

Figure 2.—Plots of \bar{n} functions pertaining to the determination of the stability quotients of mercury(II) azide at ionic strengths 0.05 (a), 0.15 (b), and 0.25 (c).

From the slopes and intercepts of plots such as those shown in Figure 2, it is possible to determine Q_1 and Q_2 for $\text{Hg}(\text{N}_3)_2$ in aqueous solution. The results are: $Q_1 = 3.0 \pm 0.6 \times 10^7$, $Q_2 = 1.8 \pm 0.2 \times 10^7$ at ionic strength 0.05; $Q_1 = 2.0 \pm 0.4 \times 10^7$, $Q_2 = 1.2 \pm 0.2 \times 10^7$ at ionic strength 0.15; $Q_1 = 1.4 \pm 0.3 \times 10^7$, $Q_2 =$

$9.4 \pm 1.2 \times 10^6$ at ionic strength 0.25. The uncertainties listed are experimental deviations observed in several different experiments at each ionic strength. Plots of $\log Q_1$ and $\log Q_2$ vs. \sqrt{I} give stability constants at zero ionic strength of: $K_1^0 = 5.6 \pm 1.1 \times 10^7$ and $K_2^0 = 3.1 \pm 0.4 \times 10^7$. More rigorous methods of extrapolation to zero ionic strength seemed unwarranted considering the probable limits of accuracy of the results as obtained by the method described.

It is of interest to compare the stability quotients of aqueous mercuric azide with stability quotients of the mercuric halides and other "pseudo-halides." The following published values¹³ are listed in order of increasing magnitude: HgCl_2 , $Q_1 = 5.5 \times 10^6$, $Q_2 = 3.0 \times 10^8$ (ionic strength 0.50, 25°, perchlorate media); HgBr_2 , $Q_1 = 1.1 \times 10^9$, $Q_2 = 1.9 \times 10^8$ (ionic strength 0.50, 25°, perchlorate media); $\text{Hg}(\text{SCN})_2$, $Q_1 Q_2 \cong 3 \times 10^{17}$ (varied media, 25°); HgI_2 , $Q_1 = 7.4 \times 10^{12}$, $Q_2 = 8.9 \times 10^{10}$ (ionic strength 0.50, 25°, perchlorate media); $\text{Hg}(\text{CN})_2$, $Q_1 = 1 \times 10^{18}$, $Q_2 = 5 \times 10^{16}$ (ionic strength 0.10, 25°, nitrate media). Thus, it would seem that the azide ion with respect to its tendency to form HgX^+ and HgX_2 species in aqueous solution may be placed in the following series, where derivatives of CN^- are the most stable: $\text{Cl}^- < \text{N}_3^- < \text{Br}^- < \text{SCN}^- < \text{I}^- < \text{CN}^-$. The values which are available for formation constants for azido complexes make it clear that the above order is not necessarily a general one. For example, the FeN_3^{2+} ion is far more stable than either FeCl^{2+} or FeBr^{2+} , whereas the formation constant for CuCl^+ is probably greater than that for CuN_3^+ .¹³

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Raman and Infrared Spectra of Nitronium Perchlorate

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The Raman spectrum of crystalline nitronium perchlorate exhibits ten well-resolved lines plus an additional tentative line appearing as a weak shoulder. The infrared spectrum, with sodium chloride optics, contains moderately intense absorptions at 940 and 2300 cm^{-1} and a strong broad absorption in the region of 1100 cm^{-1} which shows some tendency to resolve into three peaks. The spectra have been interpreted in terms of structural features shown by X-ray structure data. In addition, an interpretation is given correlating the bending mode of the nitronium ion with cation-anion interaction in crystalline nitronium salts.

Introduction

Nitronium perchlorate has classically been considered to be an ionic compound, with discrete nitronium ions and perchlorate ions. Evidence of its ionic character is well documented in the literature. Infrared data^{2a} and Raman spectra^{2b} are generally what

should be expected of a linear NO_2^+ ion isoelectronic with CO_2 and a tetrahedral ClO_4^- ion. We have obtained a more highly resolved Raman spectrum of nitronium perchlorate which cannot be interpreted using a model of isolated linear nitronium ions and isolated tetrahedral perchlorate ions. Our infrared data and those of earlier workers^{2a} are generally consistent with one another. The spectral data for solid nitro-

(1) (a) Midwest Research Institute; (b) Callery Chemical Co.
 (2) (a) J. R. Soulen and W. F. Schwartz, *J. Phys. Chem.*, **66**, 2066 (1962);
 (b) D. J. Millen, *J. Chem. Soc.*, 2606 (1950).

TABLE I
 INFRARED AND RAMAN FREQUENCIES OBSERVED IN NITRONIUM PERCHLORATE

Frequencies obsd., cm.^{-1}		Frequencies reported from other sources, cm.^{-1}		
Infrared	Raman	Infrared ^a	Raman ^b	
	448		461	Symmetric ClO_4^- bend
	471			
	571	570		NO_2^+ bend
	625	625	626	Antisymmetric ClO_4^- bend
	640			
	642 sh (?) ^c			
940	936	936	937.8	Symmetric ClO_4^- stretch
1060?	1080		1082	
1080?	1095	1100 vb		Antisymmetric ClO_4^- stretch
1130	1139		1143	
	1396		1396.2	Symmetric NO_2^+ stretch
2360		2360		Antisymmetric NO_2^+ stretch

^a Ref. 2a. ^b Ref. 2b. ^c sh, shoulder.

nitronium perchlorate are listed in Table I along with assignments of vibrational modes.

X-Ray investigations³ have shown that in nitronium perchlorate the NO_2^+ ion is slightly nonlinear and ClO_4^- is similarly distorted from a tetrahedron. These facts and other features of the crystal structure have been correlated with the observed spectra using the rigorous theory of vibrations in crystals.^{4,5} This analysis has shown that our spectral data are consistent with basic aspects of the crystal structure. Examination of existing information about other nitronium salts has, in addition, revealed fundamental differences in the character of the nitronium ion as it exists in different compounds.

Experimental

Crystalline nitronium perchlorate as produced by Callery Chemical Co. was employed in the studies. Samples were handled in a drybox atmosphere, with exposure even to a dry atmosphere being minimized as much as possible.

Raman Spectra.—The most highly resolved spectra were obtained with crystals approximately 1 mm. in diameter. Finely divided powder and crystals yielded spectra with the same features, but the best signal-to-noise ratio was found with larger particles. Spectra were obtained with a Cary Model 81 spectrometer without rearrangement of instrument optics.

Various types of sample holders were investigated. The holder which gave the best response and resolution is worthy of special mention, as it has not apparently been described in the literature. Sample holders were constructed of Pyrex tubing of the same outside diameters as liquid sample holders supplied for the instrument. A standard taper joint was sealed to one end of the holder. The other end of the tube contained a conically shaped configuration which held the sample. One method of construction consisted of fabricating a test tube end which was then indented (Vigreux type indentation) by means of a carbon rod with a conically shaped tip. The cone and tube were coaxial, and the height of the cone was 1 to 1.5 times the diameter of the tube. The radius of the cone varied from less than 1 mm. at the tip to slightly less than the inside radius of the tube. The sample of nitronium perchlorate, 1 to 2 g., was contained in the space between the tube and the cone, so that varying thicknesses of sample were exposed to incident radiation. Some holders were equipped with a hollow tubular extension about 3 in. long,

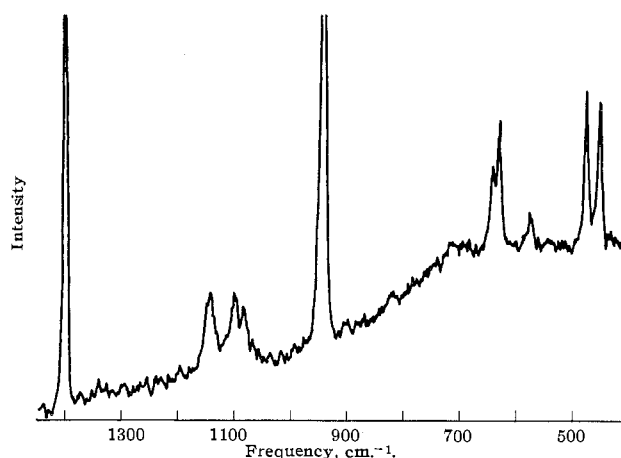


Figure 1.—Raman spectrum of solid nitronium perchlorate.

which was sealed to the end of the tube containing the cone. The extension was painted black and its end fitted flush against the cell optics. The latter arrangement generally gave stronger signals. The spectrum of nitronium perchlorate presented in Figure 1 was obtained, however, with a 22-mm. o.d. sample holder with the base of the cone flush against the cell optics.

Infrared Spectra.—Finely divided powders or Nujol mulls were dispersed thinly between two paired windows of sodium chloride and various other available materials. The best spectra were obtained with barium fluoride windows. The windows were sealed as tightly as possible with pressure-sensitive tape. Spectra were recorded with a Perkin-Elmer Infracord; resolution was sacrificed for speed, since the appearance of most spectra changed within a matter of minutes. The changes in the spectra with time are attributed primarily to unavoidable hydrolysis. Exposed samples exhibited a single sharp, strong band peaking at about 1100 cm.^{-1} and very weak absorptions at 2360 and 940 cm.^{-1} . The 2360 and 940 cm.^{-1} absorptions were sharp and of moderate intensity in the best spectra of freshly prepared samples (Table I), and a strong broad absorption occurred between about 1150 and 1000 cm.^{-1} . This broad band peaked fairly sharply at 1130 cm.^{-1} and exhibited evidence of weakly resolved peaks at 1100–1080 and 1060–1030 cm.^{-1} .

Discussion

Nitronium perchlorate crystallizes in a monoclinic unit cell (space group $C/2c-C_{2h}^6$) containing four formula units.³ The crystal contains discrete units of nitronium cation (NO_2^+) and perchlorate anion (ClO_4^-). The nitrogen and chlorine nuclei are located on twofold

(3) M. R. Truter, D. W. J. Cruikshank, and G. A. Jeffrey, *Acta Cryst.*, **13**, 855 (1960).

(4) R. S. Halford, *J. Chem. Phys.*, **14**, 8 (1946).

(5) D. F. Hornig, *ibid.*, **16**, 1063 (1948).

axes within the unit cell, and the two ions are alternately spaced along these axes. The location of these atoms in the unit cell requires that the two oxygens in the nitronium ion be equivalent (but not necessarily collinear with the nitrogen nucleus) and that the four oxygens in the perchlorate ion be divided into two pairs which are not necessarily equivalent. This condition permits the observed bend (*ca.* 5°) in the NO_2^+ cation and the observed distortion in the ClO_4^- anion.

Consider first the transitions due to the nitronium ion. An isolated linear nitronium ion would be expected to exhibit three vibrations. The nondegenerate symmetric stretching mode would be Raman-active. The nondegenerate antisymmetric stretching mode and the doubly degenerate bending mode would both be infrared-active. Since there is a center of symmetry in the species, dual Raman and infrared activities are not permitted. In the crystal, on the other hand, symmetry would cause each of these vibrations to become both Raman- and infrared-active and the degenerate bending mode to become split. However, since the nitronium ion is bent in its equilibrium configuration in crystalline nitronium perchlorate, only one bending mode would be expected in both the Raman and infrared spectra.

The infrared absorption at 2360 cm^{-1} and the Raman line at 1396 cm^{-1} clearly belong to the antisymmetric and symmetric stretching vibrational modes, respectively. The absence of a Raman transition near 2360 cm^{-1} and an infrared band near 1400 cm^{-1} shows that the stretching modes do not exhibit dual activity. However, a weak line appears at 571 cm^{-1} in the Raman spectrum and a strong band at 570 cm^{-1} in the infrared.^{2a} The exactness of these frequencies, plus the fact that a vibration due to ClO_4^- has never been reported in this area, leads us to the conclusion that this frequency is the NO_2^+ bend in both spectra.

The lack of dual activity for the stretching motions cannot be used to dispute this interpretation, since the theory of Raman and infrared transitions in crystals^{4,5} can only predict the numbers and activities of observed transitions. On the basis of symmetry alone, theory cannot predict the positions or the intensities of these components.

Let us now consider the perchlorate ion. In solutions of perchlorate compounds, four vibrations corresponding to a simple tetrahedral configuration are observed.⁶ The nondegenerate breathing vibration at 935 cm^{-1} and the doubly degenerate in-phase bending vibration at 462 cm^{-1} are both Raman-active but not infrared-active. The remaining two vibrations are the triply degenerate modes at 1082 and 628 cm^{-1} corresponding to the antisymmetric stretching and bending motions, respectively. These two vibrations are active in both the Raman and infrared. Since symmetry permits two nonequivalent pairs of oxygen in the ClO_4^- anion, the degenerate vibrations should be split into individual components, and all vibrations should become both

infrared- and Raman-active. Thus we should see nine fundamentals with both techniques. The triply degenerate vibrations should give a group of three lines, and the doubly degenerate vibrations should give rise to two. The nondegenerate breathing mode should be observed as a singlet in both spectra. As can be seen from Table I, this pattern is followed closely.

The strong line at 936 cm^{-1} in the Raman and the weak band at 940 cm^{-1} in the infrared are due to the symmetric breathing vibration of the perchlorate ion. The two transitions at 448 and 471 cm^{-1} in the Raman spectra arise from the doubly degenerate in-phase bending of the perchlorate ion. Infrared data are not available for these low-lying vibrations. However, one would expect a weak doublet, or more likely a weak, unresolved absorption. The group of three vibrations at 1080 , 1095 , and 1139 cm^{-1} in the Raman spectrum and the broad absorption region around 1100 cm^{-1} in the infrared arise from the triply degenerate antisymmetric stretching mode of the ClO_4^- anion.

Finally, we come to the triply degenerate antisymmetric bending mode for the ClO_4^- anion. In the infrared,^{2a} this transition is observed as a band at 625 cm^{-1} with a shoulder on the high-frequency side. In the Raman, it appears as a doublet at 625 and 640 cm^{-1} . Theory says that this mode should appear as a group of three separate transitions. The question immediately arises whether the Raman band at 571 cm^{-1} is the third component of the perchlorate antisymmetric bend or whether it indeed belongs to the NO_2^+ species where we have assigned it. The shift from 628 cm^{-1} in tetrahedral perchlorate⁶ to 571 cm^{-1} is very large, and it is highly questionable whether this large shift can be attributed to resolution of degeneracy. A close examination of the Raman spectrum reveals a small shoulder on the high-frequency side of the 640 cm^{-1} band which might account for the missing third frequency.

Fundamental Implications.—The Raman spectrum of nitronium perchlorate is strikingly similar to spectra observed by Hathaway and Underhill⁷ for certain transition metal perchlorates. These authors advanced an explanation involving a bidentate ClO_4 group, and their treatment implies structures substantially covalent in nature. Nitronium perchlorate is clearly ionic, and one must interpret its spectra in terms of ions. It is apparent that interpretations of bonding on the basis of symmetry alone must be made with caution. The X-ray and spectral data for nitronium perchlorate are nevertheless indicative of an interaction between cation and anion. In nitronium perchlorate we have a relatively rare case in which spectra are capable of indicating change in both cation and anion, and the data should therefore be examined for evidence of the nature of bonding in crystalline ionic compounds.

Additional insight can be gained from considerations of NO_2^+ in other salts and of the isoelectronic carbon dioxide molecule in the solid state. Pertinent data are

(6) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945, p. 167.

(7) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

TABLE II
 INFRARED AND RAMAN FREQUENCIES IN VARIOUS NITRONIUM SALTS AND SOLID CARBON DIOXIDE (CM.⁻¹)

—NO ₂ ClO ₄ —		—NO ₂ NO ₃ —		—NO ₂ BF ₄ —		—CO ₂ (s)—		
Infrared	Raman	Infrared ^a	Raman ^b	Infrared ^c	Raman ^c	Infrared ^d	Raman ^e	
570 ^f	571	538	...	590 } 605 }	...	653 } 660 }	...	ν_2 , bending mode
...	1396	...	1400	...	1399	...	1388	ν_1 , symmetric str. mode
2360	...	2375	...	2380	...	2344	...	ν_3 , antisymmetric str. mode

^a Ref. 8. ^b Ref. 9. ^c Ref. 11. ^d W. E. Osberg and D. F. Hornig, *J. Chem. Phys.*, **20**, 1345 (1952). ^e J. C. McLannan and H. D. Smith, *Can. J. Res.*, **7**, 551 (1932). ^f Ref. 2a.

available for nitronium nitrate (infrared,⁸ Raman,⁹ and structure by X-ray¹⁰) and nitronium fluoroborate (Raman and infrared¹¹). The fundamental frequencies of the nitronium ions and carbon dioxide are presented in Table II. While the stretching frequencies are very nearly identical in all cases, the only NO₂⁺ bending mode closely equal to that of carbon dioxide is that of nitronium fluoroborate (doublet centered at 598 cm.⁻¹). In nitronium perchlorate and nitronium nitrate, the bending modes are shifted to lower frequencies (570 and 538 cm.⁻¹, respectively). These shifts clearly indicate decreased resistance to bending. This transformation is accomplished with little effect on nitrogen-oxygen bonding energies, as the stretching frequencies are almost identical for all four cases.

It can be inferred from the above comparisons that NO₂⁺ bending frequencies are a measure of the extent of interaction, in crystals, between the nitronium cation and companion anion. In nitronium fluoroborate little cation-anion interaction is indicated, and one predicts a linear NO₂⁺ ion. On this basis, NO₂⁺ in nitronium fluoroborate is deemed to be more completely ionic than in nitronium perchlorate and nitronium nitrate. The cation of nitronium nitrate is by the same reasoning the least ionic; this conclusion is supported by the ease with which this compound volatilizes and reverts to appropriate covalent species.

(8) R. Teranishi and J. C. Decius, *J. Chem. Phys.*, **22**, 896 (1954).

(9) J. Chedin, *Compt. rend.*, **201**, 552 (1935).

(10) E. Grison, K. Eriks, and J. L. deVries, *Acta Cryst.*, **3**, 290 (1950).

(11) J. C. Evans, H. W. Rinn, S. J. Kuhn, and G. A. Olah, *Inorg. Chem.*, **3**, 857 (1964).

Walsh¹² has shown that addition of an electron to NO₂⁺ should theoretically be accompanied by the observed change in angle from 180 to 143°. The small change in angle observed in nitronium perchlorate can therefore be considered to result from a partial transfer of charge from perchlorate ion to nitronium ion. The transferred charge would be concentrated on the nitrogen atom and would not be expected to contribute significantly to the nitrogen-oxygen bond energy. Thus, the stretching frequencies should remain unchanged. On the other hand, the additional charge on the nitrogen atom would significantly affect the bending frequency. In nitronium nitrate, linearity is enforced by crystal symmetry, and the excess charge is evidenced only by a lowering of the bending frequency.

The proposed partial charge transfer can be treated as a resonance phenomenon, which implies a contribution of neutral NO₂ and neutral ClO₄ species to the overall wave function of the crystal. This minor contribution is exclusive of those for the individual NO₂⁺ cations and ClO₄⁻ anions. From a molecular orbital point of view, the model implies a small overlap between orbitals of the nitronium and perchlorate ions. The overlap would be much too small to interpret as covalency. Our interpretation presents a picture of the observed interactions which is consistent with the concept that ionic crystals are inadequately described by purely electrostatic forces.

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(12) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

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The Preparation and Thermal Stability of Trichloroboroxine

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The preparation of trichloroboroxine as a low-temperature photoinitiated reaction of boron trichloride and oxygen has been investigated. Trichloroboroxine was shown to be relatively stable as a gas-phase species at normal temperatures but to undergo decomposition when condensed on glass surfaces. A suggested reaction mechanism involves the initial photolysis of boron trichloride followed by reaction with oxygen to yield boron monochloride.

Introduction

The present work had its origin in a study of the photochemistry of volatile boron compounds. In the

case of BCl₃ it seemed likely that the continuous absorption of radiation beginning at about 2200 Å. and extending into the vacuum ultraviolet would give rise