Theoret. Chim. Acta (Berl.) 42, 145–154 (1976)

THEORETICA CHIMICA ACTA

Semi-Empirical Calculations on the Structure of the Oxonium Ion in Various Crystal Sites and Relative Acidity Scale

Michel Fournier
Faculté des Sciences, F–66025 Perpignan, France

Marcel Allavena
Centre de Mécanique Ondulatoire Appliquée (C.N.R.S.), 23 rue du Maroc, F–75019 Paris, France

Antoine Potier
Laboratoire des Acides Minéraux, U.S.T.L., F–34060 Montpellier, France

The structure of the H_3O^+ ion embedded in a solid environment ($H_3O^+X^-$, $X^- = Cl^-$, NO_3^-, ClO_4^-) is studied using a modified version of CNDO/2. In this calculation the effect of the first shells of nearest neighbours is taken into account and the effects of second nearest neighbours are introduced by a simulation procedure. Electronic effects are also included. The ion structure is more planar in nitrate than in perchlorate environment and the hydrogen bonds are slightly bent. Trends in structural parameters are compared with chemical properties of the hydrogen bonds and parallels the Hammett acidity scale $HNO_3 < HCl < HClO_4$.

Key words: Oxonium ion in solid environment

1. Introduction

The importance of the oxonium ion in the chemistry of acid solution has been recognized for a long time [1]. However there is no way to observe this species in the liquid state. It is found in the cystals of monohydrates and one can hope to obtain from these solids information on the behaviour of the corresponding acid solutions. A great number of crystallized monohydrates of strong acids are in fact oxonium salts

$$HX \cdot H_2O \rightarrow H_3O^+X^-$$

with, for example, $X^- = Cl^-$, NO_3^-, ClO_4^-.

In these ionic compounds, the H_3O^+ ion is hydrogen bonded to the various anions: Cl^-, NO_3^- and ClO_4^-. A proposed structure for H_3O^+, as deduced from experiments such as X-ray diffraction [2, 10], neutron diffraction [11, 12] and N.M.R. [13, 14] or from spectroscopic experiments (I.R. [15–19] and Raman [20–21]), is shown in Fig. 1. Unfortunately most of these methods lead to an incomplete description of the cation. In the case of X-ray diffraction, only the $O \ldots X^-$ bond length and its spatial orientation in the solid can be determined as well as an estimate of the HOH angle provided that the H atom lies on the $O \ldots X^-$ axis. A better estimate of the bond angle can be obtained from neutron diffraction studies and an $H \ldots H$ bond length by N.M.R. investigations. In Table 1

Table 1. Experimental data: X-ray diffraction, neutron diffraction and nuclear magnetic resonance

			$d(\mathrm{OH}\ldots\mathrm{X}^-)$A	$d(\mathrm{X}^-\ldots\mathrm{X}^-)$A	$(\widehat{\mathrm{XOX}^-})°$	$d(\mathrm{O}\ldots\mathrm{H})$A	$(\widehat{\mathrm{HOH}})°$	$d(\mathrm{H}\ldots\mathrm{H})$ A
2	$HClH_2O$	X-Ray Diffraction	2.95 ± 0.01	(4.84)[a]	110.4 ± 0.2	0.96 ± 0.08	117	(1.65)
3	$HClO_4H_2O$		2.92 ± 0.02				107	
			2.93 –				102	
			2.86 –				102	
4	$HClO_4H_2O$		2.64 ± 0.01	(4.37)	118.9 ± 0.5	0.78 ± 0.06	113 ± 9	(1.37)
			2.71 –		110 –	0.82 ± 0.05	110 ± 4	
			2.63 –		104.3 –	0.91 ± 0.11	112 ± 5	
5	HNO_3H_2O		2.54	(4.44)	120			
6			2.61		117			
7			2.68		113			
8	HNO_3H_2O[b]		2.608 ± 0.003	(4.29)	115.6 ± 0.2	0.88 ± 0.006	117 ± 5	(1.49)
			2.589 –		113.7 –	0.89 – 4	101 ± 6	
			2.589 –		105.9 –	0.96 – 6	111 ± 4	
9	$H_2SO_4H_2O$		2.566 ± 0.005	(4.24)	125.5 ± 0.2			
			2.649 – 6		100.9 –			
			2.538 – 6		106.4 –			
10	$CF_3SO_3H\ H_2O$[c]		2.668 ± 0.004	(4.32)	132.1 ± 0.1	$0.93 \leqslant \ldots \leqslant 1.04$	$100 \leqslant \ldots \leqslant 131$	$(1.42 \leqslant \ldots \leqslant 1.89)$
			2.546 –		108.2 –2			
			2.585 –		101.3 –1			
11	$CH_3C_6H_4SO_3H\ H_2O$	Neutrons	2.538 ± 0.005	(4.13)	114.9 ± 0.2	1.013 ± 0.008	111.2 ± 0.5	(1.66)
			2.525 –		110.0 –	1.011 –	110.7 –	
			2.520 –		103.8 –	1.008 –	111.2 –	
12	$CH_3C_6H_4SO_3D\ D_2O$		2.537 ± 0.004	(4.14)	114.4 ± 0.2	1.020 ± 0.003	110.2 ± 0.4	(1.66)
			2.537 –		109.6 ± 0.1	1.011 –	110.2 –	
			2.549 –		103.4 ± 0.1	1.008 –	108.6 ± 0.3	
13	HNO_3H_2O $HClO_4H_2O$	N.M.R.						1.72 ± 0.02
14	$3Ga_2O_34SO_3$ $9H_2O$							1.71 ± 0.03

[a] Mean value calculated from experimental data. [b] Structural data at 225°K. [c] Structural data at 298°K.

Table 2. Experimental data. I.R. and Raman spectroscopy

		Symetrie	HOH (°)
I.R.	$H_3O^+ClO_4^-$ [17]	C_{3v}	112
Raman	$H_3O^+ClO_4^-$ [20]	C_{3v}	107
	$H_3O^+SbCl_6^-$ [21]	C_{3v}	108

a list of structural parameters determined by these techniques is given. The spectroscopic data, mainly I.R. and Raman, provide another source of structural information. The molecular symmetry C_{3v} and some qualitative estimate of the bond length and angle can be obtained from a vibrational analysis (G.F. method) and isotopic studies of the fundamental frequencies. The uncertainty of the assignment as well as precise isotopic shift (due to inhomogeneous broadening) introduces the possibility of large error. The bond angle estimated from such data is given in Table 2.

An inspection of the data in Tables 1 and 2 suggests a rather large range of structural parameters for the oxonium ion. This may, in part, be due to experimental error or uncertainty in the assumptions used in extricating the results from the data. On the other hand, it may also reflect the importance of the environment in determining the structure. In this paper we investigate the role of the environment both with regard to its effect on the structure of the oxonium ion and the acidity of the corresponding aqueous solutions. Initially, the structure of the isolated or free ion is calculated by a minimization of the electronic energy with respect to both bond angle and bond length; the effects of environment are then explored through a second calculation which takes into consideration the nearest neighbours interaction in the solid. Since the energy minimization is for a system, oxonium ion plus several atoms or molecules containing a large number of electrons, the semi-empirical CNDO/2 method [22] has been used. This method gives a remarkably good description of the hydrogen bond. Further, the geometry of the free molecule, H_3O^+ calculated by CNDO/2 [23], is in good agreement with the result of the most recent *ab initio* calculations [24–28]. The latter is illustrated in Table 3. Finally it should be noted that for the structural calculations of H_3O^+ in various environments a modification of CNDO/2 is requested in order to introduce long-range effects.

2. Method

The bulk crystal is divided into two parts: a part consisting of the oxonium ion surrounded by its first shell of neighbours (6 or 3, each case being discussed separately in the text),

Table 3. *Ab initio* and CNDO/2 calculations for the force ion

Ref.	Methods	d(O–H) A	$\widehat{HOH}$°
24	SCF	0.95	120
25	SCF	0.96	117
26	SCF + IEPA PNO	0.964	113.5
27	SCF	0.963	112.5
28	SCF	0.963	114.3
23	CNDO/2	1.05	111

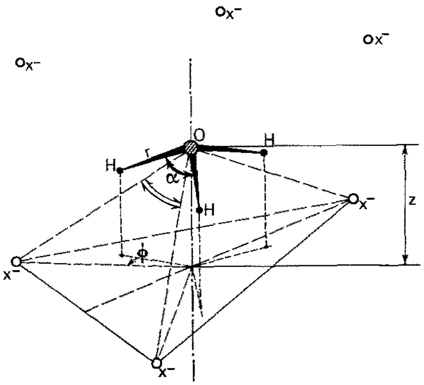
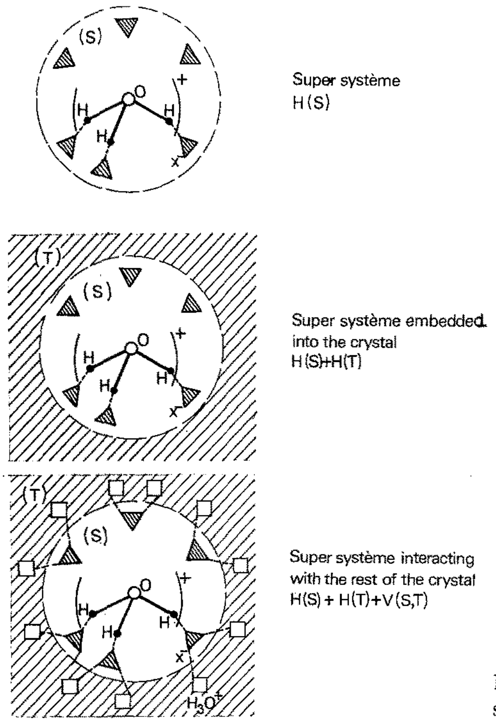


Fig. 1. A typical structure for the $H_3O^+X^-$ group

referred to as the super system, and a second part consisting of the rest of the crystal. In the super system the environmental effects to which the oxonium ion is subjected are restricted to the influence of the first shell of neighbours. Let (S) and (T) designate the super system and the rest of the crystal respectively. In terms of perturbation theory, if H(S) and H(T) are the Hamiltonians associated with systems (S) and (T), then in the zeroth-order approximation both systems are treated separately. As a further simplification, referred to here as the super system approximation, the minimization of electronic energy can be restricted to system (S). This approximation, which completely neglects the interaction between systems (S) and (T), does not take account of (a) the presence of long-range electrostatic forces, due to the ionic structure of the crystal, and (b) the existence of hydrogen bonds which also couples both systems (S) and (T). Effectively, the atomic/molecular groups forming the first shell of neighbours in system (S) are not only



Super système
H(S)

Super système embedded into the crystal
H(S)+H(T)

Super système interacting with the rest of the crystal
H(S) + H(T)+V(S,T)

Fig. 2. Illustrative representation of the different stages of approximation

hydrogen bonded to the H_3O^+ ion located inside (S) but also to other oxonium ions situated outside of (S) in system (T) (see Fig. 2). As a consequence the strength of the hydrogen bond formed between an H_3O^+ and its nearest neighbours inside system (S) will differ depending on whether or not the latter are hydrogen bonded to the atomic/molecular groups of (T). Thus to each nearest neighbour of H_3O^+ included in system (S) a coordination number is associated which determines the character of the hydrogen bonds formed inside that system. In principle the Hamiltonian in this representation of the system should now be written as $H = H(\mathrm{S}) + H(\mathrm{T}) + V(\mathrm{S}, \mathrm{T})$, where $V(\mathrm{S}, \mathrm{T})$ is an intermolecular potential representing the interaction between the atomic/molecular groups included in (S) and the complete set of atomic/molecular groups belonging to (T). Formally $V(\mathrm{S}, \mathrm{T})$ can be developed in a multipole series, and provided zero-order wave functions are known for both systems perturbation theory can be applied to determine the increase in stabilizing energy resulting from the interaction of electrostatic, inductive and dispersive forces between the (S) and (T) systems. In practice, such a calculation cannot be achieved, since the zero-order wave function of the (T) system is not available. An alternative, the approach used in this work, is to treat system (T) as the thermal bath for system (S). The contributions of $V(\mathrm{S}, \mathrm{T})$ associated with the two effects mentioned above, namely electrostatic and coordination effects, will be evaluated as follows. First, the electrostatic contribution is represented by the charge-charge interaction and is a sum of Coulombic terms:

$$E = \sum_{(\mathrm{S})(\mathrm{T})} \frac{q_{(\mathrm{S})} q_{(\mathrm{T})}}{R_{(\mathrm{S},\mathrm{T})}}$$

This can be easily evaluated when the size of the system (T) is restricted to a finite number of unit cells. This is a Madelung constant type calculation. Secondly, the contribution to $V(\mathrm{S}, \mathrm{T})$ due to coordination is estimated by a procedure which takes advantage of the fact that a semi-empirical method involving several adjustable parameters is used in the present calculation. The procedure is as follows: Let X^- be one of the nearest neighbours of system (S). We first optimize the hydrogen bond length (R) of the system $H_3O^+ \ldots X^-$ for

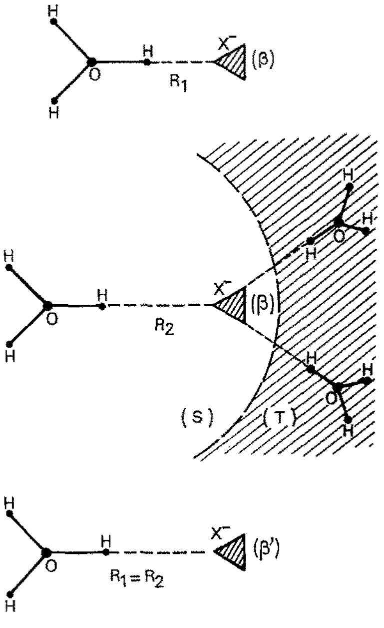


Fig. 3. Schematic representation of the reparametrization procedure

both cases shown in Fig. 3: coordination number of X^- equal to zero (R_1) (uncoordinated case) and for a coordination number greater than zero (R_2). The difference between R_1 and R_2 gives the magnitude of the coordination effect. We then adjust a chosen parameter (the β parameter of the CNDO/2 method, see section 3.2.3) so that the optimization gives $R_1 = R_2$; the coordination effect is then, at least partially, taken into account without the necessity of describing the interaction between the (S) and (T) systems.

2. Application to the Cases: $H_3O^+Cl^-$, $H_3O^+NO_3^-$, $H_3O^+ClO_4^-$

2.1. Super Systems

The structural data of the super systems used in these calculations are the unit cells of the corresponding crystals determined from X-ray diffraction experiments (See Fig. 4).

For $H_3O^+Cl^-$ the crystal is trigonal and the space group is $R\bar{3}m$, as determined by Yoon and Carpenter [2]. The unit cell is rhombohedral, and the H_3O^+ is hydrogen bonded to three Cl^-. The super system consists of one H_3O^+ surrounded by six Cl^-, three of them being hydrogen bonded to H_3O^+. Since only nearest neighbours are considered in this calculation the two Cl^- atoms on the C_{3v} are ignored.

The orthorhombic $Pna2_1$ Luzzati [5, 6, 7] structure has been used for the $H_3O^+NO_3^-$ crystal. This structure has recently been confirmed by Delaplane and coworkers [8]. The hydrogen bonded systems are arranged in layers perpendicular to the C crystallographic axis and each H_3O^+ ion is hydrogen bonded to the NO_3^- cations of the same layer and do not interact with cations of other layers. Since the layers are separated by a distance of

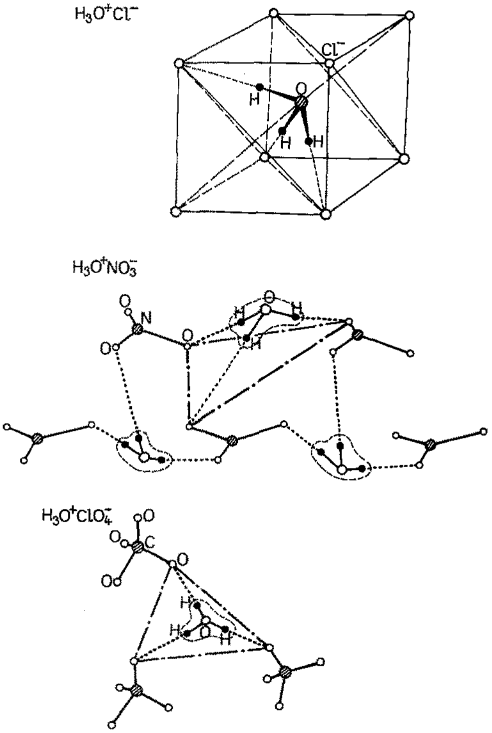


Fig. 4. Arrangement of the anions around the H_3O^+ ion

3.15 Å and interaction between the two layers is negligible, the super system is simply one H_3O^+ ion surrounded by nearest neighbour NO_3^- cations.

For $H_3O^+ClO_4^-$ we have used the structural data of the low temperature form reported by Nordman [4]. It is a monoclinic crystal which belongs to the spatial group $P21/c$. As in the preceding case, the oxonium ion and the ClO_4^- cations form layers of hydrogen bonded systems and only the interactions within the same layer are significant. In any given layer, the H_3O^+ ion is hydrogen bonded to three ClO_4^- and the super system is restricted to these four interacting species.

2.2. Optimization of the Total Energy

In this section an outline of the general method of energy minimization of the super system is presented (2.2.1) followed by an evaluation of the long-range electrostatic energy, section (2.2.2.), and the reparametrization of the CNDO/2 method to simulate the effect of coordination, section (2.2.3.).

2.2.1. Energy Minimization

The energy minimization is made with respect to the internal coordinates of the H_3O^+ ion, namely the bond angle $\alpha = \widehat{HOH}$ and the bond length $r = d(O \ldots H)$, as well as the external coordinates Z and ϕ shown in Fig. 1. The distance (Z) is measured from the oxygen atom to the plane defined by the three nearest neighbours which are hydrogen bonded to the oxonium ion, and the angle (ϕ) fixes the orientation of the H_3O^+ pyramid around the C_{3v} axis. The minimization of the total energy $E(r, \alpha; Z, \phi)$ is started by assuming some reasonable values for two coordinates, α^0 and Z^0, and minimization is performed with respect to r and ϕ. Once the minimum of the $E(r, \phi)$ surface is obtained for $(r^{(1)}, \phi^{(1)})$, we further minimize $E(r^{(1)}, \alpha; Z, \phi^{(1)})$ to obtain a new set $\alpha^{(2)}, Z^{(2)}$, and so on, this iterative procedure is continued until the results are self-consistent. It turns out, E is very sensitive to r and ϕ so that the energy minimization is mainly one of determining the parameters α and Z.

2.2.2. Long-Range Electrostatic Energy

The interacting ions outside the super system (S) are assumed to be point charges located at their centre of masses. The electrostatic energy is calculated by the direct summation of Erikson and Linnett [29]. In the three cases studied, $H_3O^+X^-(Cl^-, NO_3^-, ClO_4^-)$, the summations are extended to 343 unit cells.

2.2.3. Coordination Effect

As previously mentioned the coordination effect can be simulated by a procedure which, in effect, recalibrates the CNDO/2 parametrization. Since the effect of coordination is to

Table 4. Result of the recalibration of the β parameter

	Standard Values	β of Coordinated Atom
β(Cl)	−22.33	−12.33 ($H_3O^+Cl^-$)
β(O)	−31	−26 ($H_3O^+ClO_4^-$) −31 ($H_3O^+NO_3^-$)

reduce the hydrogen bond strength then the parameter to be varied is one which primarily affects the resonance integrals (an essential factor determining the bond strength in MO theory) associated with electronic distribution on the OH bond of H_3O^+ and the electron donor atom of X^- (Cl^- and one of the oxygen atom of NO_3^- and ClO_4^-). In the CNDO/2 method these parameters are the β_{Cl^-} and the β_O of the hydrogen bonded oxygen atom. It is to be noted that in the nitrate and chlorate ions only the β of the oxygen atom forming the hydrogen bond has to be varied, the β parameters of the other oxygen atoms being maintained at standard value.

The results of the recalibration of the β parameters for the above ions are given in Table 4 and require a few comments. As expected, the absolute value of β is always diminished by coordination, which tends to weaken the hydrogen bond. The magnitude of the change is greater when lone pair orbitals involved in hydrogen bonding belong to a unique atom (case of Cl^-) rather than a radical ion involving several atoms (NO_3^-, ClO_4^-). The super-system approximation is thus more appropriate in an environment consisting of polyatomic radical ions than simple atomic ions.

The interaction of the H_3O^+ ions in the crystal is considerably increased when going from the first case to the latter.

3. Results and Discussion

The structural data calculated by the procedure described in the text are given in Table 5. It should however be noted that in the case of NO_3^-, convergence could not be obtained and we had to use the dumping procedure suggested by Chesnut and Wormer [30]. Results for three different approximations have been included to illustrate the importance of the coordination, lines *b*, and electrostatic interaction, lines *c*. It can be seen that the simple super-system approximation, line *a*, which neglects the above effects, fails to represent correctly the geometry (angle α) and the position (Z) of the H_3O^+ ion in its cage. Both in the case of Cl^- and ClO_4^- the H_3O^+ ion is too close to the plane containing the negative ions. Coordination effects not only correct this situation but also give a more realistic value of the $\widehat{X^--O-X^-}$ angle. The electrostatic effect is important in establishing the two structural parameters Z and $d(O \ldots H)$, in the case of Cl^- it tends to shorten these distances, whereas it has the reverse effect in the others cases.

In comparing the results for the three anions given in Table 5 some general observations can be made. Except for the r_{OH} bond distance, which is constant in the three cases, there is a monotonic trend of the other structural parameters in going from NO_3^- to Cl^- to ClO_4^-. For the calculation which includes both coordination and electrostatic effects the H_3O^+ is more nearly planar in the NO_3^- crystal than in the perchlorate, an observation also consistent with the value of Z, the nearest neighbours anion distances. Further, from the value of $\phi = 0$, the same for all crystals, it would appear that the orientation of the OH bonds of the cation parallels very closely the orientation of the nearest neighbour anions in the plane above and below (see Fig. 1), i.e. there is no bifurcation of the H bonds. Since the $\widehat{X-O-X}$ angles are always less than α, the $\widehat{H-O-H}$ angle, the H bonds to the anion are no longer collinear with the OH bonds of the oxonium ion, a fact confirmed by recent neutron diffraction experiments. Finally if the $O-Cl^-$ bond distance is corrected [31] to obtain the corresponding $O \ldots O$ bond distance, the above-mentioned trend on structural parameters is also maintained for $d(O \ldots X^-)$.

Table 5. Comparison of experimental and theoretical results. (a) Super-system only, (b) super-system and coordination effect, (c) super-system and both coordination and electrostatic effect

		X^-					
		NO_3^-		Cl^-		ClO_4^-	
		Th.	Exp.	Th.	Exp.	Th.	Exp.
r (A)	a	1.05		1.05		1.05	
	b	1.05		1.05		1.05	
	c	1.05	0.92	1.05	0.95	1.05	0.83
α (°)	a	116		120		113	
	b	116		113		112	
	c	116	111	113	110	112	112
Z (A)	a	0.28		0.0		0.50	
	b	0.28		1.30		0.75	
	c	0.55	0.65	0.85	0.94	1.15	0.91
ϕ (°)	a	0.0		0.0		0.0	
	b	0.0		0.0		0.0	
	c	0.0	0.0	0.0	0.0	0.0	0.0
$\widehat{X^-OX^-}$ (°)	a	114		120		117	
	b	114		112		109	
	c	114	112	112	110	109	110
$\widehat{X^-HO}$ (°)	a	178		180		177	
	b	178		179		177	
	c	178	177	178	171	177	178
$d(O\ldots X^-)$ (A)	a	2.50		2.80		2.54	
	b	2.50		3.08		2.61	
	c	2.58	2.59	2.92	2.95	2.75	2.66

It is also interesting to note that the trend in structural parameters closely parallels some of the chemical properties of the hydrogen bonds in the monohydrate crystal. The increase in hydrogen bond energy E (Table 6), in going from the perchlorate ion to nitrate, can be viewed as a consequence of the distortion of the H-O-H bond angle by the solid environ-

Table 6. Theoretical results giving, successively, hydrogen bond energy, charge on the O atom and the H atoms of the H_3O^+ ion, charge transfer from X^- to H_3O^+, and Wiberg bond orders

	NO_3^-	Cl^-	ClO_4^-
$E(OH\ldots X^-)$ kcal/mole	5.40	3.86	0.02
q_O	−0.1171	−0.1754	−0.1205
q_H	+0.3698	+0.3605	+0.3721
Transfer e^- $X^- \rightarrow H_3O^+$	0.003	0.030	0.001
P_{OH} (in OH...X)	0.8244	0.8228	0.8372
$P_{H\ldots X}$ (in OH...X)	0.0431	0.0415	0.0229

ment (compare with result for free ion, Table 3) which is greatest in the nitrate case. This could suggest a greater delocalization of charge for the nitrate, which is not inconsistent with the trend of the Wiberg bond orders given in Table 6, namely $NO_3^- > Cl^- > ClO_4^-$. Another interesting comparison is the trend of acidities which for liquid solutions, based on the Hammett acidity scale is

$$HNO_3 < HCl < HClO_4$$

again a trend which parallels what can be concluded from the structural changes in the solids containing the same anions, reported earlier. The implication here is that the character and behaviour of liquid solutions closely resemble that of the solid. This, incidentally, is not true for the gas, where from the behaviour of the gaseous binary compounds $HX \cdot H_2O$ it has been shown by CNDO/2 calculation [32] that the order of acidity is

$$HCl < NHO_3 < HClO_4.$$

References

1. Giguère, P. A.: Revue Chim. Miner. **3,** 627 (1966)
2. Yoon, Y. K., Carpenter, G. B.: Acta Cryst. **12,** 17 (1959)
3. Lee, F. S., Carpenter, G. B.: J. Phys. Chem. **63,** 279 (1959)
4. Nordman, C. E.: Acta Cryst. **15,** 18 (1962)
5. Luzzati, V.: C.R. Acad. Sc. **230,** 101 (1950)
6. Luzzati, V.: Acta Cryst. **4,** 239 (1951)
7. Luzzati, V.: Acta Cryst. **6,** 157 (1953)
8. Delaplane, R. G., Taesler, I., Olovson, I.: Acta Cryst. **B31,** 1486 (1975)
9. Taesler, I., Olovsson, I.: Acta Cryst. **B24,** 299 (1968)
10. Spencer, J. B., Lundgren, J. O.: Acta Cryst. **B29,** 1923 (1973)
11. Lundgren, J. O., Williams, J. M.: J. Chem. Phys. **58,** 788 (1973)
12. Finholt, J. E. Williams, J. M.: J. Chem. Phys. **59,** 5114 (1973)
13. Richards, R. E., Smith, J. A. S.: Trans. Faraday Soc. **47,** 1261 (1951)
14. Kydon, D. W., Pintar, M., Petch, H. E.: J. Chem. Phys. **48,** 5348 (1968)
15. Ferriso, C. C., Hornig, D. F.: J. Chem. Phys. **23,** 1464 (1955)
16. Savoie, R., Giguère, P. A.: J. Chem. Phys. **41,** 2698 (1964)
17. Fournier, M., Mascherpa, G., Rousselet, D., Potier, J.: C.R. Acad. Sc. **269,** 279 (1969)
18. Fournier, M., Rozière, J.: C.R. Acad. Sc. **270,** 729 (1970)
19. Basile, L. J., La Bonville, P., Ferraro, J. R., Williams, J. M.: J. Chem. Phys. **60,** 1981 (1974)
20. Taylor, R. C., Vidale, G. L.: J. Am. Chem. Soc. **98,** 5999 (1956)
21. Huong, P. V., Desbat, B.: J. Raman Spectry. **2,** 373 (1974)
22. Pople, J. A., Beveridge, D. L.: Approximate molecular orbital theory. New York: McGraw-Hill 1970
23. De Paz, M., Ehrenson, S., Friedman, L.: J. Chem. Phys. **52,** 3362 (1970)
24. Moskowitz, J. W., Harrison, M. C.: J. Chem. Phys. **43,** 3550 (1965)
25. Almlöf, J., Whalgren, U.: Theoret. Chim. Acta (Berl.) **28,** 161 (1973)
26. Kollman, P. A., Bender, C. F.: Chem. Phys. Letters **21,** 271 (1973)
27. Lischka, H., Dyczmons, V.: Chem. Phys. Letters **23,** 167 (1973)
28. Allavena, M., Le Clec'h, E.: J. Mol. Struct. **22,** 265 (1974)
29. Erickson, W. D., Linnett, J. W.: J.C.S. Faraday II **68,** 693 (1972)
30. Chesnut, D. B., Wormer, P. E. S.: Theoret. Chim. Acta (Berl.) **20,** 250 (1971)
31. Bellamy, L. J., Owen, A. J.: Spectr. Chim. Acta **25A,** 319 (1969)
32. Fournier, M., Potier, A., Allavena, M. (to be published).

Received January 19, 1976