

Hydrogen Bond Studies

66*. *Ab initio* Studies of the Conformation of the Oxonium Ion in Solids

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The oxonium ion, H_3O^+ , has been studied with the MO-LCAO method in order to determine its equilibrium geometry. The main purpose has been to study effects of the external electrostatic forces exerted on the ion situated in crystals whose structures are experimentally known. Calculations have also been performed on the free ion, where the energy minimum is found for a non-planar conformation with H-O-H angles of 116.6° and O-H distances of 0.96 Å. The effect of an external field is essentially to lengthen the O-H distances and decrease the H-O-H angles in order to form approximately linear hydrogen bonds.

Die Gleichgewichtsgeometrie des Oxoniumions H_3O^+ wurde mit Hilfe der MO-LCAO Methode bestimmt. In erster Linie sind die Effekte, die von externen elektrostatischen Kräften auf das Ion in Kristallen mit bekannter Struktur ausgeübt werden, untersucht worden. Es wurden aber auch Rechnungen für das freie Ion durchgeführt, wobei die minimale Energie im Falle der nicht planaren Konformation mit H-O-H-Winkeln von $116,6^\circ$ und einem O-H-Abstand von 0,96 Å erhalten wurde. Der Effekt eines externen Feldes besteht hauptsächlich in einer Verlängerung der O-H-Bindung und einer Verringerung des H-O-H-Winkels, so daß näherungsweise lineare Wasserstoffbindungen gebildet werden.

Introduction

The properties of the oxonium ion have long attracted great interest, both from a theoretical and experimental standpoint. A number of X-ray investigations have therefore been performed on crystal structures containing this ion. Unfortunately, this method gives very poorly resolved hydrogen atom positions. Experimental difficulties have hitherto prevented the use of the neutron diffraction technique which is a more powerful tool in that context. Hence, not even the geometry of the oxonium ion has yet been established accurately. In all crystals studied so far, however, the H_3O^+ ion is pyramidally surrounded by three electro-negative atoms at short distances. This is usually taken as evidence for short and hence approximately linear hydrogen bonds, indicating a pyramidal geometry for the oxonium ion. A non-planar conformation for the free ion was also suggested by Joshi [1], who performed a non-empirical MO-LCAO calculation with an all-electron one-centre wavefunction. In this case an H-O-H angle of 111° was obtained for the equilibrium geometry.

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In contrast, Grahn [2,3] found a planar geometry both from MO and from VB calculations, and the same result was reported by Moskowitz and Harrison [4] and by Kollman and Allen [5] after much more elaborate calculations. The potentials for symmetric bending in these cases were very shallow, however. In the calculations presented below, the energy minimum was found with a non-planar geometry for the free ion, but, since the inversion barrier found is only $0.3 \text{ kcal/mole}^{-1}$, there is no fundamental difference between our results and the previous ones. They all indicate, in fact, that the energy difference between a planar and a pyramidal geometry of the free ion is too small to make any safe conclusion to be drawn as to the conformation of the ion in solids.

The calculations reported below were therefore undertaken in an attempt to study the oxonium ion when subjected to force fields created by a real crystal environment.

Method and Calculations

The molecular calculations were carried out using the MO-LCAO method, allowing an external electrostatic field to be taken into account when appropriate. A local modification of the program IBMOL IV [6] was used to perform these calculations. The MO's were expanded into a set of basis functions, each consisting of a linear combination of single Gaussians. The basis set used contained four *s*- and two *p*-type contracted functions centred on an oxygen, and two *s*- and one *p*-type function on each hydrogen. Thus, a total of 25 contracted basis functions were employed. The orbital exponents and contraction coefficients are given in Table 1.

When an ion is situated in an ionic crystal, it is assumed that the predominant effects on its properties can be attributed to the electrostatic influence from surrounding ions. As this is a long-range effect, the electrostatic potential from the whole crystal ought to be taken into account in the calculations. (Indeed, test calculations have shown that the electrostatic forces on an ion in a crystal cannot be satisfactorily described by including only a small number of neighbouring atoms). This potential can easily be evaluated following a method proposed by Ewald [9] and further developed by Bertaut [10], a brief description of which is given in the Appendix.

The ion was studied in four different surroundings: in solid hydrochloric acid monohydrate [11] and in the three non-equivalent positions in solid sulfuric acid dihydrate [12]. For each surrounding, the potential was evaluated at a large number of points within the van der Waals surface of the ion in its approximate equilibrium position. The surroundings of the ion were then approximately described by 45 suitably placed point charges, the values of which were determined by a least-squares fit to the calculated potential values. In order to obtain the best fit the positions of the point charges were also varied. However, point charges were always placed at the sites of the three hydrogen-bonded acceptor atoms around the H_3O^+ ion.

Using this approach, the inclusion of external electrostatic forces in the Hartree-Fock scheme is a trivial matter, since these point charges will contribute to the one-electron part of the Fock-operator in exactly the same way as they would if they were atomic nuclei.

The total energy of the ion was calculated with 12–14 conformations in each environment, as well as for the free ion. The equilibrium geometry for each case was obtained by fitting an analytic expression to these energy values and determining its minimum. The energy expressions used were of the form

$$A \cdot [1 - \exp \{-\beta(r - r_0)\}]^2 + p(r, \theta),$$

where the first term is simply a Morse function, p is a polynomial of second degree in r and θ , r denotes the O–H distance and θ the H–O–H angle.

The Ewald method applied for the potential calculation requires a description of the crystal structure in terms of point charges. This was no problem in the case of the sulfate and chloride ions, where the atomic positions are experimentally known. The sulfur and oxygen atoms in the sulfate ion were assigned formal charges of +1.34 and –0.835 from previous *ab initio* calculations [13]. The same strategy could obviously not be used for the oxonium ions, since only the positions of the oxygen atoms were known from experiments.

Instead, the orientation of each oxonium ion was systematically varied with the oxygen atom fixed in its experimentally determined position. For each orientation the classical electrostatic energy of the crystal was calculated, using a method described by Baur [14]. The geometry and charge distribution used for the H_3O^+ ion in these calculations were chosen from the calculations made on the free ion. These properties were not quite the same as those obtained in the final calculations. However, these slight variations turned out to have little effect on the final result.

The conformation of the H_3O^+ ion was restricted to obey C_{3v} symmetry in all calculations, although, in the case of sulfuric acid dihydrate the surroundings did not possess perfect threefold symmetry. This restriction was not considered to be a serious drawback, since the deviations were quite small and would not affect the general picture of the effect of a crystal environment.

Results and Discussion

As mentioned earlier, previous calculations using similar methods have indicated a planar conformation for the H_3O^+ ion. The calculations made by Kollman and Allen were slightly better than ours energywise (–76.316 a.u., compared to –76.222 a.u. in the present work). However, the geometry was not fully optimized in their calculation, and a similar strategy would have resulted in a planar conformation in our case also. Moskowitz and Harrison made a more careful search of the energy surface. Their basis set was quite small, however ($E_{\text{min}} = -75.846$ a.u.), and especially the lack of polarization functions on hydrogen may be responsible for the discrepancy between their results and ours.

The calculated total energies for the different conformations and environments are shown in Table 2. A comparison with equivalent calculations on the water molecule [15] gives a proton affinity for the water molecule of $189 \text{ kcal} \cdot \text{mole}^{-1}$. The experimental value for the proton affinity is $182 \pm 7 \text{ kcal} \cdot \text{mole}^{-1}$ [16].

The equilibrium geometries in the five different environments are shown in Table 3. The equilibrium O–H distance of 0.944 \AA . agrees well with the value 0.958 \AA . found by Kollman and Allen. The application of an external field results

Table 1. Orbital exponents (α) and contraction coefficients (c). The constants for oxygen were selected from the work of Roos and Siegbahn [7]. The s exponents and coefficients for hydrogen are those given by Huzinaga [8], and scaled by a factor 1.25. The contraction of primitive Gaussians is shown with brackets

		α	c	
Oxygen	s	{	2714.89	0.007355
			415.725	0.054884
			91.9805	0.266058
			24.4515	0.761744
			7.22296	1.0
			1.06314	1.0
	p	{	0.322679	1.0
			7.75579	0.232222
			1.62336	0.863870
			0.36503	1.0
Hydrogen	s	{	16.7019	0.032828
			2.51663	0.231208
			0.567196	0.817238
			0.154146	1.0
			0.8	1.0
	p			

Table 2. Total energies and geometries for the H_3O^+ ion. d denotes the distance between the oxygen atom and the plane of the three hydrogen atoms, a is the projection of the H-O vector onto this plane. I, II and III denote the three independent oxonium ions in $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ in order corresponding to O(7), O(8) and O(9) in Ref. [12]. An asterisk* denotes the minimum energy for the environment under consideration

d	a	Free ion	HCl · H ₂ O	I	II	III
0.0	1.85	-76.22062	-76.51992	-76.49454	-76.38835	-76.55127
0.1	1.80	0.22225	0.52495	0.49925	0.39505	0.54012
0.2	1.75	0.22009	0.52417	0.50092	0.39830	0.53540
0.2	1.80	0.22223	-	-	-	-
0.2	1.85	0.22023	-	-	-	-
0.3	1.65	-	-	0.48913	0.38719	0.52628
0.5	1.70	0.21992	0.52939	0.51164	0.41252	0.55479
0.5	1.75	0.22179	0.53395	0.51331	0.41484	0.56081
0.5	1.80	0.21981	0.53481	0.51112	0.41329	0.56323
0.5	1.85	-	0.53257	0.50364	0.40010	0.55416
0.7	1.65	-	0.52613	0.51563	0.41672	0.55786
0.7	1.75	-	0.53108	0.51424	0.41727	0.56613
0.8	1.70	0.21627	0.52574	0.51472	0.41716	0.56276
1.0	1.65	-	-	0.50496	0.40594	0.56022
1.0	1.75	-	0.53108	0.49397	0.39713	0.54717
0.351	1.780	0.22245*	-	-	-	-
0.496	1.788	0.22067	0.53490*	-	-	-
0.709	1.688	0.21701	-	0.51660*	-	-
0.708	1.700	0.21702	-	-	0.41874*	-
0.676	1.776	0.21436	-	-	-	0.56653*

Table 3. Equilibrium geometries for the oxonium ion. α_{exp} denotes the mean value of the three experimentally determined X ... O ... X angles around each ion. The notations I, II and III are the same as in Table 2

		$r_{\text{O-H}}(\text{\AA})$	$\alpha_{\text{H-O-H}}$	α_{exp}
Free ion		0.96	117°	—
HCl · H ₂ O		0.98	113°	110°
H ₂ SO ₄ · 2H ₂ O	I	0.97	106°	109°
	II	0.98	106°	105°
	III	1.00	108°	108°

Table 4. Atomic formal charges for the oxonium ion. Column A gives the charges for the equilibrium geometry as in the crystal. The charges in B were calculated using the same geometries, but without an external field. The notations I, II and III are the same as in Table

		A		B	
		q_{O}	q_{H}	q_{O}	q_{H}
Free ion				+0.015	+0.328
HCl · H ₂ O		-0.074	+0.358	-0.014	+0.338
H ₂ SO ₄ · 2H ₂ O	I	+0.050	+0.275	+0.095	+0.302
			+0.336		
			+0.339		
	II	+0.006	+0.303	+0.077	+0.308
			+0.341		
			+0.350		
	III	-0.154	+0.378	-0.027	+0.342
			+0.386		
			+0.390		

in relatively small increases in the O–H distances (0.01–0.04 Å). In contrast, there are considerable changes in the H–O–H angles, tending to make the O–H ... X arrangement approximately linear. The magnitudes of these changes correspond to displacements of the protons of 0.08–0.20 Å. These distortions of the molecular geometry are much greater than those observed in the solid state for similar molecules such as NH₃ or H₂O. It is therefore tempting to assume that the angles in H₃O⁺ are usually easily distorted. However, the vibrational force constants for H₂O and NH₃ indicate that some 0.1 kcal/mole⁻¹/degree⁻¹ are required to distort the angles in these molecules. This compares well with the inversion barrier of 0.3 kcal/mole⁻¹ and the equilibrium angle of 116.6° in H₃O⁺. The above assumption is therefore unjustified, and the large distortions must instead be attributed to H₃O⁺ carrying a positive charge. This will result in an ability to form much stronger hydrogen bonds than in the case of a neutral molecule. The H–O–H angles obtained agree fairly well with the averaged X ... O ... X angles, as obtained from experiment (cf. Table 3).

It follows from the population analysis, that there are two main sources of charge redistribution within the ion (cf. Table 4). Firstly, there is a considerable change in charge distribution due to the alterations of the geometry only. This can be seen from Table 4 by comparing the populations in column B for different geometries. A lengthening of the O–H distance results in an electron flow towards

oxygen, whereas a decrease in the H–O–H angle will have the opposite effect. Secondly, the application of an external field will bring about an increase of negative charge at the oxygen atom. This is to be expected since it will increase the dipole moment of the ion and make the interaction with the field more energetically favourable. As these effects are of the same order of magnitude, it is not possible to obtain accurate information about the charge distribution unless the geometry of the ion is properly optimized, as in the case of HCl·H₂O. In H₂SO₄·2H₂O, the restrictions mentioned above (C_{3v} symmetry) will render the values of the charges obtained somewhat unreliable. However, the most spectacular effect of introducing an external field is not the charge redistribution but rather the large changes in geometry.

The decrease in H–O–H angles obviously expresses the tendency to form as short –H ... X hydrogen bond contacts as possible, as does the lengthening of the O–H distances. There is no experimental evidence for these changes but similar effects are known for other cases of hydrogen bonding (i.e. H₂O₂ in Na₂C₂O₄·H₂O₂ and in Li₂C₂O₄·H₂O₂ [17, 18]).

Appendix

Provided that the crystal can be described as an assembly of point charges, the electrostatic potential at a point not identical to an atom site can be written as

$$P(\mathbf{r}) = \sum_{i,l} \frac{Q_i}{|\mathbf{r} - \mathbf{r}_i - \mathbf{t}_l|}.$$

The summations over i and l are to be taken over all atoms i in a unit cell and over all unit cells l , respectively. Q_i and \mathbf{r}_i are the charge and position of atom i , and \mathbf{t}_l denotes a lattice translation in direct space. In practice, it is found that this sum is very slowly convergent or even divergent, and it must therefore be rewritten according to Ewald [9] to make the evaluation possible.

Consider the function

$$F(\mathbf{r}, \varrho) = \frac{2}{\sqrt{\pi}} \sum_l \exp\{-\varrho^2(\mathbf{r} - \mathbf{t}_l)^2\} \quad (1)$$

F is periodic in space and can be expanded in a Fourier series:

$$F(\mathbf{r}, \varrho) = \sum_k F_k \exp(2\pi i \mathbf{k} \cdot \mathbf{r}), \quad (2)$$

where

$$\begin{aligned} F_k &= \frac{2}{\sqrt{\pi V}} \int \sum_l \exp\{-\varrho^2(\mathbf{r} - \mathbf{t}_l)^2 - 2\pi i \mathbf{k} \cdot \mathbf{r}\} d\tau \\ &= \frac{2}{\sqrt{\pi V}} \sum_l \int \exp(-\varrho^2 r^2 - 2\pi i \mathbf{k} \cdot \mathbf{r}) d\tau = \frac{2\pi}{v\varrho^3} \exp(-\pi^2 k^2/\varrho^2). \end{aligned} \quad (3)$$

V and v denote the volumes of the whole crystal and of one unit cell, respectively.

(1), (2) and (3) give

$$\frac{2}{\sqrt{\pi}} \sum_l \exp \{-\varrho^2(\mathbf{r}-\mathbf{t}_l)^2\} = \frac{2\pi}{v\varrho^3} \sum_{\mathbf{k}} \exp(-\pi^2 k^2/\varrho^2 + 2\pi i\mathbf{k}\cdot\mathbf{r}). \quad (4)$$

Consider the identity

$$\frac{1}{|\mathbf{r}-\mathbf{t}_l|} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp\{-\varrho^2(\mathbf{r}-\mathbf{t}_l)^2\} d\varrho.$$

If this equation is summed over all l and the integration is split at some arbitrary point χ , Eq. (4) can be used to give

$$\begin{aligned} \sum_l \frac{1}{|\mathbf{r}-\mathbf{t}_l|} &= \frac{2\pi}{v} \sum_{\mathbf{k}} \int_0^\chi \frac{1}{\varrho^3} \exp(-\pi^2 k^2/\varrho^2 + 2\pi i\mathbf{k}\cdot\mathbf{r}) d\varrho \\ &+ \frac{2}{\sqrt{\pi}} \sum_l \int_\chi^\infty \exp\{-\varrho^2(\mathbf{r}-\mathbf{t}_l)^2\} d\varrho = \frac{1}{\pi v} \sum_{\mathbf{k}} \frac{1}{k^2} \exp(-\pi^2 k^2/\chi^2 + 2\pi i\mathbf{k}\cdot\mathbf{r}) \\ &+ \sum_l \frac{1}{|\mathbf{r}-\mathbf{t}_l|} \operatorname{erfc}(\chi|\mathbf{r}-\mathbf{t}_l|). \end{aligned}$$

Finally, substituting $\mathbf{r}-\mathbf{r}_i$ for \mathbf{r} , multiplying by Q_i and summing over i :

$$\begin{aligned} \sum_{i,l} \frac{Q_i}{|\mathbf{r}-\mathbf{r}_i-\mathbf{t}_l|} &= \sum_{i,l} \frac{Q_i}{|\mathbf{r}-\mathbf{r}_i-\mathbf{t}_l|} \operatorname{erfc}(\chi|\mathbf{r}-\mathbf{r}_i-\mathbf{t}_l|) \\ &+ \frac{1}{\pi v} \sum_{\mathbf{k}} A_{\mathbf{k}} \exp(-\pi^2 k^2/\chi^2 + 2\pi i\mathbf{k}\cdot\mathbf{r})/k^2, \end{aligned}$$

where $A_{\mathbf{k}} = \sum_j Q_j \exp(-2\pi i\mathbf{k}\cdot\mathbf{r}_j)$, sometimes termed the electrostatic structure factor. Given a suitable choice of χ , both series are rapidly convergent.

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