	IR	Raman	
		3459 s		3431 s		
3327 s	3349 w	3312 s	3353 w	3344 s	3347 w	$\nu_{as}(NH_2)$
3225 w				3232 s		FR (2 x 1617 or 2 x 1632)
3167 s	3131 s	3171 s	3165 w	3121 m, br	-	$\nu_{s}(NH_2)$
	3014 m	3111 s	3110 vs		3103 m	ν(C8H)
	2953 s	2949 m, br	2954 vs	2952 w	2947 vs	$\nu(CH_3)$
2882 m, br						ν(N1H1)
2764 m, br						ν(N1H1)
2714 m, br	2702 w, br					ν(N1H1)
1695 vs		1685 vs	1681 m	1687 sh	1697 w	ν(C=O)
1683 vs	1682 m	1646 w	1673 m	1671 vs	1670 vw	
1669 a	1670 m		1643 m			
1617 m	-	1629 m		1632 s	1626 vw	$\delta(NH_2)$
1560 m	-			1597 m		$\nu(R)+\delta(NH_2)$
1394 m	-					δ(N1H1)
892 s	886 vw					γ(N1H1)
609 or 570	-	617 m		600 b		$\omega(NH_2)$

v = very, s = strong, m = medium, w = weak, br = broad, ν = stretching, δ = in-plane deformation, γ = out-of-plane deformation, ω = wagging, R = ring, a = weak shoulder overlapping with the coupled with ν(C=O) vibration; b = weak shoulder at the low frequency side of the ring vibration observed at 632 cm^{-1}. FR = Fermi resonance

(Raman) and 3289 cm^{-1} (IR) to the $\nu_{as}(NH_2)$ vibration of the NH bonds characterized by distances of 3.09 and 2.85 Å. In the IR spectrum the bands are broad and only a shoulder is observed at 3340 cm^{-1}. The strong band at 3154 cm^{-1} is ascribable to the $\nu_s(NH_2)$ of the two molecules, since the distance of 1,89 Å between $H(2)_A$ and $O(6)_B$ or $H(2)_B$ and $O(6)_A$ involved in principal hydrogen bond for both molecules is almost identical. The superposition of $\nu_s(NH_2)$ of the two molecules probably explains the high intensity of this band. This absorption corresponds to the broad band observed at 3155 cm^{-1} in diffusion.

The ν(N1H1) vibration is assigned to the absorption observed at 2714 cm^{-1} and indeed similar absorption persists in infrared spectra of guanine derivatives, N(1)H tautomer. The broadness and asymmetry of the absorption is ascribed to the fact that two different N(1)H(1)...N(7) hydrogen bonds are formed in the crystal. In guanine, this vibration is observed at 2696 cm^{-1} [13].

The ν(C=O) vibration is observed at 1680 cm^{-1} and the bands at 1668, 1650 and 1635 cm^{-1} (IR) and 1647, 1637 and 1625 cm^{-1} (Raman) are ascribed to the NH_2 scissoring vibration of the free, weakly bonded and strongly bonded NH_2 groups.

9-Methylguanine

The infrared spectrum of 9-methylguanine monomer has been investigated in a N_2 matrix and the normal modes of the keto and enol forms have been calculated [1-2]. In addition, an experimental and theoretical study of its tautomers and rotamers has been performed [3].

Table 1 allows one to compare the frequencies observed in N_2 and in the polycrystalline state. Three $\nu_{as}(NH_2)$ vibrations shifted downward by 117, 152 and 203 cm^{-1} from the isolated molecule. The observation of three bands is related to the existence of three different NH...X hydrogen bonds

like in 9-ethylguanine [12]. The two observed $\nu_s(NH_2)$ bands are shifted from 239 and 300 cm^{-1} from the isolated molecule. The greater perturbation of the $\nu_s(NH_2)$ vibration can be accounted for the non-equivalence of the two bonds in the NH_2 groups. The ν(N1H1) vibration is shifted by 682 cm^{-1} from free molecule. The N1H1 group is probably hydrogen bonded to the N(3) atom like in 9-ethylguanine. The absorption at 1683 cm^{-1} involves mainly a stretching vibration of the C=O bond. The shift from the isolated molecule is 55 cm^{-1}. The great shift of this vibration can be accounted by the fact that the two NH_2 bonds of a first molecule are both hydrogen bonded to the O(6) atom of a second molecule. Only one NH_2 scissoring mode is observed at 1656 cm^{-1} (shift = +30 cm^{-1}). The absorption at 1603 cm^{-1} involves probably like in guanine, some contribution of the NH_2 scissoring mode. The assignment of Nishimura et al [14] is reinforced by the fact that in isolated N_2, this mode is observed at 1592 cm^{-1}. The two other vibrations at 1576 and 1549 cm^{-1} are pure ring modes and are observed at lower wavenumbers than in low temperature materials. The absorption at 1388 cm^{-1}, weak and broad, is assigned to the δ(N1H1) vibration. In guanine, the absorption at 1375 cm^{-1}, disappearing on N-deuteration, is assigned to the mode. Comparison with the isolated molecule is difficult; four absorption between 1372 and 1295 cm^{-1} are assigned to the coupled ν(R) + δ(NH) modes. By comparison with guanine, the band at 870 cm^{-1} is assigned to the γ(N1H1) vibration. In N_2 matrix, several absorptions at 723, 699 and 677 cm^{-1}, contribute to this mode. These upward shifts of 147, 171 and 198 cm^{-1} reflect the strength of the N(1)H(1)...N(7) hydrogen bond. The rocking and wagging vibrations of the NH_2 group are usually sensitive to hydrogen bond formation. The rocking vibration seems to be coupled with one of the ring stretching mode and a trio of bands is observed at 1060, 1053 and 1047 cm^{-1} at low temperature. The broad and weak band observed at 1121 cm^{-1} in the polycrystalline state is

probably the main component at the rocking mode. The wagging vibration of the NH_2 group is observed at 578 cm^{-1} in guanine. No absorption at this wavenumber could be detected in 9-methylguanine. The band at 638 cm^{-1} probably contribute to this modes. It is worth noting that the $\delta(C=O)$ and $\gamma(C=O)$ vibrations are both strongly coupled with other modes and only weak perturbation on going from the isolated to the polycrystalline state could be observed.

At last, some ring vibration are very insensitive to CH_3 substitution. This is the case for the vibration observed at 1550, 1510, 1262, 1010, 780 and 690 cm^{-1}.

7-Methylguanine, 1,7-Dimethylguanine and 1,9-Dimethylguanine

Some relevant infrared and Raman data for 7-methylguanine, 1,7-dimethylguanine and 1,9-dimethylguanine are indicated in Table 2. No X-ray diffraction data are available for the 7-methylguanine and 1,7-dimethylguanine molecules. The data indicate that in 7-methylguanine, the NH_2 and N1H1 groups are involved in hydrogen bond formation. The bands at 3327 and 3167 cm^{-1} are attributed the NH_2 asymmetric and symmetric stretching modes respectively. The ν(N1H1) vibration is observed at 2764 - 2714 cm^{-1}, at about the same wavenumber as in 9-methylguanine and this strongly suggest the existence of N(1)H(1)...N(7) hydrogen bonds in the crystalline state. The $\nu(C=O)$ vibration observed at 1721 cm^{-1} in argon matrix [4] is shifted downward by 26 - 38 cm^{-1} and this also suggests that the C=O bond is involved in the hydrogen bond(s). The δ(N1H1) vibration appears as a band of medium intensity. The assignment of the wagging vibration of the NH_2 group at 609 (or 570 cm^{-1}) is somewhat uncertain.

In 1,7-dimethylguanine and 1,9-dimethylguanine spectra, the $\nu_{as}(NH_2)$ vibration is observed at high frequencies, 3459 and 3431 cm^{-1} respectively.

This suggests that one of the NH bond of the NH_2 group remains essentially free from hydrogen bond. In 8-aminoquinoline, where one of the NH bond of the NH_2 group is free, the ν(NH) vibration is observed in the solid state at 3454 cm^{-1}[15]. The narrowness of the absorption band at 3459 cm^{-1} in 1,7-dimethylguanine confirms that one of the NH bond of the NH_2 group is free. In contrast, the broad band at 3312 cm^{-1} is related to the other NH bond of the NH_2 group hydrogen bonded. The absorption band observed at 3171 cm^{-1} corresponding to the band at 3185 cm^{-1} in the Raman spectrum is attributed to the $\nu_s(NH_2)$ vibration.

In the 1,9-dimethylguanine molecule, as shown by its structure determined by single crystal X-ray [10], the N(2)-H(2) groups are involved in N(2)-H(2)...N(7), N(2)-H(2)...N(3) and N(2)-H(2)...O(6) hydrogen bonds. Hence. The absorption bands at 3431, 3344 and 3241 cm^{-1} or the diffusion band at 3347 cm^{-1} are attributed to the asymmetric vibration of NH_2 group free, weakly bond and strongly bonded. The shoulder observed near 3121 cm^{-1} may be assigned to $\nu_s(NH_2)$ vibration.

The absence of absorption between 2800 and 2700 cm^{-1} in 1,7-dimethylguanine and 1,9-dimethylguanine confirms the assignments of ν(N1H) vibration in the 7-methylguanine and 9-methylguanine spectra. The C=O function is probably involved in hydrogen bond formation. Indeed, on observes more than one band between 1695 - 1643 cm^{-1} which are related to more than one C=O...H-N hydrogen bond. Substitution of a hydrogen atom by CH_3 group lowers the ν(C=O) frequency. In N,N,1,9-tetramethylguanine, the ν(C=O) vibration is observed at 1691 cm^{-1}[16], and this frequency will be probably higher in the free 1,7-dimethylguanine or 1,9-dimethylguanine derivatives. In 1,9-dimethylguanine, the main ν(C=O) absorption observed at 1671 cm^{-1} is most probably the band shifted by hydrogen bond formation. In solution, the preferred hydrogen bond interaction site is the O atom and this also likely to be the same in solid state.

The ring breathing vibration is observed with a very strong Raman intensity at 641 cm^{-1} (7-methylguanine) 632 cm^{-1} (1,7-dimethylguanine) and 630 cm^{-1} (1,9-dimethylguanine).

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