

The absorption intensities of water trimer symmetric stretches: A QTAIM/CCFDF atomic approach

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Introdução

Through hydrogen bond formation some of the most dramatic changes in chemical properties occur. Among them, changes in the infrared spectrum, such as frequency shifts and huge intensity enhancements of H-X stretching vibrations are especially notable. However the vast information that could be contained in infrared spectra is not always directly accessible and sometimes correct band assignments are difficult. In this work the infrared enhancement effect observed experimentally for the water trimer is investigated at the QCISD/cc-pVTZ level with the QTAIM/CCFDF model.

Resultados e Discussão

The experimentally proposed most stable¹ water trimer geometry does not exhibit molecular symmetry (i.e. C_1), since it consists of three water molecules cyclically bonded through their hydrogens with all oxygen atoms in a plane. The free hydrogen atoms are angled alternating above and below the oxygen plane. Another often used approximate geometry consists of a C_{3h} planar complex, since the torsion barrier of the free water trimer is rather low. Both geometries are presented in Figure 1.

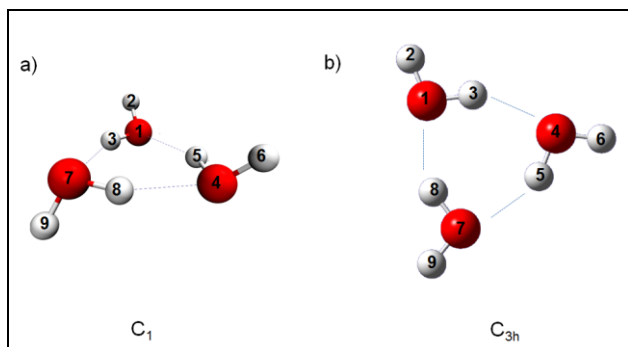


Figure 1. Two most stable structures for the water trimer, a) C_1 and b) C_{3h}

The results were obtained using the protocol explained in previous papers². The water trimer has three symmetric stretches. The atomic contributions and total intensity of these normal coordinates are represented in Table 1

Table 1. Atomic contributions for the symmetric stretches in the water trimer

Atom	Sym. Str. 1	Sym. Str. 2	Sym. Str. 3
O(1)	0,8	0,0	0,5
H(2)	0,8	0,0	0,4
H(3)	188,0	9,5	121,0
O(4)	0,0	0,6	0,3
H(5)	14,2	163,4	64,2
H(6)	0,5	1,3	0,7
O(7)	0,4	0,3	0,5
H(8)	98,2	78,4	97,1
H(9)	0,8	0,9	0,8
H(3)H(5)	46,4	37,8	-83,5
H(3)H(8)	97,5	-20,3	-78,1
H(5)H(8)	-46,6	149,9	-103,8
Other	1,0	6,1	3,4
Total	401,7	427,9	23,5

Two of these vibrations have one of the water molecules stretching in an opposite phase compared with the others. These normal coordinates have the strongest (1 and 2) absorptions, i.e. enhancement effects, with QCISD/cc-pVTZ intensities of 401.7 and 427.9 km.mol^{-1} . The remaining stretching band consists of the three water units vibrating with the same phase. It is clear from Table 1 that almost all the intensity of the normal coordinates can be explained by the hydrogens involved in the hydrogen bonding, and their interactions. This is true for all three stretches but for the third one. Owing to its high symmetry, all the intensity contributed by the hydrogens is cancelled by their interactions, resulting in a rather small intensity

Conclusões

The high infrared intensity of the symmetric stretches 1 and 2, can be described almost exclusively by the hydrogens involved in the hydrogen bonding, as they account for 397,7 and 418,7 km.mol^{-1} respectively. The last normal coordinate (3) has a much lower intensity since the hydrogen contributions are annulled by their interactions.

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