509. *Vibrational Spectra of Ionic Forms of Oxides and Oxy-acids of Nitrogen. Part IV. Raman Spectral Evidence of Ionisation in Crystalline Nitronium Salts. The Constitution of Solid Dinitrogen Pentoxide. Note on the Spectrum of the Perchlorate Ion.*

By D. J. Millen.

The structural lattice components of some of the nitronium compounds described by Goddard, Hughes, and Ingold (*J.*, 1950, 2559) are identified by means of the Raman spectra of the crystalline substances. The diagnostic frequencies of certain of the structural units which are present in these compounds were originally established by measurements in solution, largely as is described in Parts I and II (*J.*, 1950, 2576, 2589). Some of these identification characters have been confirmed, and others have been newly determined, by means of a study here reported, of crystalline salts of alkali metals. With the aid of the data obtained in these ways, the substances named nitronium perchlorate, nitronium hydrogen disulphate, nitronium disulphate, and nitronium fluorosulphonate have been proved to be salts, having the ionic structures $(NO_2^+)(ClO_4^-)$, $(NO_2^+)(HS_2O_7^-)$, $(NO_2^+)_2(S_2O_7^{--})$, and $(NO_2^+)(FSO_3^-)$, respectively. In all cases, the molecular vibration spectra consist of, and display nothing more than, the superposed spectra of the ions.

Ingold, Millen, and Poole concluded, on Chédin's evidence concerning the Raman spectrum of solid dinitrogen pentoxide, that this substance has the ionic constitution of nitronium nitrate $(NO_2^+)(NO_3^-)$. The experimental evidence has been questioned, but Chédin's work has been repeated and confirmed. Despite suggestions to the contrary, the high vapour pressure, and allegedly high chemical constant, of dinitrogen pentoxide are not necessarily difficulties in relation to its ionic constitution.

Incidentally to this work, an obscure point concerning the vibration frequencies of the perchlorate ion is cleared up.

(1) *Raman Spectra of Crystalline Nitronium Salts.*

(1.1) *Scope of this Work.*—In accompanying papers, physical evidence of various kinds has been provided for the ionisation of nitric acid by certain very strong acids. It has been shown that the products of ionisation of nitric acid by a strong acid HX include the nitronium ion NO_2^+ and the anion X^-. The isolation of certain solid products, which involve the ionisation of nitric acid in this manner, has been described by Goddard, Hughes, and Ingold (*J.*, 1950, 2559). Some of these solids have compositions corresponding to the general formula NO_2X.

The present paper describes the identification of the crystalline-lattice components of some solids isolated by these authors. In addition, solid dinitrogen pentoxide, which is the member of the series NO_2X with $X = NO_3$, has been re-examined. The method of investigation was Raman spectroscopy, by which the structural units of the crystals were identified from their known spectra. The diagnostic characteristics of some of these constituents have been established in Parts I and II. The identification of a number of the constituents was confirmed by a special study of the Raman spectra of certain comparison substances.

(1.2) *Solids derived from the System* HNO_3–$HClO_4$.—Goddard, Hughes, and Ingold obtained two solid materials of definite composition from this system. One of these corresponded to the formula $NClO_6$, and the other to $H_3NCl_2O_{11}$. It was important to establish the nature of the compounds, since the structure of the second had been claimed to be $(H_3NO_3^{++})(ClO_4^-)_2$, in support of the view that the ionisation of nitric acid in strong acids produces the ion $H_3NO_3^{++}$.

The frequencies observed in the Raman spectra of these two solids are recorded in Table I, together with the frequencies of the perchlorate ion as observed in an aqueous solution of sodium perchlorate (Redlich, Holt, and Bigeleisen, *J. Amer. Chem. Soc.*, 1944, **66**, 13). All the frequencies of the two solids were observed as Stokes lines excited by nitrite-filtered Hg 4358 A. A microphotometer trace of part of the spectrum of $NClO_6$ is reproduced in Fig. 1.

It is evident from Table I that the Raman spectrum of solid $NClO_6$ consists simply of the superposed Raman spectra of the perchlorate and nitronium ions. (The reason for the observation of a doublet in place of a band is considered in Section 3.) This establishes that, as was first reported in a preliminary note (*Nature*, 1946, **158**, 480), the solid has the ionic structure $(NO_2^+)(ClO_4^-)$. The crystal structure of this substance has also been investigated by *X*-ray methods (Cox, Jeffery, and Truter, *Nature*, 1948, **162**, 259), with results which confirm the assigned constitution.

TABLE I.

Raman frequencies (cm.$^{-1}$) of crystalline solids derived from the system HNO_3–$HClO_4$. *Comparison with the Raman frequencies of the perchlorate ion.*

Solid $NClO_6$.	Solid $H_3NCl_2O_{11}$.	ClO_4^- ion (R, H., and B.).	Solid $NClO_6$.	Solid $H_3NCl_2O_{11}$.	ClO_4^- ion (R., H., and B.).
461 (mw)	460 (mw)	461 (m)	1082 (mw)	—	1058 to 1167 (w, band)
626 (m)	625 (m)	631 (ms)	1143 (mw)	—	
937·8 (vs)	926 (s)	940 (vs)	1396·2 (vs) *	1395·4 (s) *	—

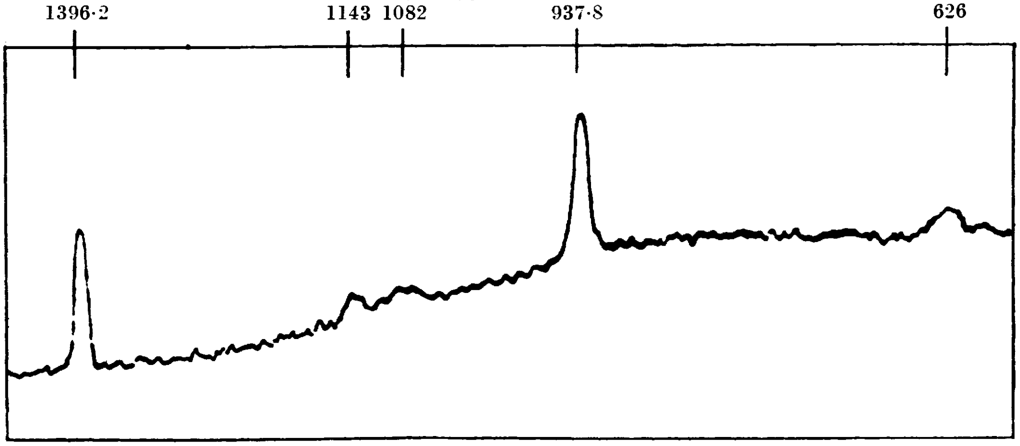
* Nitronium ion frequency.

The Raman spectrum of the solid $H_3NCl_2O_{11}$ contains the three strongest fundamental frequencies of the perchlorate ion and the Raman-active nitronium ion frequency. The solid must therefore contain the nitronium and perchlorate ions. Its composition can be explained by supposing it to be a mixture of nitronium perchlorate and the well-known monohydrate of perchloric acid in equimolecular proportions. The monohydrate doubtless has the ionic constitution $(H_3O^+)(ClO_4^-)$. Its Raman spectrum is simply that of the perchlorate ion, since, as is well known, the hydroxonium ion does not give a distinct Raman spectrum.* For stoicheiometric reasons the two substances $(NO_2^+)(ClO_4^-)$ and $(H_3O^+)(ClO_4^-)$ are necessarily produced from nitric and perchloric acids in equimolecular proportions, and some of the preparative methods which have been employed leave little opportunity for even partial separation.

FIG. 1.

Microphotometer trace of part of the Raman spectrum of solid $NClO_6$.

ν (*cm.*$^{-1}$) *from* Hg 4538 A.



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* Further attempts will be made to find a hydroxonium ion spectrum in solid hydroxonium perchlorate; but all that can be seen on the Raman spectrograms so far secured is the perchlorate ion spectrum.

(1.3) *Solids derived from the System* N_2O_5–SO_3–H_2O.—Two of the solid phases that Goddard, Hughes, and Ingold obtained from this system have been examined spectroscopically. They have compositions corresponding to the formulæ $(NO_2)HS_2O_7$ and $(NO_2)_2S_2O_7$. The spectral characteristics of the anions $HS_2O_7^-$ and $S_2O_7^{--}$ were considered in Part II (*J.*, 1950, 2589) on the basis of a study of the Raman spectra of solutions in sulphuric oleum. In order to confirm the conclusions thus derived and to establish a sound basis for the spectroscopic identification of these anions, solid potassium disulphate $K_2S_2O_7$, and solid potassium hydrogen disulphate KHS_2O_7 have now been examined. The results obtained for both the nitronium salts and the reference potassium salts are assembled in Table II. These frequencies were measured as Stokes lines excited by Hg 4358 A. Only the strongest Raman frequencies of the hydrogen disulphate and normal disulphate ions are recorded clearly enough for measurement in the spectra of the solid salts.

It is obvious from Table II that the two nitrogen compounds are nitronium hydrogen disulphate $(NO_2^+)(HS_2O_7^-)$ and nitronium disulphate $(NO_2^+)_2(S_2O_7^{--})$. Their Raman frequencies correspond to those of potassium hydrogen disulphate and potassium disulphate, respectively, except for the additional frequency, 1400 cm.$^{-1}$, given by the former pair of compounds, which is evidently due to the nitronium ion.

TABLE II.

Raman frequencies (cm.$^{-1}$) of solid potassium and nitronium salts derived from disulphuric acid.

$(NO_2)HS_2O_7$.	$(NO_2)_2S_2O_7$.	KHS_2O_7.	$K_2S_2O_7$.
1075	1096	1073	1096
1396 *	1401 *	—	—

* Nitronium ion frequency.

(1.4) *Solid derived from the System* N_2O_5–$F{\cdot}SO_3H$.—In the Raman spectrum of this solid substance which has the composition $(NO_2)FSO_3$, strong sharp lines were observed at 1405 cm.$^{-1}$ and 1083 cm.$^{-1}$. The former is attributed to the nitronium ion, and the latter to the fluorosulphonate ion. The Raman spectrum of the latter ion had not been previously studied, but the suggested assignment of the strong line at 1083 cm.$^{-1}$ to this ion has been confirmed by the observation of a single strong and sharp line at 1087 cm.$^{-1}$ in the Raman spectrum of solid lithium fluorosulphonate. The Raman frequencies of solid nitronium fluorosulphonate are thus accounted for on the basis that the solid is an ionic crystal $(NO_2^+)(SO_3F^-)$.

(2) *The Constitution of Solid Dinitrogen Pentoxide.*

(2.1) *The Raman Spectrum of Dinitrogen Pentoxide.*—The Raman spectra of solutions of dinitrogen pentoxide in carbon tetrachloride, chloroform, or phosphorus oxychloride (Chédin, *Compt. rend.*, 1935, **201**, 552) contain lines at the following frequencies, which Chédin has attributed to the N_2O_5 molecule :

707, 860, 1033, 1240, 1335 cm.$^{-1}$

The existence of dinitrogen pentoxide in the molecular form in phosphorus oxychloride solution is consistent with the cryoscopically determined molecular weight of the substance in that solvent (Walden, *Z. anorg. Chem.*, 1910, **68**, 314).

Chédin (*Compt. rend.*, 1936, **203**, 722) found that the Raman spectrum of solid dinitrogen pentoxide contains none of the lines found for its solutions in the solvents mentioned above. Instead, there appeared two sharp lines having frequencies of 1051 cm.$^{-1}$ and 1400.$^{-1}$. Chédin accounted for these spectral differences by supposing that dinitrogen pentoxide exists in the solid state, not in the molecular form, but in some modified form. This modified form has been interpreted by Ingold, Millen, and Poole (*Nature*, 1946, **158**, 480) as the ionic form $(NO_2^+)(NO_3^-)$. They assigned the frequency of 1400 cm.$^{-1}$ to the nitronium ion, and the frequency 1050 cm.$^{-1}$ to the nitrate ion, and supposed that the other two fundamental frequencies of the nitrate ion were not observed in the spectrum of the solid because of their low intensity compared with that of the frequency of 1050 cm.$^{-1}$ (cf. Part V, *J.*, 1950, paper no. 510).

An alternative explanation of the origin of the lines at 1050 cm.$^{-1}$ and 1400 cm.$^{-1}$ in the Raman spectrum of the solid has, however, been suggested in certain widely circulated documents. This is that small quantities of nitric acid might have been present among the crystals Chédin employed, and that dinitrogen pentoxide, although covalent in the solid state, dissolved and ionised in this nitric acid to produce nitronium and nitrate ions. The Raman spectrum of a solution of these ions in nitric acid does contain sharp lines at 1050 cm.$^{-1}$ and 1400 cm.$^{-1}$, as has been directly observed (cf. Part V). This explanation is, however, not satisfactory, because none of the lines of molecular nitric acid was observed by Chédin in the spectrum.

In order to establish conclusively which of these interpretations is correct, the observation of the Raman spectrum of solid dinitrogen pentoxide has been repeated, under conditions which ensure the absence of nitric acid from the crystals. Dinitrogen pentoxide was distilled in a stream of ozonised oxygen on to phosphoric oxide, and redistilled through phosphoric oxide into a Raman cell. The cell was then closed by ground-glass caps which were externally sealed with metaphosphoric acid. The spectroscopic result confirms that of Chédin : the spectrum of the solid at $-40°$ contains sharp lines at 1047 cm.$^{-1}$ and 1394 cm.$^{-1}$, and naturally no vestige of any lines of molecular nitric acid.

All the collateral evidence in this paper shows that the Raman-spectral method is a valid one for identifying the structural units in crystals. The constitution of nitronium perchlorate, which was first established in this way, has since been confirmed by *X*-ray methods (Cox, Jeffery, and Truter, *loc. cit.*). It is therefore impossible to escape the conclusion * that solid dinitrogen pentoxide has the ionic structure $(NO_2^+)(NO_3^-)$, just as solid phosphorus pentachloride has the ionic structure $(PCl_4^+)(PCl_6^-)$. In the vapour phase the anhydride consists of N_2O_5 molecules, just as sodium chloride vapour consists essentially of NaCl molecules.

(2.2) *The Volatility of Dinitrogen Pentoxide.*—We are accustomed to regarding low volatility as one of the characteristics of ionic crystalline substances. Dinitrogen pentoxide has, however, a sublimation pressure of approximately 200 mm. at 15°. The comparatively high volatility of dinitrogen pentoxide is connected with its low latent heat of sublimation in comparison with the latent heats of the majority of ionic crystals. Whereas the latent heats of sublimation of the alkali chlorides are of the order of 50 kcals./g.-mol., the latent heat for dinitrogen pentoxide is approximately 13 kcals./g.-mol. (Russ and Pokorny, *Monatsh.*, 1913, **34**, 1040; Daniels and Bright, *J. Amer. Chem. Soc.*, 1920, **42**, 1131). The energy required for the vaporisation of an ionic crystal depends upon the difference between the lattice energy of the crystal and the energy obtained from the pairing of the ions to form the gaseous molecules. In the case of sodium chloride, for instance, the high value of the lattice energy (about 180 kcals./g.-mol.), and the considerably smaller energy of formation of sodium chloride molecules from Na^+ and Cl^- ions (about 125 kcals./g.-mol.), results in a large latent heat of sublimation. In the sublimation of dinitrogen pentoxide, the energy gained in the formation of a covalent N–O bond, and the consequent electron redistribution, much more nearly compensates for the expenditure of the lattice energy.

Chédin's inference that the dinitrogen pentoxide molecule is modified in the solid state is particularised in our conclusion that the molecule is ionised; but the opposite form of particularisation, *viz.*, that the molecule is associated or polymerised, has been made, and has been quoted, so that the basis of the idea should be examined. It was first advanced by Russ and Pokorny (*loc. cit.*), in consequence of their conclusion that dinitrogen pentoxide has a high " chemical constant." This conclusion was derived by a consideration of the vapour pressure of dinitrogen pentoxide, the connexion being the dependence of vapour pressure on the vapour-pressure constant.

The equilibrium vapour pressure of a solid at a temperature T is given by the equation

$$\ln p = -\frac{L_0}{RT} + \int_0^T \frac{dT}{RT^2} \int_0^T \Delta C_p dT + i$$

provided that we may assume the vapour to behave as an ideal gas. Here L_0 is the molar heat of sublimation at the absolute zero of temperature, ΔC_p is the difference between the heat capacities of the two phases ($\Delta C_p = C_{p(\text{gas})} - C_{p(\text{solid})}$), and i is the vapour-pressure constant of the substance. Thus a high vapour pressure may arise either from a low latent heat of sublimation, or from a high vapour-pressure constant, or (except at low temperatures) from a high heat-capacity difference; or, of course, from any combination of these causes.

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* [*Added in proof,* 14.7.50.] A very recent paper by Grison, Ericks, and de Vries (*Acta Crystall.*, 1950, **3**, 290) gives *X*-ray confirmation of the ionic structure, together with the complete crystal geometry. The linear centrosymmetric NO_2^+ ions lie normal to the planes of the trigonal planar NO_3^- ions. The bond-length of the NO_2^+ ion, $1{\cdot}154 \pm 0{\cdot}01$ A., is the most accurate yet recorded. It is of interest to compare it with the spectroscopically measured bond-length of carbon dioxide, *viz.*, 1·163 A., and with the *X*-ray bond-length of the ion N_3^-, *viz.*, $1{\cdot}15 \pm 0{\cdot}02$ or $1{\cdot}165 \pm 0{\cdot}02$ A.

The constant i is connected with other thermodynamic functions through the equation

$$i = (\Delta S^\circ - C^\circ_{p(\text{gas})})/\boldsymbol{R}$$

where ΔS° is the difference between the molar entropies of the phases at the zero of temperature ($\Delta S^\circ = S^\circ_{(\text{gas})} - S^\circ_{(\text{solid})}$), and $C^\circ_{p(\text{gas})}$ is the molar heat capacity of the vapour at the zero of temperature. The conditions for a high value of i are therefore a high entropy for the vapour and a low entropy for the solid. The following conditions are some of those which would contribute to such a situation: (1) no disorder in the solid at the absolute zero of temperature; (2) no degeneracy in the ground state of the solid; (3) a molecular symmetry number equal to unity; (4) degeneracy in the ground state of the gaseous molecule. If we assume that orientation in the crystal at the absolute zero of temperature is perfect, that there is no degeneracy in either the solid or the gas, and that the symmetry number of the non-linear gaseous molecule is unity (so that all rotational states are available), then i is given by the equation

$$i = \ln\{64\pi^5\boldsymbol{k}^4m^{3/2}(ABC)^{1/2}/\boldsymbol{h}^5\}$$

where m is the mass, and A, B, and C are the principal moments of inertia, of the gaseous molecule, $\boldsymbol{k}$ is Boltzmann's constant, and $\boldsymbol{h}$ is Planck's constant. Unfortunately, we do not know enough about the molecular dimensions of dinitrogen pentoxide to obtain a good value of i from this equation; but there seems to be no reason to suspect an abnormally high value. The same statement could be made if the symmetry number were two, as it might be.

The other possible method of obtaining i involves the use of the integrated vapour-pressure equation given above. However, the application of this method to dinitrogen pentoxide would require much more knowledge than we possess of the specific heat of this substance. For the vapour, at temperatures at which vibration is unexcited, we might make the approximation, $C_{p(\text{gas})} = C^\circ_{p(\text{gas})}$, which amounts to assuming that rotation is classical down to the temperature zero. But still $C_{p(\text{solid})}$ will vary in a complicated way, owing to the acoustical vibrations in the crystal lattice. Yet, without a knowledge of ΔC_p as a function of temperature, it is impossible to deduce i from the temperature variation of $\ln p$.

Now Russ and Pokorny obtained their constant, which they called the "chemical constant," by the use of an empirical vapour-pressure equation. This was in 1913, before much was known about the third law, or, for that matter, about the variation of specific heats of solids with temperature. Their constant is really no more than the temperature-independent term in their particular empirical equation. At that time, it appeared that constants so obtained were approximately the same for most substances. But water had a high "chemical constant"; and this seems to have led to the assumption that associated substances had high chemical constants. That is how the idea originated that solid dinitrogen pentoxide is associated.

(3) *Note on the Raman Spectrum of the Perchlorate Ion.*

(3.1) *The Five Raman Frequencies of the Perchlorate Ion in Crystals.*—In Section 1.2, five of the Raman frequencies of crystalline nitronium perchlorate were assigned to the perchlorate ion. A regular tetrahedral structure for the perchlorate ion requires that it should possess four fundamental vibration frequencies, all of which should be active in the Raman spectrum. The observation of the Raman spectra of aqueous solutions of perchlorates (Redlich, Holt, and Bigeleisen, *loc. cit.*) has established the existence of fundamental frequencies of approximately 460 (m), 630 (ms), and 935 (vs) cm.$^{-1}$. A fourth frequency has generally been reported as a broad, weak band extending approximately from 1050 to 1170 cm.$^{-1}$. In the Raman spectrum of solid nitronium perchlorate there appear two lines, at 1080 and 1143 cm.$^{-1}$, instead of the usual broad band. The resolution of these two lines is clearly shown on the microphotometer record reproduced in Fig. 1.

TABLE III.

Raman displacements (cm.$^{-1}$) of Stokes lines excited by Hg 4358 A. *in the spectra of some solid perchlorates.*

$KClO_4$	461 (mw)	628 (m)	938 (vs)	1073 (mw)	1121 (mw)	—
$NClO_6$	461 (mw)	626 (m)	938 (vs)	1082 (mw)	1143 (mw)	1396 (s) *

* Nitronium ion line.

Previous records of the Raman spectrum of crystalline potassium perchlorate include no mention of a frequency near 1100 cm.$^{-1}$, and the Raman spectrum of this crystal has therefore been re-examined. Again five Raman lines, which necessarily must belong to the perchlorate ion, have been found, including two in the neighbourhood of 1100 cm.$^{-1}$. The comparison in Table III of the observed frequencies of potassium and nitronium perchlorates leaves no doubt that the perchlorate ion possesses five Raman frequencies. It is accordingly necessary to consider the assignment of these frequencies.

(3.2) *Assignment of Frequencies of the Perchlorate Ion.*—The normal vibrations of a regular tetrahedral molecule XY_4 are classified according to their symmetry in Table IV. The 9 degrees of vibrational freedom are distributed over one non-degenerate, one doubly degenerate, and two triply degenerate vibrations. An assignment of frequencies of the perchlorate ion to these vibrations is indicated on the right-hand side of the Table.

It is certain that the intense Raman frequency 935 cm.$^{-1}$ belongs to the "breathing" vibration ν_1. It is equally definite that the two low frequencies, 630 and 460 cm.$^{-1}$, collectively belong to the bending vibrations ν_2 and ν_4. Redlich, Holt, and Bigeleisen (*loc. cit.*) have assigned these two frequencies in the manner indicated in the Table, on the basis of a comparison with the spectrum of perchloric acid. This particular allocation of the frequencies may be regarded as probably, but not certainly, correct. However, even if the assignments of these two frequencies should have to be interchanged,* it would make no difference to the following discussion of the remaining two observed frequencies, and of the remaining normal vibration ν_3.

The present suggestion is that the observed doubtlets near 1100 cm.$^{-1}$ in the solid perchlorates constitute the simplest type of result that can arise from Fermi resonance between the fundamental frequency ν_3 and the combination tone $\nu_2 + \nu_4$. The fundamental vibration has symmetry F_2 (Table IV). The combination state consists of two sub-states, degenerate in themselves and with each other, one of symmetry F_1,† and the other of symmetry F_2. The former is forbidden in the Raman effect, but the latter is allowed, and is of the right symmetry for resonance with the fundamental vibration. The unperturbed frequency of the combination tone would be 1090 cm.$^{-1}$, and it is assumed that this is close enough to the unperturbed fundamental frequency, ν_3, estimated as approximately 1110 cm.$^{-1}$, to permit resonance under the coupling action of anharmonicity. The result is a further separation of the frequencies, and a sharing of the intensities, so that one observes a doublet.

TABLE IV.

Normal vibrations of regular tetrahedral molecules XY_4.

Vibration.	Symmetry.	Deg. of freedom.	Approximate description.	ClO_4^- (cm.$^{-1}$).
ν_1	A_1	1	Totally symmetrical; synchronous stretching.	935
ν_2	E	2	Doubly degenerate; bending; external atoms converge in pairs synchronously.	630
ν_3	F_2	3	Triply degenerate; stretching; external atoms displaced towards a common but indefinite direction.	~1110 *
ν_4	F_2	3	Triply degenerate; bending; external atoms bent towards a common but indefinite direction.	460

* Split by Fermi resonance—see text.

(3.3) *Nature of the Raman Band around* 1100 *cm.*$^{-1}$ *of the Perchlorate Ion in Solution.*—It has now to be considered why the Raman doublet of the perchlorate ion in the crystal becomes replaced by a diffuse band in observations on the perchlorate ion in solution. The evident cause is the high degeneracy of the vibrational states concerned. Contributing to the Fermi doublets there are really six vibrational energy states, arranged, according to the preceding discussion, in two sets of three, *i.e.*, in two levels. However, strict degeneracy within each set of three will be preserved only so long as the equilibrium configuration about which the ion is vibrating has the full symmetry of a regular tetrahedron. Since ions can never be obtained in practical concentrations otherwise than under the influence of strong external fields, this condition will be fulfilled or approached only if such external fields have a high degree of symmetry. The field acting on an individual perchlorate ion in a crystal will always have a large amount of symmetry, and in some crystals at least it may be so symmetrical as to cause no serious breakdown of the degeneracies. These are the conditions in which we

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* [*Added in proof*, 14.7.50.] They have, indeed, to be interchanged; Mr. H. Cohn has found the frequency 630 cm.$^{-1}$ in the infra-red spectra of solid nitronium and metal perchlorates. This shows that it is ν_4, so that 460 cm.$^{-1}$ must be ν_2. These observations are so recent that the text above has not been altered.

† The symmetry F_1 may be described as that of an isotropic rotation, just as the symmetry F_2 is that of an isotropic translation (cf. Table IV).

observe the Fermi doublets. In aqueous solution, however, any ion which does not form a stereochemically stable polyhydrate will always be under strongly dissymmetric forces. This should cause the six energy states of the Fermi doublet to fall apart, so that instead of two levels, we shall have six levels. Furthermore, the dissymmetric forces are not steady, but are fluctuating with the thermal motion. One can readily understand how, in these circumstances, the comparable intensities of six diffuse and overlapping Raman lines integrate to the intensity distribution of a broad band, extending, according to the observations, over more than 100 cm.$^{-1}$.

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