

The Near-Infrared Spectrum of the Guanidinium Ion: A Local-Mode Analysis

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Near-infrared (near-IR) spectra at 10 K in polarized light were recorded for single crystals of guanidinium perchlorate (GuanClO₄), tetrafluoroborate (GuanBF₄), and iodide (GuanI). All these substances contain planar guanidinium ions which lie on trigonal sites and are hydrogen bonded to the anions. The spectrum of guanidinium nitrate (GuanNO₃) was also recorded, but its structure is not known. The spectra show clearly the effects of the hydrogen bonding, the strength of which increases in the order BF₄ < ClO₄ < I < NO₃. The spectra have been analyzed using local-mode theory to yield a set of local-mode parameters, ω , X , and λ . The ω and X values have been compared with those of a wide selection of N-H oscillators of various types.

Introduction

In a recent series of articles¹⁻⁵ we have studied the near-infrared (near-IR) spectra of substances containing O-H or O-D oscillators in condensed phases at low temperatures. Numerous sharp bands are found, which are principally overtones of the stretching vibrations or combinations of a single quantum of a stretch with other vibrations. The stretch overtones are of particular interest to chemists, since their energies are quite sensitive to variations in the strength of hydrogen bonding with neighboring receptors.

The local-mode theory developed for molecules in the gas phase⁶⁻⁸ gives a good account of many of the stretch overtone features. We have modified this theory to accommodate some of the extra effects associated with incorporating the molecules into condensed phases.³⁻⁵ Studies on oriented oscillators are expected to be especially useful, since the chemical environment about each oscillator is rigorously controlled by the crystal. This makes feasible the interpretation and correlation of the resulting local-mode parameters in terms of bond angles and distances.

Very little is known about the overtone spectra of N-H oscillators in hydrogen-bonded situations in crystals. Here we report a study of the guanidinium ion, C(NH₂)₃⁺, and this may be the first detailed treatment of the vibrational overtone spectra of the NH₂ group in the solid state. X-ray structures of a number of substances containing the guanidinium ion have been reported.⁹⁻¹⁸ In all cases, the CN₃ skeleton is planar and the N-anion distances are suggestive of hydrogen bonding. In some

of the crystals, as for example the chloride⁹ and bromide,¹⁰ not all the guanidinium ions are coplanar. This would complicate the polarized spectra and make them less amenable to interpretation. In the present report, we consider three cases in which the symmetry is high; this helps to simplify what might otherwise be a more intractable problem. We have also recorded the spectra of a number of ammonium salts. Because NH₄⁺ contains a larger number of oscillators, and also because in many salts the NH₄⁺ ions retain residual disorder even at low temperatures, their spectra are considerably more complex than those of guanidinium salts. Therefore the latter are better subjects for a study of N-H oscillators.

Guanidinium perchlorate (GuanClO₄) crystallizes in space group *R3m* (*C*_{3v}⁵, No. 160) with $a = 7.606 \text{ \AA}$, $c = 9.121 \text{ \AA}$, and $Z = 3$.^{15,16,19} The guanidinium ion was found to be planar within experimental error and to lie perpendicular to the trigonal axis (c) of the crystal; the perchlorate ions also lie on *C*₃ sites. The NH₂ groups from three different cations form rings of 3-fold symmetry with oxygens from three different perchlorate ions, as shown schematically in Figure 1a.

Guanidinium tetrafluoroborate (GuanBF₄) is isomorphous with GuanClO₄, and its rhombohedral unit cell has $a_r = 5.27 \text{ \AA}$ and $Z = 1$.¹⁷ The authors note that the N-H...F hydrogen bonds probably form layers of guanidinium and BF₄⁻ ions, similar to those in the perchlorate salt. No detailed structure has been reported.

Guanidinium iodide (GuanI) belongs to space group *P6₃mc* (*C*_{6v}⁴, No. 186) with $a = 7.19 \text{ \AA}$, $c = 12.30 \text{ \AA}$, and $Z = 4$.¹⁸ While all the guanidinium ions lie in planes perpendicular to the hexagonal (c) axis, the crystal contains two nonequivalent sets of guanidinium and iodide ions. The ion arrangements in two views $\perp c$ are shown schematically in Figure 1b. The H atom positions are not known but have been placed in the C-N plane with all angles in C(NH₂)₃⁺ equal to 120°. The iodide ion radius is taken to be 2.06 Å.²⁰ In the first view, the I-N distance is 3.71 Å, while in the second, it is 3.85 Å. As discussed below, the near-IR spectra of GuanI give clear indications of hydrogen

- (1) McCarthy, P. J.; Walker, I. M. *Spectrochim. Acta* **1983**, *39A*, 827.
- (2) Walker, I. M.; McCarthy, P. J. *Can. J. Chem.* **1986**, *64*, 1012.
- (3) Walker, I. M.; McCarthy, P. J. *J. Phys. Chem.* **1989**, *93*, 2230.
- (4) McCarthy, P. J.; Walker, I. M. *Inorg. Chem.* **1990**, *29*, 820.
- (5) McCarthy, P. J.; Walker, I. M. *Inorg. Chem.* **1991**, *30*, 2772.
- (6) Child, M. S.; Halonen, L. *Adv. Chem. Phys.* **1984**, *57*, 1.
- (7) Mills, I. M.; Robiette, A. G. *Mol. Phys.* **1985**, *56*, 743.
- (8) Child, M. S. *Acc. Chem. Res.* **1985**, *18*, 45.
- (9) Haas, D. J.; Harris, D. R.; Mills, H. H. *Acta Crystallogr.* **1965**, *19*, 676.
- (10) Teilacker, W. *Z. Kristallogr.* **1935**, *90A*, 256.
- (11) Schein, B. J. B.; Lingafelter, E. C.; Stewart, J. M. *J. Chem. Phys.* **1967**, *47*, 5183.
- (12) Adams, J. M. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1218.
- (13) Fröhlich, R.; Mattern, G.; Krumbe, W. *Z. Kristallogr.* **1985**, *172*, 315.
- (14) Cygler, M.; Grabowski, M. J.; Stepien, A.; Wajzman, E. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2391.
- (15) Koziol, A. E. *Z. Kristallogr.* **1984**, *168*, 313.
- (16) Pajak, Z.; Grottel, M.; Koziol, A. E. *J. Chem. Soc., Faraday Trans. 2*, **1982**, *78*, 1529.
- (17) Grottel, M.; Pajak, Z. *J. Chem. Soc., Faraday Trans. 2*, **1984**, *80*, 553.
- (18) Teilacker, W. *Z. Kristallogr.* **1935**, *90A*, 51.

- (19) The hexagonal cell parameters for GuanClO₄ can be converted to the rhombohedral cell parameters: $a_r = 5.341 \text{ \AA}$, $\alpha = 90.8^\circ$, with $Z = 1$. See: Burns, G.; Glazer, A. M. *Space Groups for Solid State Scientists*; Academic Press: New York, 1978; p 49.
- (20) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.
- (21) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

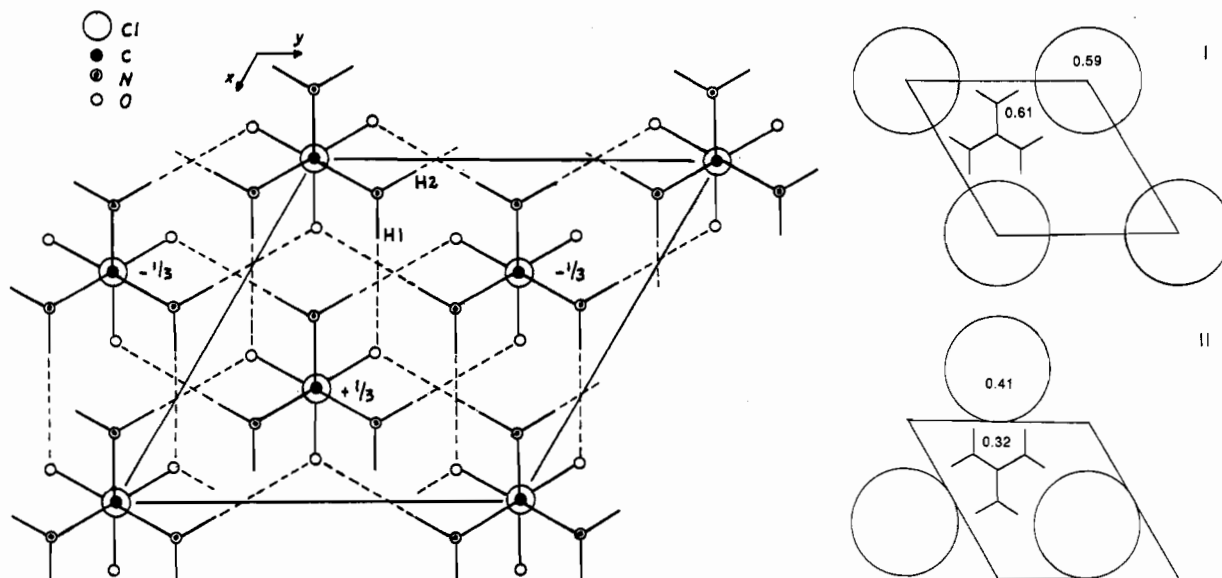


Figure 1. (a) Left: Basic hydrogen-bonded structure in guanidinium perchlorate (adapted from ref 16). A chlorine atom at (0, 0, 0), a carbon atom at (0, 0, 0.4125), and a non-hydrogen-bonding oxygen at (0, 0, -0.1563) overlap in this xy projection. The equivalent chlorine atom positions are marked $+1/3$ and $-1/3$. (b) Right: Suggested hydrogen-bonded structure in guanidinium iodide based on data in ref 18. Two views $\perp c$ are shown; the fractional c coordinates of the ions are indicated.

bonding, but because of the two different N–I distances, the hydrogen-bond strength is expected to vary slightly in the two sets of ions.

Although the crystal structure of guanidinium nitrate (GuanNO₃) is not known, the general similarity of its spectrum to those of the other guanidinium salts argues for a planar guanidinium ion hydrogen-bonded to nitrate ions.

Experimental Section

The guanidinium salts were prepared by neutralizing guanidinium carbonate (Eastman) with the appropriate aqueous acid. The solutions were evaporated to dryness in air. Crystals suitable for spectroscopy were grown by slow evaporation of a solution of the salt in a mixture of ethyl acetate and acetone.

Spectra in the range 2630–700 nm (3800–14300 cm⁻¹) were recorded on a Varian 2300 spectrophotometer with a Displex cryogenic refrigerator used to cool the samples. Polarized spectra were recorded for GuanClO₄ and GuanBF₄ with the electric vector of the incident radiation parallel and perpendicular to the extinction axes of the crystals. Polarized light was provided by a pair of matched Glan-Thompson prisms. Because of the crystal habit of GuanI, only an axial spectrum could be recorded. Likewise, because of the quality of crystals that we were able to prepare, only an unpolarized spectrum of GuanNO₃ was recorded.

IR spectra of the compounds were recorded in Nujol and Fluorolube mulls at room temperature on a Nicolet 5DX FTIR spectrophotometer. The results are very similar to the data reported for these and other guanidinium salts.²²

Results and Discussion

Fundamental Vibrations. The strong bands at 1658 (GuanClO₄), 1666 (GuanBF₄), 1646 (GuanI), and 1670 cm⁻¹ (GuanNO₃) are primarily the NH₂ bends (δ). The bands at 1567 (GuanClO₄), 1568 (GuanBF₄), 1543 (GuanI), and 1579 cm⁻¹ (GuanNO₃), in view of the strong shift to low energy on deuteration,²² must also contain considerable N–H character. Jones²³ has assigned the two analogous bands in guanidine to combinations of the NH₂ bend and the NCN antisymmetric stretch. Likewise, a detailed study of *N*-methylacetamide led to the conclusion that the lower-energy band is 60% N–H bend and 40% C–N stretch.²⁴ We will henceforth label this band μ .

The region around 3400 cm⁻¹ for GuanClO₄ and GuanBF₄ contains four sharp peaks. The highest energy features at 3454 and 3371 cm⁻¹ (GuanClO₄) and at 3485 and 3396 cm⁻¹ (GuanBF₄) can be assigned to the antisymmetric and symmetric N–H stretches, ν_a and ν_s , respectively. (In the local-mode designation these are $|01\rangle_-$ and $|01\rangle_+$.) The bands at 3220 cm⁻¹ (GuanClO₄) and 3232 cm⁻¹ (GuanBF₄) can best be assigned to the combination $\mu + \delta$, whose calculated sums are 3225 and 3234 cm⁻¹, respectively. The bands at 3291 cm⁻¹ (GuanClO₄) and 3311 cm⁻¹ (GuanBF₄) are assigned to the bend overtone (2δ). In both cases, the band appears about 20–25 cm⁻¹ lower than expected. This is due to Fermi resonance between 2δ and ν_s , which have the same symmetry. Fermi resonance will also raise the energy of ν_s and, accordingly, reduce the expected separation between ν_a and ν_s . The energies of ν_s for GuanClO₄ and GuanBF₄ are indeed found to be about 20 cm⁻¹ higher than those calculated with no correction for Fermi resonance. GuanI in this region has only a broad band with steep contour on the higher energy side and a broad envelope to lower energy. The maximum at 3292 cm⁻¹ is best assigned to ν_a with the other bands lying to lower energy under the envelope. The spectrum of GuanNO₃ shows an unresolved multiplet centered about 3340 cm⁻¹ and a distinct peak at 3202 cm⁻¹. This latter may be $\mu + \delta$ (calculated 3249 cm⁻¹).

GuanClO₄ has a very strong, complex band with principal maximum at 1066 cm⁻¹ and a shoulder at 1144 cm⁻¹. GuanBF₄ has a similar band with maximum at 1026 cm⁻¹ and shoulders at 1083 and 1150 cm⁻¹. The maxima can be assigned to the Cl–O and B–F stretching vibrations, respectively.²⁵ The shoulders at 1144 and 1150 cm⁻¹ can be assigned to ρ_r of the NH₂ group, found in guanidine at 1108 cm⁻¹.²³ While the other two compounds show no strong peak in this region, the weak bands found at 1161 (GuanNO₃) and 1159 cm⁻¹ (GuanI) can also be assigned to ρ_r of the NH₂ group. Each NH₂ group also has a wagging (ρ_w) and a twisting mode (ρ_t). From the spectrum of guanidine,²³ these are expected to lie below 800 cm⁻¹. The IR spectra also contain skeletal vibrations of the guanidinium group.

Near-IR Spectra. The most extensive near-IR investigation was carried out on GuanClO₄, since we were able to prepare crystals of varying thicknesses up to about 2 mm. The spectrum of one polarization is the same as the axial spectrum, and so has

(22) Bonner, O. D.; Jordan, C. F. *Spectrochim. Acta* 1976, 32A, 1243.

(23) Jones, W. J. *Trans. Faraday Soc.* 1959, 55, 524.

(24) Miyazawa, T.; Shimanouchi, T.; Mizushima, S. *J. Chem. Phys.* 1958, 29, 611.

(25) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley-Interscience: New York, 1978; pp 136 and 142 and references cited therein.

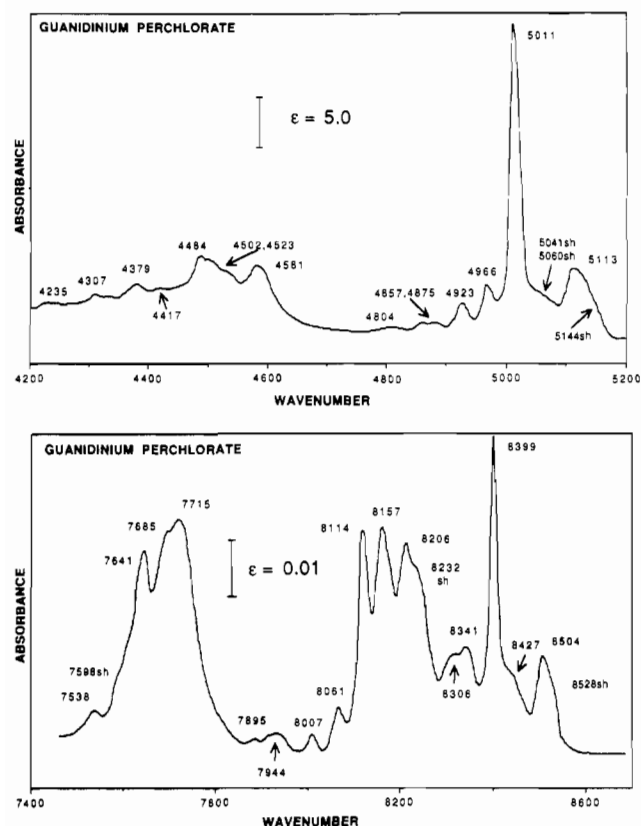


Figure 2. Crystal spectra ($E \perp C_3$) of guanidinium perchlorate at 10 K, showing combination bands (a, top) in the 4200–5200- cm^{-1} region and (b, bottom) in the 7400–8600- cm^{-1} region.

$E \perp C_3$ (σ spectrum). The spectrum of the other orthogonal polarization is about half as intense and, with two exceptions (see below), is the same as the first. If C_3 lies in the face of the crystal, this other polarization is the π spectrum ($E \parallel C_3$). If C_3 makes an angle θ ($0^\circ < \theta < 90^\circ$) with the crystal face, this other polarization is a mixture of π and σ . We do not know which situation obtains. For all the NH_2 modes except the wag and twist, the dipole change during vibration lies in the plane of the guanidinium ion and therefore is perpendicular to C_3 . Greater intensity might then be expected in the σ spectrum, an expectation which is in fact verified. The polarized spectra of GuanBF_4 are quite similar to the corresponding spectra of GuanClO_4 as regards both band position and band intensity. Therefore, we will discuss in detail only the spectra of GuanClO_4 . The axial spectrum of GuanI and the unpolarized spectrum of GuanNO_3 also show in general the same features as those of the other compounds. No definitive evidence of factor-group splitting was found in any of the spectra.

Incorporation of an XH_2 chromophore into a hydrogen-bonding environment has a profound, and not easily predictable, effect on the intensities of the electric dipole forbidden bands. We have therefore assigned the combination and overtone bands principally on the basis of their energy as compared with that expected from the sum of the fundamentals.

Combination Bands. Bands in the 3800–5200- cm^{-1} region are due to combinations of the N–H stretch with bending and librational modes of NH_2 and with other fundamental modes of the crystals. In GuanClO_4 , complex bands at 3840 and 4130 cm^{-1} , found in the weaker polarization only, most likely represent $\nu + \rho_t$ and/or $\nu + \rho_w$, since this polarization is expected to contain features polarized along the C_3 axis of the guanidinium ion.

Several of the combination bands in the 4200–5200- cm^{-1} range occur in groups, having principal maxima separated by about 100 cm^{-1} (Figure 2a). Since this is the approximate separation observed between ν_a and ν_s and between δ and μ , it has been an aid in the assignment of some bands. Those for which we could

Table I. Calculated and Observed Energies of Combination Bands for GuanClO_4 ^a

assgnt	obs ^b	calc ^c	assgnt	obs ^b	calc ^c
$ 01\rangle_+ + \rho_t$	4484	4515	$ 02\rangle_+ + \mu$	8114	8134
$ 01\rangle_- + \rho_t$	4581	4598	$ 02\rangle_- + \mu$	8157	8171
$ 01\rangle_+ + \mu$	4923	4938	$ 02\rangle_+ + \delta$	8206	8225
$ 01\rangle_- + \mu$	4966	5021	$ 02\rangle_- + \delta$	8232	8262
$ 01\rangle_+ + \delta$	5011	5029	$ 11\rangle_+ + \mu$	8399	8414
$ 01\rangle_- + \delta$	5113	5112	$ 11\rangle_+ + \delta$	8504	8505
$ 01\rangle_+ + 2\mu$	6468	6505	$ 02\rangle_+ + 2\mu$	9674	9701
$ 01\rangle_- + 2\mu$	6536 sh	6588	$ 02\rangle_+ + \mu + \delta$	9761	9792
$ 01\rangle_+ + \mu + \delta$	(6567)	6596	$ 02\rangle_+ + 2\delta$	9869	9883
$ 01\rangle_- + \mu + \delta$	6646	6679	$ 11\rangle_+ + 2\mu$	9960	9981
$ 01\rangle_+ + 2\delta$	6681	6687	$ 11\rangle_+ + \mu + \delta$	10068	10072
$ 01\rangle_- + 2\delta$	6762	6770	$ 11\rangle_+ + 2\delta$	(10145)	10163
$ 02\rangle_+ + \rho_t$	7685	7711			
$ 02\rangle_- + \rho_t$	7715	7748			
$ 11\rangle_+ + \rho_t$	7944	7991			

^a Data in cm^{-1} . ^b Observed bands in parentheses are primarily 2ν and 3ν bands (see Table II). ^c Calculated values are sums of the following: $\rho_t = 1144$; $\mu = 1567$; $\delta = 1658$; $|01\rangle_+ = 3371$; $|01\rangle_- = 3454$; $|02\rangle_+ = 6567$; $|02\rangle_- = 6604$; $|11\rangle_+ = 6847$.

make reasonable assignments are listed in Table I. It is worth noting that the splittings observed in this region are actually somewhat larger than the $\nu_a - \nu_s$ separation. This implies that Fermi resonance is a more important factor in the fundamental spectrum than in that of the combinations. Some of the weaker features in this region could be due to ternary combinations such as 3δ , $2\delta + \mu$, etc., which are calculated to lie between 4700 and 4975 cm^{-1} . Most of the features cannot at present be definitely assigned.

The 7400–8600- cm^{-1} region shown in Figure 2b contains a large number of peaks whose intensities are consistent with their being ternary combinations. The marked similarity of the sets of bands around the sharp peaks at 5011 and 8399 cm^{-1} is noteworthy. The lower energy set is about 570 times as intense as the higher energy group. This latter set lies $\approx 3380 \text{ cm}^{-1}$ above the first and contains $2\nu + \delta$ and $2\nu + \mu$. Some probable assignments of individual peaks are listed in Table I.

Stretch Overtone Bands. In the first overtone region (Figure 3a) each compound shows two strong absorptions separated by about 300 cm^{-1} , which are readily assigned as two of the three 2ν peaks. The third is expected to lie between these two, but near in energy to the lower-energy peak. So in each case an intermediate band was chosen which gave the best fit between observed and calculated energies. Some of the bands of moderate intensity which lie between the principal peaks may reasonably be assigned to $\nu + 2\delta$, $\nu + 2\mu$, and $\nu + \delta + \mu$ (see Table I). Since GuanI contains two nonequivalent guanidinium ions, all the bands in this region are probably unresolved multiplets, and so appear broader and less well resolved.

In the 3ν region of the spectrum of GuanClO_4 (Figure 3b) the peak at lowest energy is a doublet with 19- cm^{-1} separation. This doublet is assigned to the two lowest 3ν bands, whose separation is expected to be small. In GuanBF_4 and GuanI the resolution in this region is poorer and the doublet is unresolved. The same peak is accordingly assigned to both of the two lowest 3ν bands. In all three compounds the choice of the two other 3ν transitions was made on the basis of which gave the best fit between observed and calculated energies. The 3ν bands in these crystals are about 1.5 orders of magnitude weaker than the 2ν bands. The other features in this region can best be assigned to $2\nu + 2\delta$, $2\nu + 2\mu$, and $2\nu + \delta + \mu$ (see Table I). No 3ν absorptions could be observed for GuanNO_3 .

For GuanClO_4 , GuanBF_4 , and GuanI extremely weak absorptions were observed where the 4ν bands are expected. They are about 3 orders of magnitude weaker than the 2ν bands and about 5–6 orders of magnitude weaker than the stretch fundamentals.

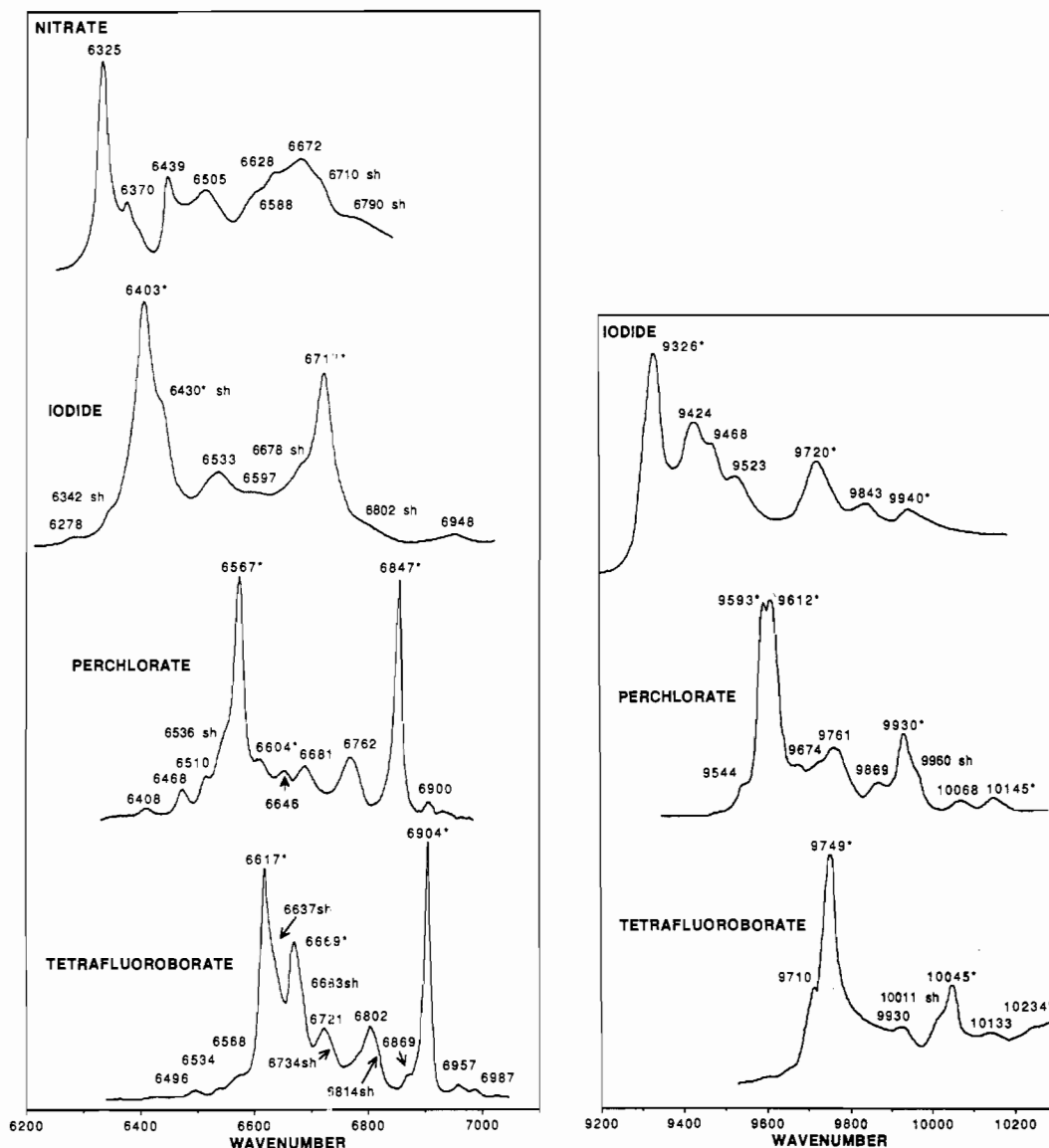


Figure 3. (a) Left: Spectra at 10 K of guanidinium salts in the region of the first overtone of the N–H stretch. Bands marked with asterisks were used in the fitting procedure. The band for GuanClO₄ at 6567 cm⁻¹ has $\epsilon \approx 3.6$. (b) Right: Same as (a), but in the second overtone region. The strongest bands for GuanClO₄ have $\epsilon = 0.070$.

Due to large uncertainties in their energy, they were not included as bands to be fitted by the minimization program.

While we consider it likely that most of the extra features in the 2ν and 3ν regions are due to combinations such as those listed in Table I, some of the bands could be due to coupling of an N–H...F or N–H...O vibration to the 2ν or 3ν band. In the spectrum of GuanBF₄, where the structure is best defined, the principal absorptions have associated bands which can be interpreted as short progressions in about 185 and 52 cm⁻¹. These may represent stretching and deformation vibrations of the N–H...F group, which in the CH₃CN–HF complex in the gas phase are found at 181 and 45 cm⁻¹, respectively.²⁶ The matter is discussed in more detail by Sandorfy.²⁷

Local-Mode Theory. Application of the local-mode model to the guanidinium ion follows the approach we used for water molecules in solids.³⁻⁵ Since the guanidinium spectra offer no evidence of coupling between the N–H bonds on different NH₂ groups, the model used is that of an isolated NH₂ group. In this group the two N–H bonds are equivalent, and the matrices needed

to calculate the eigenvalues are identical to those listed by Child and Halonen⁶ for gas-phase water. The parameters used in the calculations are as follows: ω , the local-mode harmonic frequency; X , the local-mode anharmonicity constant; and λ_{ij} , the coupling energy between oscillators i and j . Only coupling between functions having the same number of quanta of excitation is considered.

Table II shows the calculated and observed energies for the ν , 2ν , and 3ν bands for three guanidinium salts. The energies were calculated by solving the appropriate secular equations. An initial set of parameters was chosen and, by means of the program described previously,⁴ was systematically varied to minimize the sum of the squares of the differences between calculated and observed values. The process was stopped when another iteration produced no better fit. The standard deviations were calculated by the method suggested by Cowan.²⁸ Since we could not observe 3ν for GuanNO₃, no comparable fit was attempted for this compound. With only the ν and 2ν band energies, however, one can obtain a fit for GuanNO₃ with rms = 26 cm⁻¹ using the parameters $\omega = 3682$, $X = -168$, and $\lambda = -33$ cm⁻¹.

(26) Legon, A. C.; Millen, D. J.; Rogers, S. C. *Chem. Phys. Lett.* **1976**, *41*, 137.

(27) Sandorfy, C. *Vibrational Spectra of Hydrogen Bonded Systems in the Gas Phase*; Topics in Current Chemistry 120; Springer-Verlag: Berlin, 1984; pp 41–84.

(28) Cowan, R. D. *The Theory of Atomic Structure and Spectra*; University of California Press: Berkeley, CA, 1981; p 468 ff.

Table II. Stretch Overtone Energies and Local-Mode Parameters for Guanidinium Salts^a

Stretch Overtone Energies										
band	GuanBF ₄			GuanClO ₄			GuanI			assgnt ^c
	obs	calc ^b	diff	obs	calc ^b	diff	obs	calc ^b	diff	
1	3396	3376.6	19.4	3371	3352.3	18.7		3280.6		01)+
2	3485	3479.9	5.1	3454	3456.4	-2.4	3392	3396.8	-4.8	01)-
3	6617	6636.0	-19.0	6567	6566.9	0.1	6403	6405.4	-2.4	02)+
4	6669	6684.3	-15.3	6604	6611.7	-7.7	6430	6455.0	-25.0	02)-
5	6904	6904.8	-0.8	6847	6853.5	-6.5	6717	6727.0	-10.0	11)
6	9749	9738.7	10.3	9593	9596.3	-3.3	9326	9320.6	5.4	03)+
7	9749	9751.1	-2.1	9612	9606.2	5.8	9326	9331.5	-5.5	03)-
8	10045	10038.9	6.1	9930	9937.7	-7.7	9720	9705.9	14.1	12)+
9	10234	10233.0	1.0	10145	10135.9	9.1	9940	9927.4	12.6	12)-

Parameters Used in Best Fit ^d							
	GuanBF ₄	GuanClO ₄	GuanI		GuanBF ₄	GuanClO ₄	GuanI
ω	3600.4 (11.1)	3601.4 (8.0)	3561.1 (10.8)	λ	-51.6 (4.0)	-52.0 (3.0)	-58.1 (4.1)
X	-86.1 (3.5)	-98.5 (2.5)	-111.2 (3.4)	rms dev	11.3	8.4	12.1

^a All data in cm⁻¹. ^b Results of computer calculations are listed to one decimal; because of estimated standard deviations some digits cannot be regarded as significant. ^c For mixed states the average percent of the principal component is listed. ^d Standard deviations in parentheses.

Local-Mode Parameters. The shift of the stretch overtone bands to lower energies in the series GuanBF₄ > GuanClO₄ > GuanI > GuanNO₃ is a qualitative indication of increasing hydrogen-bond strength in that same order.²⁹ The local-mode analysis is an attempt to quantify this in terms of the parameters, ω, X, and λ. The increase in hydrogen-bond formation is clearly mirrored in the increase in magnitude of |X| for the N-H bond in the series GuanBF₄ < GuanClO₄ < GuanI < GuanNO₃. Sandorfy²⁷ has noted that there is much evidence that hydrogen-bond formation causes an increase in the anharmonicity of the X-H stretching motion and that the stronger the hydrogen bond, the larger the anharmonicity constant. It is interesting to note that hydrogen bonding to fluorine in tetrafluoroborate is weaker than that to oxygen in perchlorate. This is in sharp contrast to the very strong hydrogen bonding to ionic fluoride, which can be deduced from the infrared spectrum of guanidinium fluoride.³⁰

The values of ω for GuanBF₄, GuanClO₄, and GuanI are similar. It is not clear whether the small difference between the value for GuanBF₄ and GuanClO₄ and that for GuanI has any significance. It is difficult to relate this difference to hydrogen-bond strength, since the observed decrease in vibrational frequency appears to be largely due to the increase in value of |X|. Furthermore, it is not known how the harmonic stretching frequency of the N-H bond is expected to change as the hydrogen-bond strength increases. While the slight increase in |λ| in the series appears to be real, the explanation in terms of hydrogen-bond strength is also not clear in the present case. It has, however, been shown⁷ that the local-mode coupling constant, λ, can be written as a sum of kinetic (K) and potential (P) energy terms: λ = K + P. The kinetic term is generally the dominant one, and is given by

$$K = (\omega/2)(\cos \phi)m_H/(m_H + m_N) \quad (1)$$

where φ is the angle between N-H oscillators. With ω = 3600 cm⁻¹ and φ = 120°, K is about -60 cm⁻¹. Since the calculated values of λ for NH₂ in the guanidinium ion range from -51.6 to -57.9 cm⁻¹, λ-coupling is clearly dominated in this ion by the kinetic term. The potential term, P, appears to be small and opposite in sign, that is, about 2-8 cm⁻¹.

Upon hydrogen-bond formation, there is often an increase in δ as ν decreases.²⁹ In these guanidinium salts no real trend is observable. It may be that our data are not sufficiently precise to mirror such small changes or the strong mixing between δ and μ alters the expected relationship.

Table III. Local-Mode Parameters for Selected N-H Oscillators (cm⁻¹)

	harmonic freq (ω)	anharmonicity (X)	ref
Amines and Ammonia			
isopropylamine	3481	-77	a
n-propylamine	3527	-84	a
n-butylamine	3504	-80	a
sec-butylamine	3494	-79	a
tert-butylamine	3492	-82	a
methylamine	3538	-79	b
diethylamine	3536	-81	b
ammonia	3550	-75	c
Nonassociated Amides and Pyrrole			
pyrrole	3667	-68	d
N-ethylformamide	3610	-85	e
N-methylacetamide	3630	-80	e
N-methylbenzamide	3660	-90	e
trans-lactams	3675	-102	f
Associated Amides and Related Compounds			
N-methylbenzamide	3460	-35	e
Cu(thioacetamide) ₄ Cl	3446	-80	g
acetamide	3477	-42	e
Hg(thiourea) ₂ Cl ₂	3456	-71	g
thiourea	3513	-46	h
Ni(s-Me ₂ en) ₂ (TCA) ₂	3370	-40	g
Ni(s-Me ₂ en) ₂ Br ₂	3345	-60	g
trans-lactams	3460	-75	f
Ammonium Salts			
NH ₄ Cl	3252	-52	g
(NH ₄) ₂ SiF ₆	3471	-73	g
NH ₄ ClO ₄	3416	-65	g
Guanidinium Salts			
GuanBF ₄	3600	-86	i
GuanClO ₄	3601	-98	i
GuanI	3561	-111	i
GuanNO ₃	3682	-168	i

^a Data for ν = 4, 5 for liquid amines from ref 31. ^b Data for gaseous amines from: Fang, D. L.; Swofford, R. L.; Compton, D. A. *Chem. Phys. Lett.* **1984**, *108*, 539. ^c Data from ref 6. ^d Data for gaseous pyrrole (ν = 1, 4) from: Douketis, C.; Reilly, J. P. *J. Chem. Phys.* **1992**, *96*, 3431. Data for ν = 3 from: Carlotti, M.; Di Lonardo, G.; Galloni, G.; Trombetti, A. *J. Chem. Soc., Faraday Discuss.* **1972**, *68*, 1473. ^e Data for ν = 1, 2 from: Krikorian, S. E.; Mahpour, M. *Spectrochim. Acta* **1973**, *29A*, 1233. Nonassociated amides studied in CHCl₃ solution; associated amide studied in dioxane solution. Data for acetanilide and benzanilide are identical with those for N-ethylformamide. ^f Data for ν = 1, 2 from: Krikorian, S. E. *Spectrochim. Acta* **1991**, *47A*, 193. Nonassociated lactams studied in CCl₄ solution; associated lactams studied in solid state. ^g Unpublished results. Data are for ν = 2, 3 for single crystals at 10 K. s-Me₂en = N,N'-dimethylethylenediamine; TCA = trichloroacetate. ^h Data for acetone solution from: Bala, S. S.; Ghosh, P. N. *J. Mol. Struct.* **1985**, *127*, 277. ⁱ This report.

(29) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Francisco, CA, 1960; p 70.

(30) Bonner, O. D. *J. Phys. Chem.* **1977**, *81*, 2247.

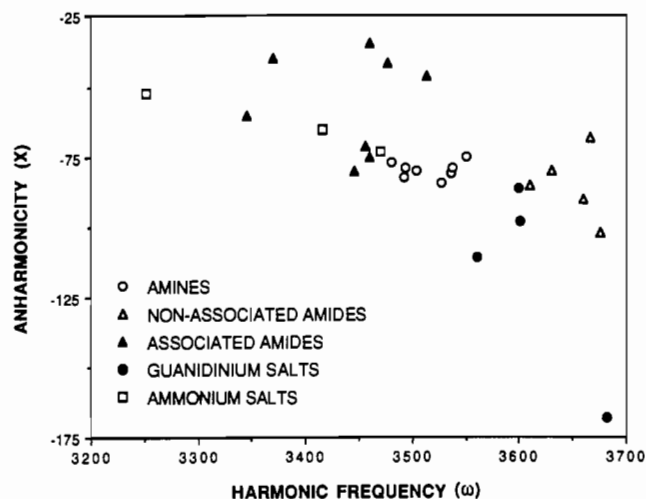


Figure 4. Plot of harmonic frequency (ω) versus anharmonicity (X) for N-H oscillators of compounds listed in Table III. All data are in cm^{-1} .

Parameters of Other N-H Oscillators. It is of interest to compare the local-mode parameters which we have obtained in this study with those of other compounds. In Table III and Figure 4 we present a selection, taken from a variety of sources, of such parameters. In areas where the literature is meager, we have used data from our unpublished low-temperature crystal studies. Furthermore, published data vary in extent of coverage. For the amides, for example, data are available for only the $\nu = 1$ and $\nu = 2$ levels, while, for ammonia, pyrrole, and the selected amines, data are available for several vibrational excited states. Nonetheless, certain trends are clear. If we group the oscillators by chemical environment, it can be seen that liquid- and gas-phase amines fall into a region characterized by a small range of ω and X values. Of the amines listed in Table III, the three in the gas phase show slightly higher values of ω . Snavely and Oref³¹ have noted that the N-H stretching frequency for liquid amines is in fact about 110–150 cm^{-1} lower than that of gaseous amines. This is due to weak association in the liquid state. The nickel complexes in Table III represent examples of coordinated amines, and the values of ω are considerably reduced from those of typical free amines. Nonassociated amides generally have harmonic frequencies somewhat greater than those of the amines, but there is rather little difference in the anharmonicity values between the two series.

(31) Snavely, D. L.; Oref, I. *J. Phys. Chem.* **1991**, *95*, 3076.

On passing to situations where hydrogen bonding is expected, it is seen that the amides undergo a substantial decrease in ω , as does ammonia when it forms crystalline ammonium salts. Worthy of note is the extremely low harmonic frequency of NH_4Cl , as well as the wide range of ω values in the ammonium salts. This may reflect variations in hydrogen-bond strength, just as was found in the guanidinium salts.

NH oscillators in coordinated thiourea, such as in $\text{Hg}(\text{thiourea})_2\text{Cl}_2$, and in $\text{Cu}(\text{thioacetamide})_4\text{Cl}$ are involved in hydrogen bonding to chloride ions, and their local-mode parameters fall into the same class as those of the associated amides. Guanidinium salts, which might be expected to behave much like associated amides, do not do so. Since both the guanidinium ion and the amide group are planar, or nearly so, each C-N bond has some double-bond character and each nitrogen is partially sp^2 -hybridized. This makes the nitrogen atom more electronegative than that of an amine in a similar associated or hydrogen-bonded state.³² This in turn causes the N-H bond to be stronger and ω to be greater than expected for a hydrogen-bonded NH group. A similar argument can be made for the ω value of pyrrole. The differences between the parameters for guanidinium salts and those for associated amides appear to be a reflection of the strength of hydrogen bonds formed. In general, as the strength of the hydrogen-bond donor increases, there is a discernible increase in the anharmonicity. This mirrors that observed for O-H oscillators in hydrogen-bonding situations.

We may conclude that guanidinium salts, which typically contain nitrogen with a formal positive charge, have much higher harmonic frequencies than ammonium salts, to which they might be expected to bear some resemblance. Their harmonic frequencies are as a group higher than those of chemically similar amides in hydrogen-bonding situations. In addition, the anharmonicities found in the guanidinium series represent some of the largest which we have found for NH oscillators under associated conditions.

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Registry No. GuanClO₄, 10308-84-6; GuanBF₄, 36595-00-3; GuanI, 19227-70-4; GuanNO₃, 506-93-4.

(32) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; p 149 ff.