The Structure of I⁻(H₂O)₄ Cluster: *Ab initio* study

Masao Masamura*

Okayama University Graduate School of Medicine and Dentistry, Shikata-cho 2-5-1,

Okayama, 700-8525 Japan

E-mail address: tokin@mx3.tiki.ne.jp

Phone number: 81-86-235-6712

FAX number: 81-86-235-6714

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Abstract

For $\Gamma(H_2O)_4$ cluster, it has long believed that the C₄ symmetry structure is most stable isomer at low temperature. However, calculated vibrational spectra values using *ab initio* disagree with experimental values. Therefore, we calculated the structure of $\Gamma(H_2O)_4$ using extensive *ab initio* calculation. Hence, we found most stable isomer for $\Gamma(H_2O)_4$ at low temperature. The isomer has C₂ symmetry. The C₄ symmetry structure was transition structure. These findings are useful for solving the confusion between the experiment and *ab initio* results.

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1 INTRODUCTION

The hydration of ions is a subject of interest in solute and biochemistry [1]. An iodide anion is of particular interest in hydration, since it has large polarizability and large ionic radius [2]. The various structures of $\Gamma(H_2O)_n$ cluster (where n = 1-6) have been examined using extensive *ab initio* calculations [2]. Also, experimental vibrational spectra was recorded at low temperature [3,4].

The *ab initio* results are in excellent agreement with the low temperature experimental data except for n =4 [2]. In the case of n = 4, it has long believed that the C₄ symmetry structure is most stable isomer [2,5]. However, the calculated vibrational spectra values disagree with the experimental values. Therefore, we calculated the structure of $\Gamma(H_2O)_4$ using extensive *ab initio* calculation. Hence, we found other more stable isomer.

The purpose of this paper is to propose the most stable isomer at low temperature.

2 MATERIALS AND METHODS

We used the Gaussian 94 [6] and Gaussian 98 [7] programs, operating on the SX-7 and VPP5000 computers located at the Research Center for Computational Science.

For $I^{-}(H_2O)_4$, we substituted I for Br in the isomers of Br⁻(H₂O)₄ in Ref. [8] and then optimized the resulting structures at MP2 level. Also, we optimized the structure near the C₄ symmetry structure. We used the following basis sets:

I: CEP-121G [9] with augmented diffuse sp and d in Ref. [2].

Water molecules: 6-31++G(2d,2p).

We also performed vibrational analysis for all of the isomers having the optimized structures to confirm that all of the vibrational frequencies are real. The core electrons were frozen.

3 RESULTS AND DISCUSSION

The most two stable isomers are the structures (1) and (2) in Figure 1. The structure (1) has C_4 symmetry. The structure (2) has C_2 symmetry. The isomer (1) is transition state structure with one imaginary frequency. The isomer (2) is local minima. The isomer (2) is more stable than the isomer (1) by 0.2 kcal/mol.

Table 1 shows the OH harmonic frequencies for $\Gamma(H_2O)_4$. The values in the isomer (1) disagree with the experimental values. The values in the isomer (2) agree with the experimental values.

The results suggest that the isomer (2) is most stable isomer at low temperature.

The C₄ structures for X⁻(H₂O)₄ (X = F, Cl, Br) are local minima. When X is heavier element, the X⁻...(H₂O) distance for the C₄ structures is longer: F⁻ (1.714 Å) [10]; Cl⁻ (2.386 Å) [11]; Br⁻ (2.549 Å) [8]; I⁻ (2.967 Å). Therefore, it is not surprising that the C₄ structure for I⁻(H₂O)₄ is transition structure.

We will calculate the structures of $\Gamma(H_2O)_n$ using higher level ab initio molecular orbital methods.



FIGURE 1. The optimized structures of $I^{-}(H_2O)_4$. The values are distances in Å.

TABLE 1. Shift of the OH harmonic frequencies for I'(H₂O)₄ cluster.^a

Isomer (1)	Isomer (2)	Experiment ^b
	378 (729)	370
297 (610) [2]	273 (587)	230
126 (73) [2]	207 (242)	180/160
109 (611)	199 (650)	

^a The shifts are given with respect to the corresponding mean of the symmetric OH strech in water (3913 cm⁻¹). The parentheses are IR intensities. The numbers in square brackets denote degeneracy. The frequency shifts are given in cm⁻¹ and the IR intensities in km/mol.

^b Based on Ref. [2-4].

4 CONCLUSIONS

We found the most stable isomer for $\Gamma(H_2O)_4$ at low temperature. The isomer has C₂ symmetry. It has long believed that the C₄ symmetry structure is most stable isomer at low temperature. However, this structure was transition structure. These findings are useful for solving the confusion between the experiment and *ab initio* results.

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