Intermolecular Vibration Coupling between Libration of Water and ν_2-SOH for Clusters $HSO_4^-(H_2O)_n$

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S *Supporting Information*

ABSTRACT: The hydrated bisulfate ion clusters ($HSO_4^-(H_2O)_n$, $n = 1-10$) were optimized at the M06/6-311++G(d,p) level. The factors affecting ν_2-SOH of the clusters involved vibration coupling between ν_2-SOH and the water wagging libration mode (W-H_2O) and hydrogen bonding effect. In order to understand the vibration coupling between W-H_2O and ν_2-SOH for the bisulfate clusters, D_2O instead of H_2O and Se instead of S were used to estimate the uncoupling frequency of ν_2-SOH and W-H_2O, respectively. For $HSO_4^-\cdot H_2O$-I, the uncoupling frequencies of ν_2-SOH and W-H_2O were obtained at 752.0 and 753.4 cm^{-1}. After coupling, the frequencies appeared at 782.2 and 732.6 cm^{-1}. H_2S and NH_4^+ instead of D_2O in $HSO_4^-\cdot D_2O$-II were compared to analyze the effect of hydrogen bond. The sequence of hydrogen bond strength was found to be $HSO_4^-\cdot H_2S$-II < $HSO_4^-\cdot D_2O$-II < $HSO_4^-\cdot NH_4^+$-II with the respective ν_2-SOH at 736.7, 740.5, and 802.2 cm^{-1} increasing in the same order. In $HSO_4^-\cdot(H_2O)_n$, coupling appeared when n was from 1 to 8. For $HSO_4^-\cdot(D_2O)_n$, no coupling between ν_2-SOH and D_2O librations made it possible to understand the hydrogen bonding effect on the ν_2-SOH. The frequencies of ν_2-SOH for clusters $HSO_4^-(D_2O)_n$ almost linearly decreased from 752.0 to 854.6 cm^{-1} with n from 1 to 10.
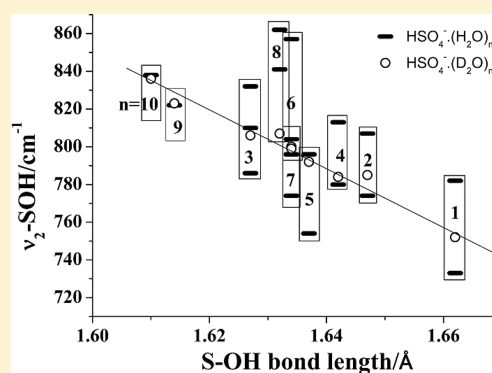
I. INTRODUCTION

Sulfate ion and bisulfate ion are both important species in forming aerosols in the atmosphere[1-3] and act with water molecules[4,5] owing to the hygroscopic property of aerosols.[6-9] The interaction between sulfuric acid (including sulfate and bisulfate ions) and water molecules is a fundamental issue in order to understand how cloud droplets grow in their initial phase.[10,11]

Many investigations about sulfate ion and bisulfate ion as well as their complexes were carried out both in experiments[12-20] and calculations[21-29] in the past years. Bisulfate ion was derived from the production of the deprotonation of sulfuric acid in the first step, exhibiting amphoteric properties owing to the fact that it has several binding sites acting both as a proton donor and a proton acceptor for hydrogen bonding.[30]

The presence of the hydrogen in HSO_4^- breaks the ideal symmetry T_d structure possessed by SO_4^{2-}. The OH group for bisulfate ion has a free rotation; thus, the bisulfate ion can be considered as approximately C_{3v} symmetry.[31] This reduces the symmetry T_d with presentation $\Gamma_{vib} = 2F + E + A$ to symmetry C_{3v} with presentation $\Gamma_{vib} = 3A + 3E$. The triply degenerate unsymmetrical stretch ν_3-SO_4^{2-} (F mode) and symmetric stretch ν_1-SO_4^{2-} (A mode) of SO_4^{2-} transfer to doubly degenerate modes unsymmetrical stretch ν_4-SO_3 (E mode), ν_2-SOH (A mode), and symmetric stretch ν_1-SO_3 (A mode) of the HSO_4^-, which is shown in Figure 1. Keeping this

approximation, bisulfate ion adds three OH vibration modes on the basic C_{3v} symmetry vibration modes, that is, O−H stretching (ν-OH)), S−O−H bending (δ-OH), and S−O−H torsion (γ-OH), which is similar to the change between PO_4^{3-} and HPO_3^{2-}.[32]

The ν_2-SOH band is very sensitive to characterize the interaction between HSO_4^- and solvent molecules and aggregation between HSO_4^- anions.[33-36] A temperature-dependent Raman spectra study was carried out on NH_4HSO_4 single crystals in the temperature range 77−298 K, and the frequency of ν_2-SOH was reported in the 850−900 cm^{-1} range.[37] A theoretical understanding on its change depending on the environment is that it is affected by the intermolecular hydrogen bonds, which form between bisulfate ions or between bisulfate ion and solvent molecules.

Water exists extensively in the atmosphere. The spectroscopy of water is very complex. The water molecule may vibrate in a number of ways. In the gas state, the vibrations involve combinations of symmetric stretch (ν_1), asymmetric stretch (ν_3), and scissoring (ν_2) of the covalent bonds. Gas phase rotations are complex and combined with these vibrations. Rotations in the liquid phase are totally dominated by hydrogen
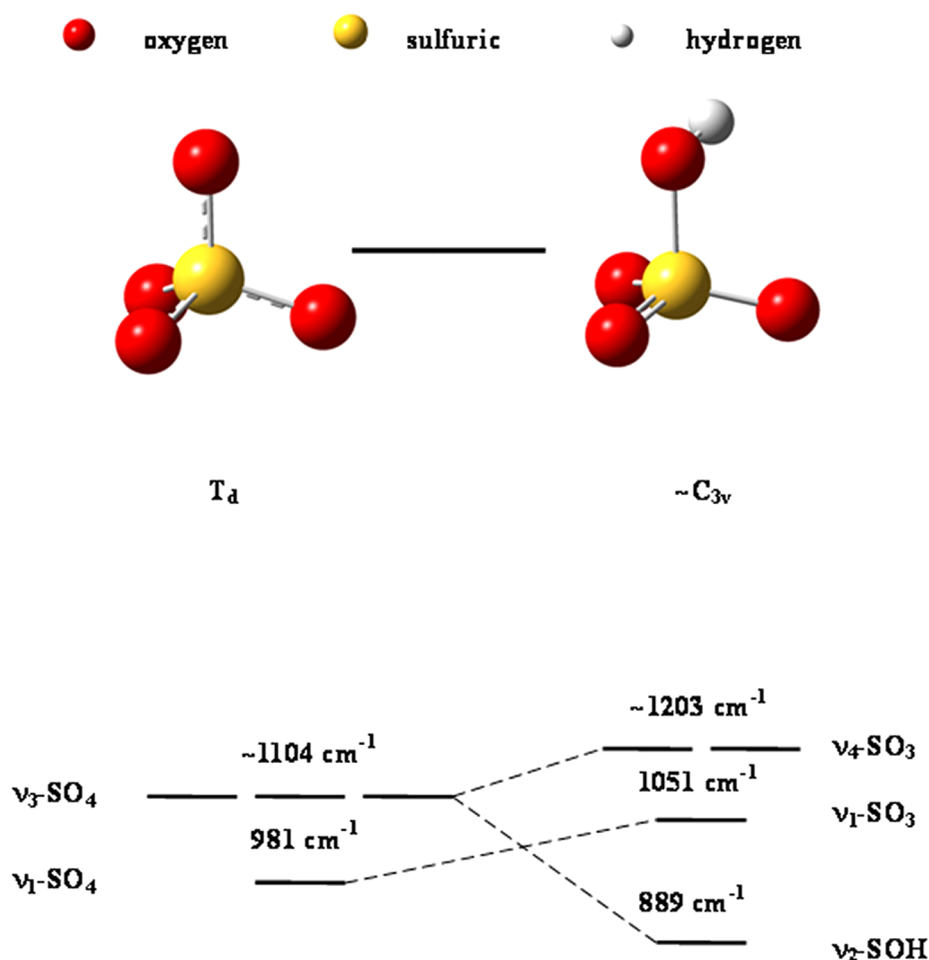
Figure 1. The relationship between SO_4^{2-} and HSO_4^- for the four stretching bands.

bonds. And the rotations transfer to librations when water molecules form hydrogen bonds with other molecules.

Several theoretical investigations about the interaction between bisulfate ion and water molecules were carried out.[38−41] When it interacts with water molecules and forms clusters $HSO_4^-(H_2O)_n$, its spectra will change and the characterized vibration band will be affected. It was found that the ν_2-SOH band had a blue shift and became broadened in the clusters $HSO_4^-(H_2O)_n$.[38] The effect of temperature and pressure on blue shift was reported, and it was conjectured that the hydrogen bond strength was affected by temperature and pressure and thus affected the vibration band.[23] However, it remains an open question about the effect of hydrogen bond strength.

The broadening ν_2-SOH vibration band still has no clear explanation because there is a strong resonance energy coupling between the ν_2-SOH vibration band and H_2O libration in addition to the hydrogen effect between HSO_4^- and H_2O.

The isotope probe is one of the most useful means to solve the difficulty of spectroscopic assignment, and it is used in experimental investigation. However, it has many restrictions in experiment because it cannot realize the accurate located substitution especially for intermolecular systems. The theoretical calculation can settle this difficulty easily, and some theoretical researchers have used it in the past years. It was introduced to understand the coupling effect between librations of H_2O with the ν_1-SO_4^{2-} band in the magnesium sulfate system.[21]

In order to understand the shift of the ν_2-SOH band in this work, the density functional theory was used to investigate the effects of hydrogen bond and coupling between the libration of water molecules and ν_2-SOH of HSO_4^-. The isotope probe was used for the investigation of coupling effects. The investigated results were helpful for understanding the intrinsic mechanism of the ν_2-SOH vibration frequency dependent on intra- and intermolecular interactions.

II. COMPUTATIONAL METHODOLOGY

All geometries were optimized at the M06/6-311++G(d,p) level by using the Gaussian 09 program package.[42] The frequency was calculated by employing the same method and by using the same basis set, as it has been shown that M06 is a more accurate density functional theory in calculating the frequency of a similar system.[43] All stable geometries obtained in this work possessed all real frequencies. All stable structures of the clusters were set up by the help of the software GaussView 5.0.

In order to obtain stability quickly, the structure parameters of stable structures optimized at the B3LYP/6-311G(2d,2p)[44] and MP2/6-311G+(d,p)[38] levels were referred to as the initial structures and optimized at the M06/6-311++(d,p) level.

The hydrated clusters $HSO_4^-·(H_2O)_n$ ($n = 1-10$) were optimized. The calculated frequencies of ν_2-SOH for these clusters were compared with the frequency of ν_2-SOH in the bisulfate.

Isotopic substitution[45] was used to estimate the coupling effect and get the uncoupling frequency of ν_2-SOH. $HSeO_4^-$ instead of HSO_4^- was calculated to get the uncoupling frequency of water libration for $HSO_4^- \cdot (H_2O)_n$. The coupling modes were gotten by comparing the uncoupling frequencies of ν_2-SOH and the libration of water molecule with their coupling frequencies.

III. RESULTS AND DISCUSSION

The Structure and Raman Spectra of Bisulfate Ion. Figure 2 shows the structure of bisulfate ion, and its structure parameters are listed in Table 1.
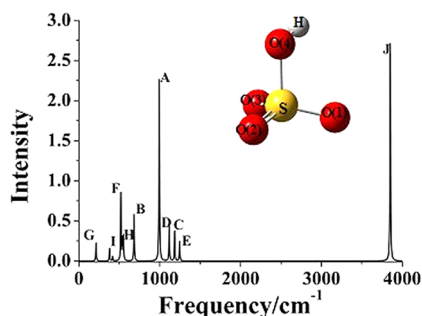

Figure 2. The structure and Raman spectroscopy of HSO_4^- obtained at the M06/6-311++G(d,p) level.

Table 1. Structure Parameters for the Geometry of HSO_4^- Obtained at the M06/6-311++G(d,p) Level

structure parameters	calculated results
S—O$_1$	1.4795
S—O$_2$	1.4696
S—O$_3$	1.4795
S—O$_4$	1.7140
O$_4$—H	0.9652
∠O$_1$SO$_2$	115.69
∠O$_1$SO$_3$	113.79
∠O$_1$SO$_4$	103.87
∠SO$_4$H	105.02
O$_3$SO$_1$O$_2$	−137.53
O$_4$SO$_1$O$_2$	110.22
HO$_4$SO$_1$	59.63

Compared with SO_4^{2-}, the bond length of S—OH becomes longer, from 1.5107 to 1.7140 Å, and the bond length of the other three bonds becomes shorter—both S—O(1) and S—O(3) are 1.4795 Å, and S—O(2) is 1.4696 Å of HSO_4^-.

Bisulfate ion involves 6 atoms and has 12 vibrational modes.[31] If we consider that the symmetry of HSO_4^- is C$_{3v}$, the 12 modes should involve the SO$_3$ symmetry stretching band (ν_1-SO$_3$, A), the SO$_3$ antisymmetry stretching band (ν_4-SO$_3$, E), SO$_3$ symmetry deformation (δ_s-SO$_3$, A), antisymmetry deformation (δ_{as}-SO$_3$, E), O=S—O deformation vibration (δ-O=S—O), S—OH stretching band (ν_2-SOH) and S—(OH) torsion vibration (τ-S—OH), O—H stretching (ν-O—H), S—O—H bending (δ-OH), and S—O—H torsion (γ-OH).[38] These frequencies are shown in Figure 2. The frequencies of ν_1-SO$_3$ (labeled A in Figure 2), ν_2-SOH (labeled B in Figure 2), δ-OH (labeled D in Figure 2), δ_s-SO$_3$ (labeled F in Figure 2), γ-O—H (labeled G in Figure 2), and ν-O—H (labeled J in Figure 2) are 994.9, 683.7, 1118.6, 520.5, 213.2, and 3851.5 cm^{-1}, respectively. The ν_4-SO$_3$ band splits at 1185.4 and 1246.5

cm^{-1} (labeled C and E in Figure 2), indicating that the HSO_4^- is not a critical C$_{3v}$ symmetry. The splitting of δ_{as}-SO$_3$ (labeled H in Figure 2) show the two peaks at 541.2 and 553.1 cm^{-1}, respectively. The frequencies of δ-O=S—O and τ-S—OH (labeled I in Figure 2) are 380.4 and 417.2 cm^{-1}, respectively. The presence of the hydrogen atom in bisulfate ion eliminates the degeneracy of ν_4-SO$_3$ and δ_{as}-SO$_3$ and causes their frequencies to split into two frequencies, which is a good explanation for the wider ν_4-SO$_3$ band than the other vibrational bands for bisulfate ion in experiment.

The Raman spectra of bisulfate ion vary after interacting with water molecules. The stable isomers of the clusters $HSO_4^- \cdot (H_2O)_n$ ($n = 1-10$) are shown in Figure 3, calculated at the M06/6-311++G(d,p) level.

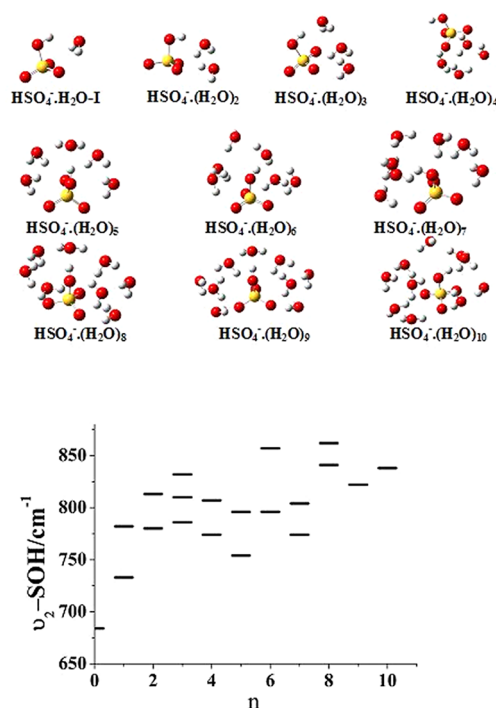**Figure 3.** Stable isomers of $HSO_4^-(H_2O)_{1-10}$ and the frequencies of V_2-SOH of them.

Now let us turn our attention to the ν_2-SOH band. The frequencies of the S-(OH) stretching mode, i.e., the ν_2-SOH band, in every species are given at the bottom of Figure 3. There are two or three frequencies related to the ν_2-SOH band in the same clusters except for $n = 9$ and 10, which have a blue shift after interacting with water molecules. Coupling between the ν_2-SOH band and libration of H_2O as well as hydrogen bonding between H_2O and HSO_4^- are the two factors causing the changes of the frequency of the ν_2-SOH. In the next two parts, the coupling between ν_2-SOH and libration of H_2O and the effect of hydrogen bonding are elucidated in detail.

Coupling Effect on ν_2-SOH. The three translation vibration modes (Tr$_1$, Tr$_2$, Tr$_3$) of bound H_2O are shown in Figure 4, in which the arrowheads denote the displacement vectors of the atom in the vibrations. The three rotations generate three libration modes when a free water molecule is bound to a HSO_4^- to form two hydrogen bonds with the oxygen atoms of the bisulfate ion.[21] In the complex, rotations tend to be restricted by hydrogen bonds, giving the libration modes shown in Figure 4. The libration modes are described in
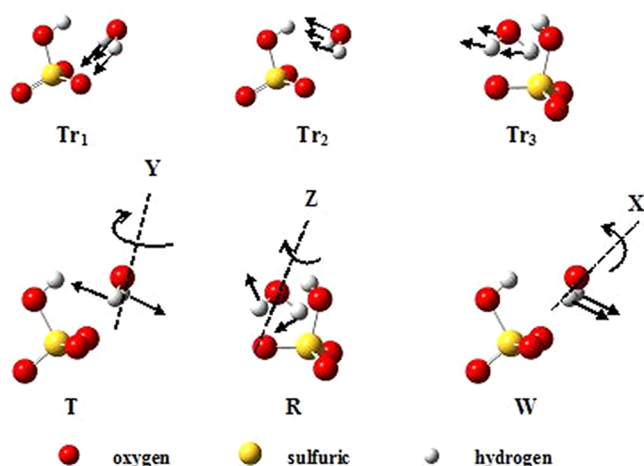
Figure 4. The translation and libration of H_2O after hydrogen bonding with HSO_4^-.

terms of motions about the three principal inertia axes of free water, whose nomenclature X, Y, Z is chosen so that $I_X < I_Y < I_Z$. The librations around the axes X, Y, and Z are conventionally named as wagging (W), twisting (T), and rocking (R) modes, respectively. The frequencies of translation and libration were determined by the location of the water molecule and the hydrogen bonds formed with bisulfate ion; therefore, they vary in the clusters containing different numbers of water molecules or in different structures containing the same number of water molecules. In the clusters, they couple with other vibrational modes. The most important coupling with the ν_2-SOH band is the W-H_2O, and in some clusters, T-H_2O also has a certain extent of coupling with the ν_2-SOH band. In the clusters $HSO_4^-\cdot(H_2O)_{1-10}$, the frequencies of the ν_2-SOH band are in the region from 733.6 to 862.5 cm^{-1} and the frequencies of T-H_2O and W-H_2O are largely in the regions from 550 to 780 cm^{-1} and from 730 to 1300 cm^{-1}, respectively. They appear at the same frequency region, which would couple with each other. The frequencies of R-H_2O are in the region from 300 to 600 cm^{-1} which is lower than the frequencies of ν_2-SOH and rarely couples with the ν_2-SOH band. The frequencies of the libration of a water molecule have a relationship with the inertia of the water molecule. The frequency of the libration of H_2O becomes lower for the clusters $HSO_4^-(H_2O)_n$, $n = 1-10$, with increasing inertia of the free water molecule.

To clarify the details of the coupling, the methods of isotopic substitution (D instead of H in the water molecule of the cluster) is utilized and this method was used to investigate the Fermi resonance between the two bending modes of CO_2 in 1996[46] and the Fermi resonance between ν_1-SO_4^{2-} and ν_1-ClO_4^- in 2006[47] by Rudolph. The same main group element substitution (Se instead of S) is utilized, respectively, to get the uncoupling vibration frequencies of ν_2-SOH and W-H_2O.

The coupling between ν_2-SOH and W-H_2O is investigated by taking the clusters $HSO_4^-\cdot(H_2O)_n$ with $n = 1$ and $n = 3$ for examples.

Figure 5a shows the case of the cluster of $HSO_4^-\cdot H_2O$, for which the water molecule forms three hydrogen bonds with bisulfate ion (structure I). There are two bands at 732.6 and 782.2 cm^{-1} related to ν_2-SOH resulting from coupling between ν_2-SOH and W-H_2O. The coupling phenomenon disappears when H_2O in the cluster is replaced by D_2O. That is, the

uncoupling frequency of ν_2-SOH is 752.0 cm^{-1} when the molecule H_2O in structure I is substituted by D_2O. The uncoupling frequency of W-H_2O can be obtained as 753.4 cm^{-1} by the method of replacing S in bisulfate ion with Se.

The uncoupling frequencies of ν_2-SOH (752.0 cm^{-1}) and W-H_2O (753.4 cm^{-1}) in structure I are so close that they couple with each other and break up into two frequencies which is in accordance with the result from the system of SO_4^{2-}.[21] After coupling, one of them appears at 732.6 cm^{-1}, much lower than both the frequencies of ν_2-SOH and the libration of water W-H_2O, while the other appears at 782.2 cm^{-1}, much higher than both of them.

In this structure, the band at 732.6 cm^{-1} corresponds to shrinking of S—OH and wagging of W-H_2O downward, while the 782.2 cm^{-1} band, to S—OH extruding and wagging of W-H_2O downward. These two bands are in contrary phase, as shown in Figure 5a.

The structure of the cluster of $HSO_4^-\cdot H_2O$ in which the water molecule forms two hydrogen bonds with O(2) and O(3) in bisulfate ion (structure II) is shown in Figure 5b. The uncoupling frequencies of ν_2-SOH and libration of water molecule W-H_2O are obtained at 740.5 and 659.5 cm^{-1}, respectively, with D instead of H and by replacing S with Se. Even though the symmetry deformation of SO_3 (δ_s-SO_3) appears at 526.6 cm^{-1}, it is involved in the coupling with ν_2-SOH, as shown in Figure 5b. In this case, the coupling frequencies of ν_2-SOH appear at 708.5 and 657.2 cm^{-1}, in which the former includes ν_2-SOH, W-H_2O, and δ_s-SO_3 and latter is from ν_2-SOH and W-H_2O. After coupling, the uncoupling frequency of W-H_2O (659.5 cm^{-1}) breaks up into two coupling frequencies where one (657.2 cm^{-1}) is lower than the uncoupling frequency and the other (708.5 cm^{-1}) is higher than the uncoupling frequency of W-H_2O, which is similar to structure I. Differently from the coupling modes of structure I, the two coupling frequencies are both lower than the uncoupling frequency of ν_2-SOH (740.5 cm^{-1}) in this structure. The participation of intramolecular coupling is the key point. At the coupling frequency 708.5 cm^{-1}, δ_s-SO_3 which appears in low frequency (526.6 cm^{-1}) couples with ν_2-SOH and W-H_2O. The participation of δ_s-SO_3 causes this coupling frequency to become lower than the uncoupling frequency of ν_2-SOH.

Figure 6 shows the case of the cluster of $HSO_4^-\cdot(H_2O)_3$, there are three bands at 786.3, 810.5, and 831.6 cm^{-1} related to ν_2-SOH, which result from coupling between ν_2-SOH, T-H_2O, and W-H_2O.

The water molecules in this cluster are marked A, B, and C, as shown in Figure 6. ν_2-SOH couples with W-$(H_2O)_A$, T-$(H_2O)_B$, and W-$(H_2O)_C$ appearing at 786.3 cm^{-1}. The coupling between ν_2-SOH, W-$(H_2O)_A$, W-$(H_2O)_B$, and W-$(H_2O)_C$ appears at 810.5 cm^{-1}. The coupling between ν_2-SOH, T-$(H_2O)_A$, W-$(H_2O)_B$, and W-$(H_2O)_C$ appears at 831.6 cm^{-1}.

The uncoupling frequencies are obtained by isotopic substitution (D instead of H) and the same group element substitution (Se instead of S). The uncoupling frequency of ν_2-SOH appears at 806.5 cm^{-1} by substituting the hydrogen atoms in three water molecules with deuterium atoms. The uncoupling frequency of the libration of every water molecule cannot be achieved only by substituting the atom S in $HSO_4^-\cdot(H_2O)_3$ with Se because the libration of the three water molecules couples with each other. The uncoupling frequency of W-$(H_2O)_B$ appears at 825.8 cm^{-1} when the hydrogen atoms (including the hydrogen atom in the bisulfate ion) in the cluster $HSO_4^-\cdot(H_2O)_3$ are all substituted with
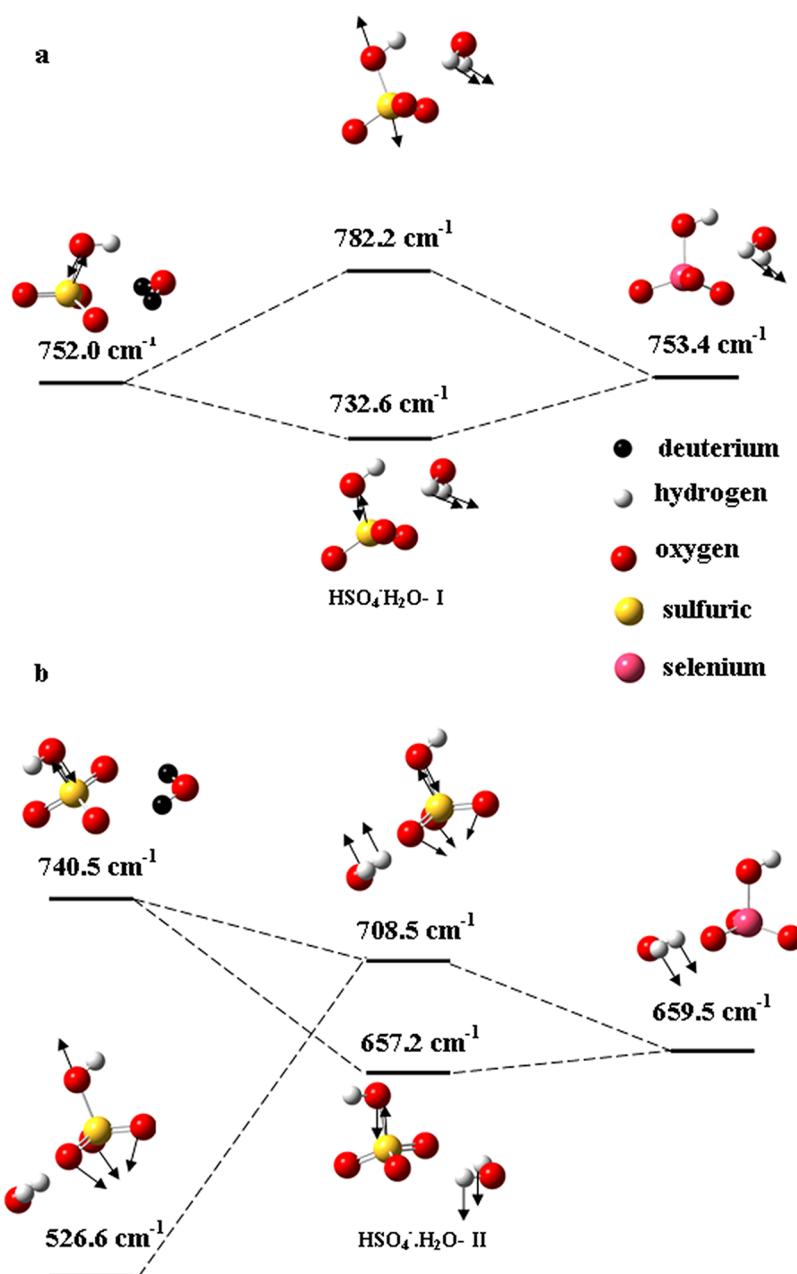
Figure 5. (a) The coupling modes between V_2-SOH and W-H_2O in the cluster $HSO_4^-\cdot H_2O$ with three hydrogen bonds in structure I. (b) The coupling modes between V_2-SOH and W-H_2O in the cluster $HSO_4^-\cdot H_2O$ with two hydrogen bonds in structure II.

deuterium atoms except the two hydrogen atoms in water molecule B. The uncoupling frequencies of W-$(H_2O)_A$ are obtained by substituting the hydrogen atoms in water molecules B and C with deuterium atoms appearing at 783.1 cm^{-1}. The uncoupling frequency of W-$(H_2O)_C$ is obtained of 756.8 cm^{-1} by substituting the hydrogen atoms in water molecules A and B with deuterium atoms.

To verify the effect of isotopic substitution in this system, the frequency of ν_2-SOH for the clusters of $HSO_4^-\cdot H_2O$-III (the hydrogen bonds forming between water molecule and O(2) and O(4)), which ν_2-SOH does not couple with other vibrational modes, is compared to the frequency of ν_2-SOH for the clusters $HSO_4^-\cdot D_2O$-III, as shown in Figure 7. The frequency of ν_2-SOH is 707.1 cm^{-1} for the cluster $HSO_4^-\cdot H_2O$-III, and it is 706.8 cm^{-1} for the cluster $HSO_4^-\cdot D_2O$-III. It can

be inferred that the frequency of ν_2-SOH has so small change if there no coupling when D instead of H.

To be more convinced, two more examples are given. ν_2-SOH for $HSO_4^-\cdot H_2S$-II is compared with $HSO_4^-\cdot D_2S$-II with the same structure. The frequencies of ν_2-SOH in $HSO_4^-\cdot H_2S$-II and $HSO_4^-\cdot D_2S$-II appear at 736.7 and 736.0 cm^{-1}, respectively. ν_2-SOH for $HSO_4^-\cdot H_2S$-III is compared with $HSO_4^-\cdot D_2S$-III. The frequencies of ν_2-SOH are 712.3 and 711.9 cm^{-1} for $HSO_4^-\cdot H_2S$-III and $HSO_4^-\cdot D_2S$-III, respectively. The frequency of ν_2-SOH has so little red shift (within 1 cm^{-1}) when D instead of H that this method is proved to be a good method to estimate the uncoupling frequencies.

These calculation results about the coupling phenomenon are good references for some experimental phenomena. In experiment, different isomers[41] exist and the coupling phenomenon appears in some of these isomers. Just as the
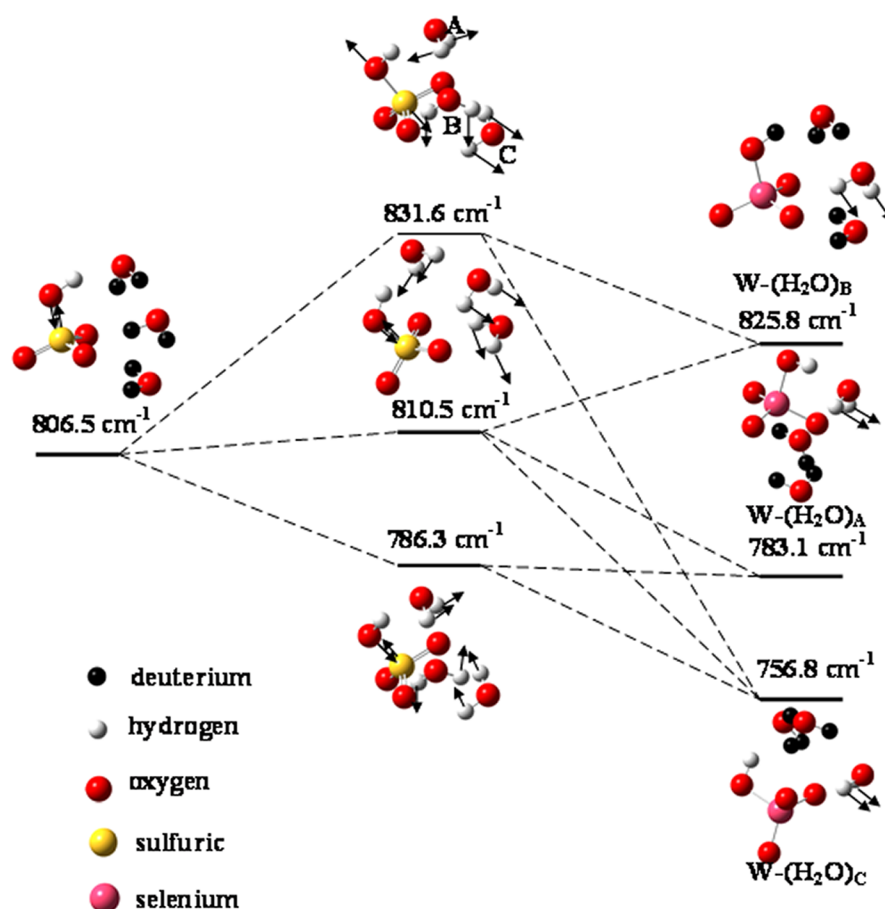
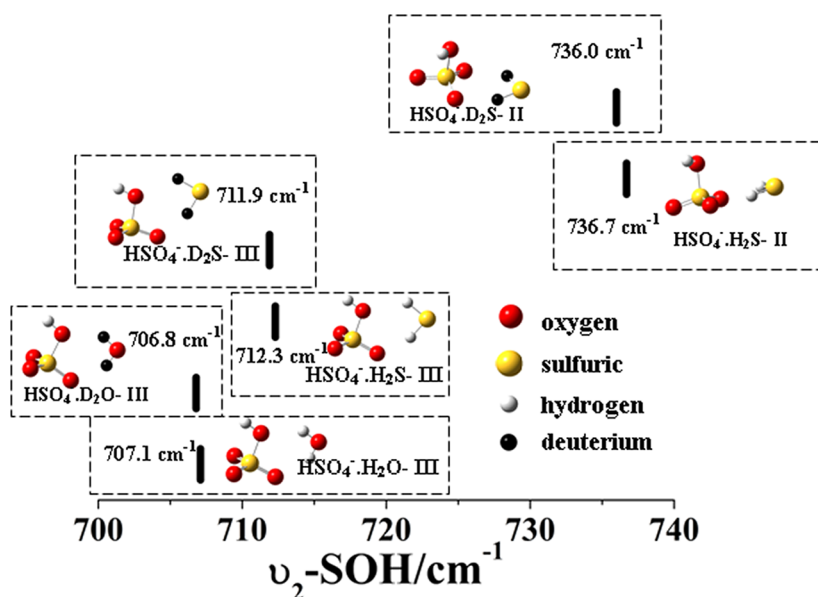**Figure 6.** The coupling modes between V_2-SOH and W-H_2O in the cluster $HSO_4^- \cdot (H_2O)_3$.

Figure 7. The frequencies of V_2-SOH in the clusters $HSO_4^- \cdot H_2X$ and $HSO_4^- \cdot D_2X$ (X = O, S).

cluster of $HSO_4^- \cdot H_2O$, the coupling phenomenon appears in structures I and II, while ν_2-SOH does not couple with other vibrational modes in structure III. At the same time, the existence of different clusters containing different numbers of water molecules[38,41,43] brings more coupling frequencies. All of these coupling and uncoupling frequencies appear near each

other. It is inferred that the overlap of these bands leads to the ν_2-SOH bands broadening.

Hydrogen Bonding Effect on ν_2-SOH. To verify the effect of hydrogen bonding, the frequency of ν_2-SOH for $HSO_4^- \cdot D_2O$-I, -II, and -III is compared with the frequency of ν_2-SOH for bisulfate ion, respectively. In these three structures, there is the biggest blue shift of ν_2-SOH in structure I, then

structure II, and finally structure III which is the smallest. The frequency of ν_2-SOH for bisulfate ion is 683.7 cm^{-1}, while the frequencies of ν_2-SOH for HSO$_4^-$·D$_2$O in structures I, II, and III are 752.0, 740.5, and 706.8 cm^{-1}. ν_2-SOH has a blue shift of 68.3 cm^{-1} in structure I, 56.8 cm^{-1} in structure II, and 23.1 cm^{-1} in structure III. The strength of hydrogen bond forming between the deuterium atom and oxygen atom in bisulfate are close to each other, but it had a different effect on the length of the S−(OH) bond because the locations of the water molecules are different. S−(OH) bond lengths are 1.6616 Å in structure I, 1.6710 Å in structure II, and 1.6943 Å in structure III. Thus, the conclusion is that hydrogen bonding will shorten the S−OH bond length[23] and lead to a blue shift for ν_2-SOH in bisulfate ion. The change of S−OH bond length is different with the changing of the locations of water molecules.

In order to investigate the effect of different strengths of hydrogen bonds, D$_2$O of HSO$_4^-$·D$_2$O-II is substituted with H$_2$S and NH$_4^+$. The optimized structures are shown in Figure 8.
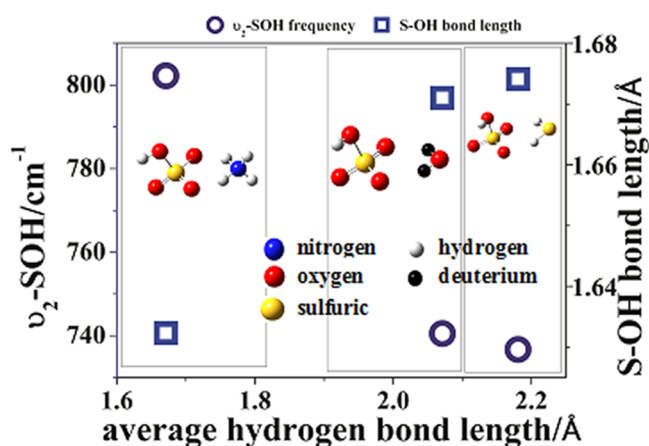

Figure 8. The relationship between hydrogen bonding strength, S−OH bond length, and the frequencies of V$_2$-SOH in the clusters HSO$_4^-$·D$_2$O, HSO$_4^-$·H$_2$S, and HSO$_4^-$·NH$_4^+$.

The lengths of the hydrogen bonds vary in these three clusters. The lengths of the two hydrogen bonds in HSO$_4^-$·H$_2$S-II are 2.1093 and 2.2520 Å, respectively. The lengths of the two hydrogen bonds in HSO$_4^-$·D$_2$O-II are 2.0588 and 2.0836 Å, respectively. The lengths of the hydrogen bonds in HSO$_4^-$·NH$_4^+$-II are 1.6361 and 1.7079 Å, respectively. The sequence of the hydrogen bond strength is HSO$_4^-$·H$_2$S-II < HSO$_4^-$·D$_2$O-II < HSO$_4^-$·NH$_4^+$-II. The S−(OH) bond length is 1.6741, 1.6710, and 1.6324 Å, respectively. The frequencies of ν_2-SOH in HSO$_4^-$·H$_2$S-II, HSO$_4^-$·D$_2$O-II, and HSO$_4^-$·NH$_4^+$-II appear at 736.7, 740.5, and 802.2 cm^{-1}, respectively. The relationship of the hydrogen bond strength, the S−(OH) bond length, and the frequencies of ν_2-SOH is shown in Figure 8. Comparing with the frequency of ν_2-SOH in bisulfate ion which is 683.7 cm^{-1}, the blue shift is 53.0 cm^{-1} for HSO$_4^-$·H$_2$S-II and 56.8 cm^{-1} for HSO$_4^-$·D$_2$O-II (we do not select HSO$_4^-$·H$_2$O-II because ν_2-SOH couples with the W-H$_2$O), while the blue shift is 118.5 cm^{-1} for HSO$_4^-$·NH$_4^+$-II. Evidently there is a blue shift for the frequency of the ν_2-SOH band with increasing hydrogen bond strength.

Both the location of the water molecule and the hydrogen bond strength[23] have an effect on the S−OH bond length and the frequency of ν_2-SOH for the clusters. The shorter the S−OH bond length, the higher frequencies of ν_2-SOH shift to. In

the clusters HSO$_4^-$(H$_2$O)$_{1-10}$, the isotopic substitution is used (D instead of H). The coupling phenomenon disappears after isotopic substitution. The frequencies of ν_2-SOH and the S−(OH) bond length in the clusters HSO$_4^-$(D$_2$O)$_{1-10}$ are shown in Figure 9. When n is from 1 to 10, the S−(OH) bond lengths

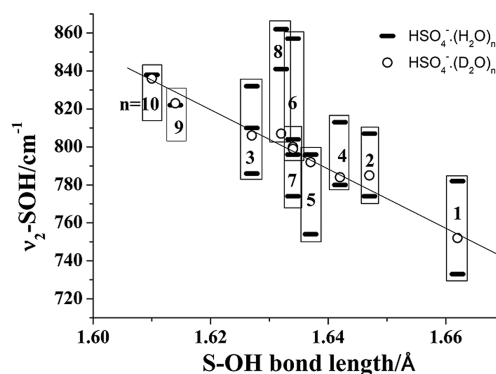**Figure 9.** The relationship between S−OH bond length and the frequencies of V$_2$-SOH in the clusters HSO$_4^-$(H$_2$O)$_{1-10}$ and HSO$_4^-$(D$_2$O)$_{1-10}$.

are almost linearly decreasing from 1.6613 to 1.6103 Å and the frequencies of ν_2-SOH are almost linearly increasing from 752.0 to 854.6 cm^{-1} with the exception of HSO$_4^-$(D$_2$O)$_3$. The hydrogen bonds increase with increasing water molecules in the clusters. And the S−(OH) bond lengths become short with the increasing hydrogen bonds. It is the nature that the hydrogen bonds shorten the length of the S−(OH) bond and cause its bond constant to increase which leads to a blue shift for ν_2-SOH.

IV. CONCLUSIONS

The coupling effect and the hydrogen bond are the factors affecting the vibration frequency of ν_2-SOH. The coupling effect causes the ν_2-SOH to relate to more bands, and this effect will lead to the ν_2-SOH band becoming broadened in experiment. With the substitution of isotope, the coupling between the libration of water W-H$_2$O and ν_2-SOH can be separated, by which way the coupling effect is abstracted. Then, we can expound the contributions of these factors. Comparing with the frequency of ν_2-SOH for bisulfate ion, the hydrogen bond leads to a blue shift of 68.3 cm^{-1} in structure I, 56.8 cm^{-1} in structure II, and 23.1 cm^{-1} in structure III for ν_2-SOH. It leads to a blue shift of 53.0 cm^{-1} for HSO$_4^-$·H$_2$S-II and leads to a blue shift of 56.8 cm^{-1} for HSO$_4^-$·D$_2$O-II, while it leads to a blue shift of 118.5 cm^{-1} for HSO$_4^-$·NH$_4^+$-II. For HSO$_4^-$·(D$_2$O)$_n$ (n = 1−10) clusters, there is no coupling between ν_2-SOH and D$_2$O librations. The hydrogen bonding effect on the ν_2-SOH can be clearly understood. The frequencies of ν_2-SOH for clusters HSO$_4^-$(D$_2$O)$_{1-10}$ are almost linearly decreasing from 752.0 to 854.6 cm^{-1}, with n from 1 to 10. The blue shift of the ν_2-SOH band has a relationship with the S−(OH) bond length. The change that this bond length becomes short causes the band of ν_2-SOH to appear at the higher frequencies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The complete author lists of refs 2 and 3 and Cartesian coordinates of optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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