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# A unique trapping by crystal forces of a hydronium cation displaying a transition state structure

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## ARTICLE INFO

## Article history:

Received 12 August 2014

Accepted after revision 21 October 2014

Available online 4 February 2015

## Keywords:

Bifurcated hydrogen bond

Protonated water structure

Electron density

Bond critical point electron density

Topology of the electron density

Quantum theory of atoms in molecules

(QTAIM)

## ABSTRACT

An hydronium cation has been discovered which is unique among all crystallographic such ions of the Cambridge Database. Of composition  $\text{H}_7\text{O}_3^+$  it has a structure that is totally different from those classically known with structures  $\text{H}_2\text{O}-\text{H}_2\text{O}-\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}-(\text{H}_3\text{O}^+)-\text{H}_2\text{O}$ . Unlike the crystallographically classical ones, the cation discussed here has a bifurcated hydrogen bond. From a central  $\text{H}_3\text{O}^+$  moiety a single hydrogen bond donor extends to two adjacent water molecules. Quantum chemical calculations in absence of the crystal environment demonstrate that the bifurcated hydrogen bond structure is that of a transition state for the  $\text{H}_7\text{O}_3^+$  complex. Thus remarkably, it appears that crystal forces have captured the ion in what would otherwise be a short-lived and unstable transition state formation.

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## 1. Introduction

In a recent publication, Bernal and Watkins [1] reviewed the entire contents of the Cambridge Crystallographic Database [2] for examples of hydronium cations and found approximately 1500 of them which were available by February 2014 and which were analyzed in detail. Among the many species described in that publication, easily one of the most interesting ones is that referenced as WIZPAX [3] which is pictured in Fig. 1. Among the 1500 crystal structures of hydronium ions examined this one is unique.

This cation has the same composition and a similar relative arrangement of the oxygen atoms as that shown in Fig. 2, both sharing the formula  $\text{H}_2\text{O}-(\text{H}_3\text{O}^+)-\text{H}_2\text{O}$ .

In the case of the ion pictured in Fig. 2 the central hydronium moiety is the same as that in Fig. 1 but it differs in that it has the “normal” or “expected” hydrogen bonding displayed by hydronium ions familiar to crystallographers for many years. In contrast to that, the crystal’s hydronium ion pictured in Fig. 1 has a bifurcated hydrogen bond connecting to a pair of adjacent water molecules. Previous work [5] has shown that crystal forces are capable of capturing protonated water structures that are highly unusual. However when the unusual protonated structures are removed computationally from the crystal environment in which they have been captured, and then subjected to theoretical calculations in the gas phase, their structure changes dramatically to one corresponding to their minimized energy geometry.

Against that experience it occurred to us to remove the bifurcated hydrogen bond structure of Fig. 1 from its crystal environment and subject it to theoretical analysis since it would be of interest to ascertain the relative

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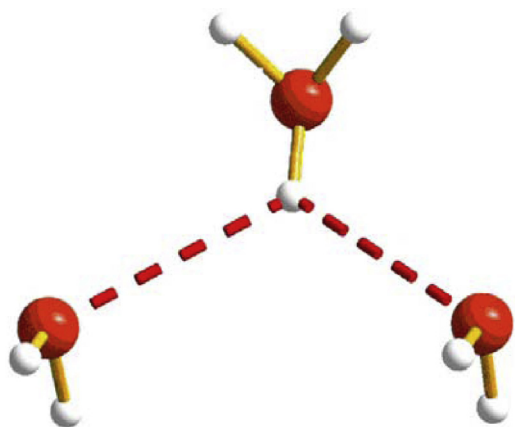


Fig. 1. (Color online.) The experimental geometry of an ion  $\text{H}_2\text{O}-(\text{H}_3\text{O}^+)-\text{H}_2\text{O}$  from the Cambridge data base (WIZPAX [3]).

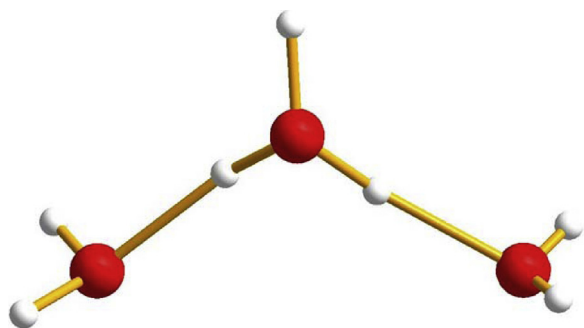


Fig. 2. (Color online.) The experimental geometry of an ion  $\text{H}_2\text{O}-(\text{H}_3\text{O}^+)-\text{H}_2\text{O}$  from the Cambridge data base (XUMQIF [4]).

stabilities of the two structures pictured in Figs. 1 and 2. If the classical structure of Fig. 2 were to be the more stable it could be expected that optimization of the bifurcated hydrogen bond structure, upon energy optimization, would revert to that classical geometry. On the other hand it was also an open possibility that the structure of Fig. 1 corresponded to an optimized minimum energy structure. As it happened however, calculations show that the optimized geometry of the bifurcated hydrogen bond structure of Fig. 1 corresponds to a transition state, with a single imaginary vibrational frequency, which appears to be unusual.

Stated differently, it appears that crystal forces have captured an hydronium ion in a geometry that would otherwise be unstable and very short-lived except for its appearance within the crystal. Such a crystallographic

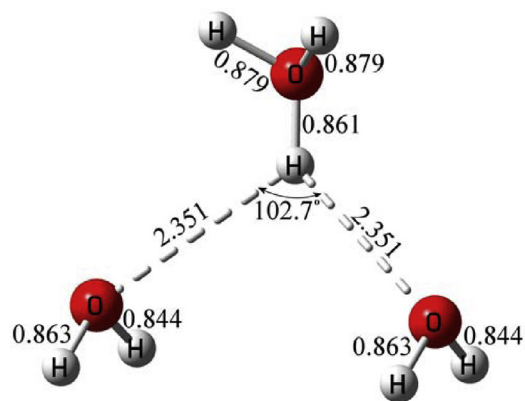


Fig. 3. (Color online.) Geometrical parameters of  $\text{H}_7\text{O}_3^+$  as it exists in the crystal.

bifurcated hydrogen bond hydronium species has never been described previously to the best of our knowledge. Considerable calculations have been invoked to test adequately the result that the structure of Fig. 1 is a transition state in the gas phase. The existence of such a transition state associated with protonated water structures may well be related to the motion of protons though the liquid state, with a possibly wide range of importance in experimental biology and material science.

## 2. Results

### 2.1. Energy and geometry

The geometrical parameters of the  $\text{H}_7\text{O}_3^+$  bifurcated hydrogen bond as it exists in the crystal structure are given in Fig. 3. The two hydrogen bonds associated with the bifurcation are perfectly symmetrical both corresponding to inter-nuclear distances to the neighboring oxygen equal to 2.351 Å. The angle subtended by the pair of hydrogen bonds is 102.7°. We optimized the geometry, and calculated the optimized energy of the  $\text{H}_7\text{O}_3^+$  complex, using Gaussian 09 program [6]. In Table 1 that energy is given for several chemical models, HF [7], B3LYP [8,9], MP2 [10], and CCSD [11] in which both the basis functions, 6-311G [12], 6-311G(d,p) [13], 6-311+G(d,p) [14], 6-311++G(3df,3pd), and the approximation for solution of the Schrodinger equation were varied.

The energy of the molecule is equal to  $-229.16835$  atomic units (a.u.) at crystal coordinates in the most accurate of the chemical models, viz., CCSD/6-311++G(3df,3pd), which stands for coupled clusters with singles and doubles

Table 1

Energy of the bifurcated  $\text{H}_7\text{O}_3^+$  complex at the crystallographic geometry before (single point, or SP) and after geometry optimization (OPT) for different chemical models.

Energy (a.u.)	HF		B3LYP		MP2		CCSD	
	SP	OPT	SP	OPT	SP	OPT	SP	OPT
6-311G	-228.24529	-228.41014	-229.43991	-229.63312	-228.64182	-228.83120	-	-
6-311G(d,p)	-228.36473	-228.49802	-229.54632	-229.70684	-	-	-	-
6-311+G(d,p)	-228.37266	-228.50529	-229.56011	-229.71922	-	-	-	-
6-311++G(3df,3pd)	-228.39201	-228.51937	-229.57873	-229.73213	-229.16237	-229.31282	-229.16835	-229.32977

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