pronounced selectivity for fluoride in contrast to the hexacoordinated intermediates,[3] $Co(NH_3)_4(NH_2)\cdots X^{n-1}$.

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Appendix

The ion-aggregation constant K_Y at $I \rightarrow 0$ for the example $A^{z+} + Y^- \rightleftarrows [A,Y]^{z-1}$ is given[10] by

$$K_Y(I \rightarrow 0) = \frac{4\pi N_A r^3}{3000} \exp\left\{\frac{ze^2 N_A}{DrRT}\right\}$$

with N_A, e, D, R, r, and T being Avogadro's number, the elementary charge, the dielectric constant of water, the gas constant, the distance of closest approach, and the absolute temperature, respectively.

The ionic strength dependence of K_Y was calculated by using the Debye–Hückel equation[11] (eq 6a) for the activity coefficients:

$$K_Y = K_Y(I \rightarrow 0) \times 10^{-2zAI^{1/2}/(1+\beta r I^{1/2})}$$

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Near-Infrared Spectra of $BaCl_2 \cdot 2D_2O$ at 10 K. A Local-Mode Approach

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The polarized crystal spectra of $BaCl_2 \cdot 2D_2O$ and of several partially deuterated crystals have been measured at 10 K in the near-infrared region. The O–D stretching bands have been analyzed by using local-mode theory, and the calculated parameters are compared with those derived from $BaCl_2 \cdot 2H_2O$. The anharmonicities are smaller than those observed for O–H oscillators in bound H_2O; this trend follows that found in the gas-phase molecules. The local-mode parameters for O–H oscillators in HOD are not the same as those in H_2O. Some possible explanations for this are presented.

Introduction

Recently, we have begun to apply local-mode theory to the vibrational overtone-combination spectra of oriented water molecules in single crystals.[1,2] These spectra occur in the near-infrared (near-IR) region, and the use of low temperature and polarized light insures optimum resolution of the vibrational bands in this region. Most recently we have measured the near-IR spectra of single crystals of $BaCl_2 \cdot 2H_2O$, and have derived local-mode parameters for water in these crystals.[2] The present study is a corollary to that report, and in it we calculate local-mode parameters for O–D oscillators in $BaCl_2 \cdot 2D_2O$ and try to assess the effect of deuteration on the local-mode parameters for O–H oscillators.

Barium chloride dihydrate (BCD) belongs to space group $P2_1/c$ (C_{2h}^5, $Z = 4$)[3] in which the formula units have a layered arrangement with the layers stacked along the crystal b axis. All atom positions have been determined by neutron diffraction,[4] and the angles and distances associated with the various hydrogen bonds have been codified by Brink,[5] whose numbering system we use in this work (see Figure 1). The lattice contains two crystallographically distinct water molecules on general positions. The spectra are therefore the superposition of features expected for two different water molecules. Oscillators 1 and 2 on water(I) and oscillator 3 on water(II) are engaged in strong hydrogen bonding to neighboring chloride ions. Oscillator 4 on water(II), on the other hand, forms weaker, bifurcated hydrogen bonds to neighboring chlorides. The local-mode parameters that we derived for these four oscillators are all different from one another. We were able to provide assignments for most of the strong bands in the spectra and also to correlate the local-mode parameters with hydrogen-bond distances and/or angles.

Experimental Section

Single crystals of BCD with varying degrees of deuteration were grown by recrystallization from aqueous solutions containing about 25%, 50%, 75%, 94%, and 98% D_2O. The solutions were slowly evaporated over concentrated H_2SO_4 in a desiccator. The crystals form as large rectangular plates showing the [010] face.[6]

Spectra were recorded at 10 K on a Varian-2300 spectrophotometer by using a Displex cryogenic refrigerator to cool the sample. Polarized light was provided by a pair of matched Glan-Thompson prisms. The incident light was perpendicular to the prominent [010] face of the crystal, and so was parallel to the crystal b axis (C_2). Two orthogonal polarizations were recorded with the electric vector of the light along the crystal extinction directions, one of which is about 8° from the a axis. Both polarizations are accordingly perpendicular to C_2. The water molecules lie in such a way that the two polarizations contain various mixtures of absorptions parallel and perpendicular to the O–H or O–D bonds. The bands differ in intensity and also are slightly different in energy in the two polarizations, the latter being due to factor-group splitting. The observed absorptions listed in this paper are the average energies of the two polarizations.

Results and Discussion

The most complete study of the fundamental vibrations of BCD and its deuterio analogue has been made by Lutz et al.,[7] and it is their 95 K data that we use in the following discussion. Our assignments differ in some instances from theirs, as we have noted previously.[2]

Spectra of $BaCl_2 \cdot 2D_2O$. The near-IR spectra of $BaCl_2 \cdot 2D_2O$ are rich in detail, but less so than those of the non-deuterated crystal. The lower frequency of the absorptions in the deuterated compound places many of the combinations outside the range of the spectrophotometer. The assignments are also less certain for the deuterated crystal, since even the most highly deuterated sample contains some HOD. This adds some weak features, which complicate the assignments. Furthermore, we were unable to grow thick crystals of $BaCl_2 \cdot 2D_2O$, which are needed to observe all of the weak 3ν overtones.

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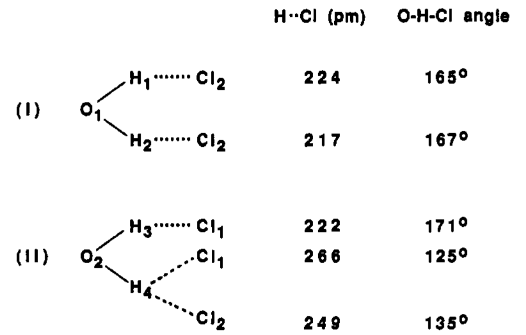

Figure 1. Structural parameters for the waters in $BaCl_2 \cdot 2H_2O$. Data are from ref 5.

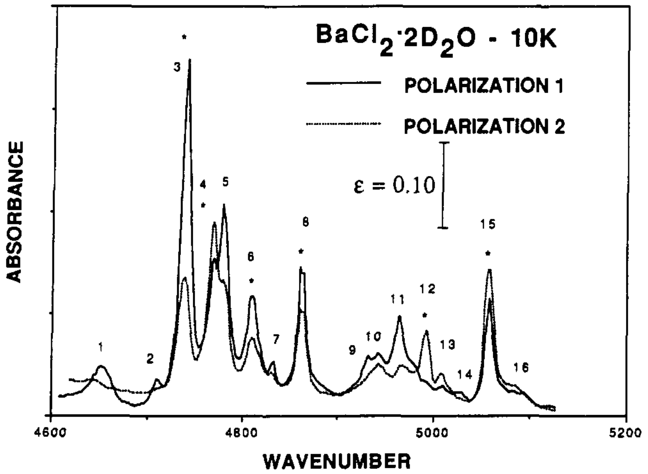

Figure 2. Polarized crystal spectra of $BaCl_2 \cdot 2D_2O$ at 10 K in the 4600–5200-cm^{-1} range. Crystals contained an H/D ratio of about 2/98. Bands marked with asterisks were used in the fitting procedure. Energy values are listed in Table I.

It is most unusual to observe IR fundamentals in a single-crystal transmission spectrum. However, in the unpolarized spectrum of a very thin (ca. 0.07 mm) crystal of $BaCl_2 \cdot 2D_2O$, we have observed in the 3300–3700-cm^{-1} region several features that are due to ν(OH) of residual HOD. If the dipole strength of an O–H oscillator lying totally in the *ac* plane is taken as 1.00, then the dipole strengths of O_1–H_2 and O_2–H_3 in the *ac* plane are calculated to be about 0.98. The data of Lutz et al.[7] place these bands at 3320 and 3305 cm^{-1}. We observe an unsymmetrical, fairly intense band at 3318 cm^{-1}. The dipole strengths of O_1–H_1 and O_2–H_4 in the *ac* plane are calculated to be about 0.21 and 0.12 and the bands are expected at 3356 and 3460 cm^{-1}. We observe weak bands at 3357 and 3460 cm^{-1}, which match this expectation. Another still weaker feature at about 3418 cm^{-1} remains unexplained. The same spectrum shows a very intense unsymmetrical band centered about 3650 cm^{-1}. This probably contains the four $\nu + \delta$ bands of D_2O, which are calculated from the sum of the fundamentals to lie between 3630 and 3771 cm^{-1}.[7]

The spectra in the 3700–4100-cm^{-1} region are much stronger in polarization 1 than in polarization 2. In this range they show more than a dozen features, all of which can most probably be associated with the HOD species present. For example, the ν(OH) + ρ_r (or ρ_t) features for HOD are calculated to lie in the 3655–3954-cm^{-1} range, the ν(OH) + ρ_w features for HOD are expected between 3919 and 4156 cm^{-1}, and the four ν(OD) + δ bands of HOD are calculated to lie between 3875 and 3965 cm^{-1}.[7] At present we cannot make more exact assignments in this region.

The spectra in the 4600–5200-cm^{-1} range are also strongly polarized. They show 16 bands where the six 2ν(OD) bands of D_2O are expected (see Figure 2 and Table I). Four ν(OD) + 2δ bands of D_2O could also appear in this region with enhanced intensity due to Fermi resonance with the 2ν bands. The presence of the small amount of H could also allow the intense ν(OH) + δ bands of HOD or the 2ν(OD) bands of HOD to appear in this same region. For these reasons the assignment of the 2ν(OD) bands is not straightforward. The manner of assigning these latter bands will be discussed below.

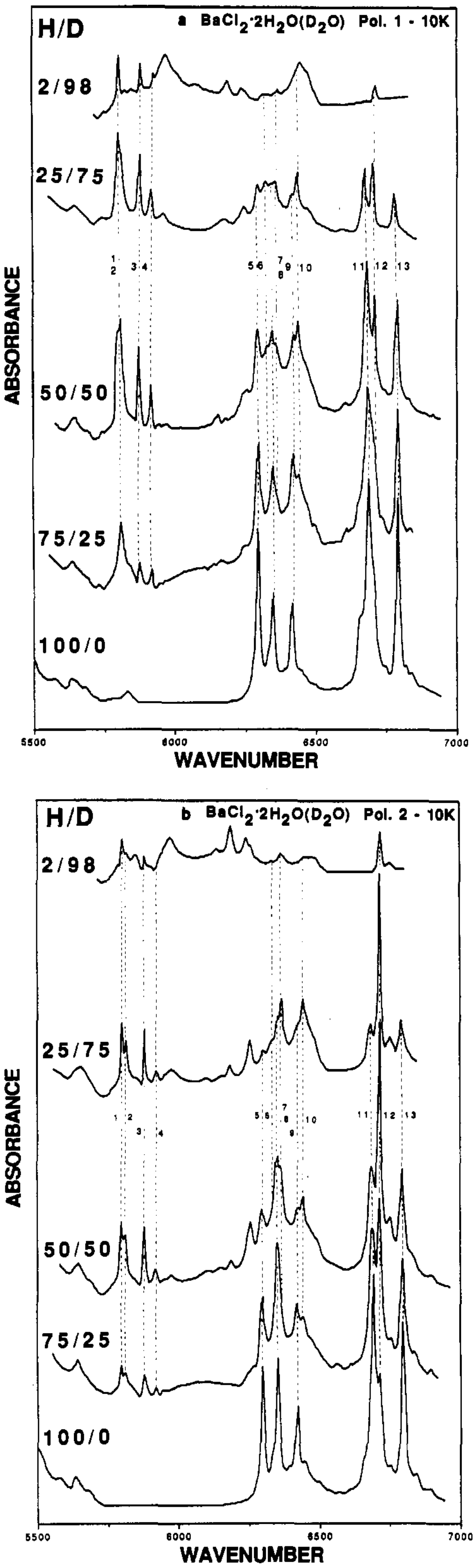

Figure 3. Polarized crystal spectra of $BaCl_2 \cdot 2X_2O$ (X = H, D) at 10 K in the 5500–7000 cm^{-1} range: (a) polarization 1; (b) polarization 2. The H/D ratio for each trace is indicated. The intensities of the bands in different traces in a given polarization are not directly comparable, since the values of ϵ are not known. Energy values are listed in Table I.

Some very weak absorptions are found in the 5500–7000-cm^{-1} range (see Figure 3 and Table I). Those between 5800 and 5925 cm^{-1} can be assigned to ν(OH) + ν(OD) of HOD, as was discussed in the previous report.[2] The remaining bands are due principally

Table I. Some Near-IR Bands of $BaCl_2 \cdot 2X_2O$ (X = H, D)

Figure 2		Figure 3	
band	energy, cm^{-1}	band	energy, cm^{-1}
1	4653	1	5801
2	4710	2	5814
3	4738.5	3	5880
4	4769	4	5922
5	4779	5	6295
6	4810.5	6	6328
7	4832	7	6349
8	4861	8	6364
9	4930	9	6418
10	4942	10	6442
11	4965	11	6688
12	4991	12	6712
13	5007	13	6793
14	5027		
15	5065.5		
16	5088		

to 2ν(OH) of HOD, and will also be discussed more in detail below. In this same region several new bands between 6000 and 6260 cm^{-1} appear on deuteration and some in the 6160–6260-cm^{-1} range remain in the 98% deuterated sample. From the sum of the fundamentals, they could be the ternary bands, ν(OH) + 2δ, in HOD molecules, which are calculated to lie between 6160 and 6380 cm^{-1}, or the 2ν(OD) + δ bands in D_2O molecules, calculated to lie in the 6100–6350-cm^{-1} range.

Finally, we observed at 7002 and 7499 cm^{-1} two very weak features that are the only bands we could observe of the eight bands in the 3ν manifold of D_2O.

In the remainder of this paper, we will focus our attention on the 2ν(OD) bands of D_2O, which are shown in Figure 2, and on the 2ν(OH) bands of residual HOD shown in Figure 3.

Local-Mode Theory. Local-mode theory is discussed in detail in several reports.[8-10] We have also developed the local-mode theory for water on general sites.[1,2] The essential theory is as follows: local-mode wave functions for the pair of anharmonic oscillators that make up the water molecule can be written as $|v_i v_j\rangle$, where v_i and v_j are the vibrational quantum numbers. The diagonal matrix elements of the local-mode Hamiltonian are written as functions of the harmonic oscillator frequency, ω, and the local-mode anharmonicity, X:

$$\langle v_i,v_j|H|v_i,v_j\rangle = \sum_{k=i,j} \omega_k(v_k + 1/2) + \sum_{k=i,j} X_k(v_k + 1/2)^2 \quad (1)$$

Coupling between the local modes takes place through the off-diagonal matrix element

$$\langle v_i + 1, v_j - 1|H|v_i,v_j\rangle = \lambda[(v_i + 1)v_j]^{1/2} \quad (2)$$

where λ is the coupling constant between the two oscillators. We consider coupling only between states of the same total vibrational excitation, V, where $V = v_i + v_j$. These considerations allow one to formulate the secular equations needed to calculate the stretch fundamentals and the first and second overtones for H_2O, D_2O, and HOD. The equations are presented in eq 5 and Table II of ref 2.

For an H_2O or a D_2O molecule on a general site in a crystal the stretch fundamentals will be unequal mixtures of states of type $|1,0\rangle$. In the first overtone region there are overtone states of type $|2,0\rangle$ as well as combination states of type $|1,1\rangle$. The latter are generally at higher energy than the former, since they are less dependent on X, which is large and negative. Since there is coupling between the overtone and combination states, the three eigenstates will in general also be mixtures.

For an HOD molecule the overtone states are little affected by the λ coupling because of the large separation between the diagonal elements. Since there are four different HOD molecules present, we expect four pure OH overtones, four pure OD overtones, and four combinations. Since the eigenfunctions maintain their purity to a large degree, the various eigenstates of HOD may for all practical purposes be equated with the diagonal energies.

Table II. Calculated and Observed Energies of $BaCl_2 \cdot 2D_2O$

	energy, cm^{-1}			assgnt[c]	
band	obs[a]	calc[b]	diff[b]	D_2O(I)	D_2O(II)
1	2434	2433.34	0.66	$\|10\rangle + \|01\rangle$	
2	2456	2450.27	5.73		$\|01\rangle + \|10\rangle$
3	2518	2520.28	−2.28	$\|01\rangle + \|10\rangle$	
4	2569	2561.99	7.01		$\|10\rangle + \|01\rangle$
5	4738.5	4737.94	0.56	$\|02\rangle + \|20\rangle$	
6	4769	4773.19	−4.19	$\|20\rangle + \|02\rangle$	
7	4810.5	4811.85	−1.35		$\|02\rangle + \|20\rangle + \|11\rangle$
8	4861	4865.32	−4.32		$\|20\rangle + \|02\rangle$
9	4991	4988.51	2.49	$\|11\rangle$ (86%)	
10	5056.5	5064.98	−8.48		$\|11\rangle$ (79%)
11		6854.81		$\|03\rangle$ (95%)	
12		6890.83		$\|30\rangle$ (95%)	
13	7002	7001.32	0.68		$\|30\rangle$ (92%)
14		7096.77			$\|03\rangle$ (88%)
15		7182.09		$\|12\rangle + \|21\rangle$	
16		7302.25			$\|21\rangle + \|12\rangle$
17		7349.01		$\|21\rangle + \|12\rangle$	
18	7499	7494.68	4.32		$\|12\rangle + \|21\rangle$

Parameters Used in Best Fit[b,d]

ω_1 = 2644.78 (61.19)	X_1 = −85.63 (15.30)
ω_2 = 2670.10 (62.24)	X_2 = −95.00 (15.63)
ω_3 = 2714.36 (22.45)	X_3 = −93.09 (5.81)
ω_4 = 2592.56 (19.60)	X_4 = −54.24 (4.92)
λ_{12} = −43.35 (1.64)	λ_{34} = −51.33 (1.80)

root-mean-square (rms) deviation = 4.31 cm^{-1}

[a] Observed bands below 3000 cm^{-1} from ref 7. [b] Results of computer calculations are listed to two decimal places; because of estimated standard deviations some decimals cannot be regarded as significant. [c] The numbers in the kets refer to oscillators 1 and 2 (water(I)) or 3 and 4 (water(II)) (see Figure 1). Coupled states are indicated only for coefficients of the eigenvectors equal to or greater than 0.40. [d] Standard deviations in parentheses; all data in cm^{-1}.

Assignment of the O–D Overtone Bands in D_2O. The choice of the six 2ν bands of D_2O was made as follows: the spectra of the 4600–5200-cm^{-1} region of the most highly deuterated sample show six major features, which in some cases are multiple. In polarization 1, for example, the strong bands at 4738.5, 4810.5, 4861, and 5056.5 cm^{-1} are clear choices for 2ν(OD). In the 4769, 4779 cm^{-1} doublet, the latter band increases greatly in intensity in a 94% D_2O sample and was accordingly assigned to HOD. The choice from within the complex multiplet, 4930, 4942, 4965, and 4991 cm^{-1}, was determined by which of the major bands gave the best fit with reasonable parameters in the expected range. The 4991-cm^{-1} band was chosen even though it is only a weak shoulder in polarization 1, but a strong feature in polarization 2. This multiplet most likely also contains ν + 2δ bands of D_2O, which from the sum of the fundamentals are calculated to lie between 4840 and 5010 cm^{-1}.

Calculation of Local-Mode Parameters. Table II shows the calculated and observed energies for the ν, 2ν, and 3ν bands for $BaCl_2 \cdot 2D_2O$ together with the assignments. As was the case for $BaCl_2 \cdot 2H_2O$,[2] no assumption was made as to which bands are associated with D_2O(I) or D_2O(II). The energies were calculated by solution of the appropriate secular equations using a reasonable set of starting parameters, namely, ω and X for each O–D bond and λ for each D_2O. The best fit was obtained by an iteration process that altered the 10 parameters systematically to minimize the sum of the squares of the differences between calculated and observed values. The process does not guarantee reaching the global minimum, but may arrive at one of a group of closely spaced local minima. The parameter sets of such minima are expected, however, to differ only slightly from one another. The standard deviations were calculated by the method outlined by Cowan.[11]

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Table III. Average Local-Mode Parameters for Coordinated and Gaseous H_2O and D_2O[a]

	$BaCl_2\cdot 2H_2O$[b]	$H_2O(g)$[c]	$BaCl_2\cdot 2D_2O$[d]	$D_2O(g)$[e]
ω	3658.5	3876.2	2655.4	2818.8
X	−146.0	−84.4	−82.0	−45.4
λ	−29.5	−49.5	−47.3	−58.3
K	−26.9	−28.5	−36.9	−39.2
P	−2.6	−21.0	−10.4	−19.1

[a] Data in cm^{-1}. [b] Data from ref 2. Average values listed. [c] Data from ref 8. [d] Average values from this work. [e] Data from ref 12.

Table IV. Local-Mode Parameters for $BaCl_2\cdot 2X_2O$ (X = H, D)[a]

	H_2O[b]	D_2O[c]	ratio (D_2O/H_2O)	av ratio
ω_1	3676.88	2644.78	0.719	0.726
ω_2	3667.27	2670.10	0.728	
ω_3	3647.36	2714.36	0.744	
ω_4	3642.62	2592.56	0.712	
X_1	−156.32	−85.63	0.548	0.562
X_2	−163.94	−95.00	0.580	
X_3	−167.35	−93.09	0.556	
X_4	−96.49	−54.24	0.562	
λ_{12}	−28.53	−43.35	1.520	1.602
λ_{34}	−30.46	−51.33	1.685	

[a] Data in cm^{-1}. [b] Data from ref 2. [c] Data from this work.

The calculations indicate that the O–D···Cl hydrogen-bonding interactions decrease in strength in the order 2 > 3 > 1 > 4. This is the same order as suggested by Brink[5] for $BaCl_2\cdot 2H_2O$. In our calculations on the latter species, O–H oscillators 2 and 3 were reversed.[2]

Comparison of Local-Mode Parameters for Coordinated and Gaseous Water. From the reported[12] fundamentals for gaseous D_2O, namely, $\nu_1 = 2671.46$ cm^{-1} and $\nu_3 = 2788.05$ cm^{-1}, one can calculate the local-mode parameters: $\omega = 2818.8$ cm^{-1}, $X = -45.4$ cm^{-1}, and $\lambda = -58.3$ cm^{-1}. These values are listed in Table III along with the values for gaseous H_2O and for water in $BaCl_2\cdot 2H_2O$ and $BaCl_2\cdot 2D_2O$.

The trends in the parameters for D_2O follow those found for H_2O. In going from gaseous H_2O (D_2O) to $BaCl_2\cdot 2H_2O$ (D_2O), ω is reduced by about 6%, X increases by 73–81%, and λ decreases by 20–40%. As was noted for $BaCl_2\cdot 2H_2O$, ω is expected to be lower in hydrogen-bonded environments.[13] X is most clearly related to hydrogen-bond strength. Sandorfy[14] has noted: "all appreciable evidence from gas and solution spectra shows that hydrogen-bond formation increases the anharmonicity of the X-H stretching motions. Furthermore, there is at least qualitative evidence that the stronger the hydrogen bond, the larger are the anharmonic constants." The decrease in λ in going from gas phase to crystal appears also to be due to hydrogen bonding, but the exact relationship is less clear. It will be discussed below.

Comparison of Local-Mode Parameters for H_2O and D_2O in Crystals. In Table IV, the parameters calculated for water in $BaCl_2\cdot 2D_2O$ are compared with those in $BaCl_2\cdot 2H_2O$.[2] Following Mills and Robiette (ref 9, eq 14), we may write

$$\omega = (g_{rr}f_{rr})^{1/2}/2\pi c \qquad (3)$$

where g_{rr} is the reciprocal effective mass ($= 1/m_O + 1/m_H$) for an O–H oscillator, and f_{rr} is the quadratic force constant. If we assume that f_{rr} is the same for H_2O and D_2O, the ratio ω_{OD}/ω_{OH} will be proportional to $[g_{rr}(OD)/g_{rr}(OH)]^{1/2}$, which is calculated to be 0.728. The corresponding ratios observed for gaseous water and for water in BCD are 0.727 and 0.726, in excellent agreement with this.

Likewise (ref 9, eq 5)

$$X = -a^2hg_{rr}/(8\pi^2c) \qquad (4)$$

where a, a parameter in the Morse equation, determines the harmonic force constant around equilibrium. On the assumption that a is the same for O–H and O–D oscillators, $X_D/X_H = g_{rr}(OD)/g_{rr}(OH)$, which is calculated to be 0.529. The corresponding ratio observed for water in BCD is 0.562. While this value is somewhat larger than expected, it is probably due to inadequacies in the model used to describe the eigenstates. Asselin and Sandorfy[15] in their study of self-associated 2-propanol and butanol also found elevated values of this ratio when they calculated vibrational parameters based on $v = 1$ and $v = 2$ data sets. When they included $v = 3$ data and used a more sophisticated Hamiltonian containing a term with $(v + {}^1/_2)^3$, the X_D/X_H ratio fell close to the expected value (0.529). As in the fully protiated crystals we find in $BaCl_2\cdot 2D_2O$ one X value that is considerably smaller than the others. This corresponds to the weak, bifurcated hydrogen bond formed by oscillator 4.

Mills and Robiette[9] following Child and Lawton[16] have also shown that the local-mode coupling constant (λ) can be written as a sum of kinetic (K) and potential (P) energy terms. Thus, $\lambda = K + P$, where

$$K = (\omega/2)(g_{12}/g_{11}) \qquad P = (\omega/2)(f_{12}/f_{11}) \qquad (5)$$

and 1 and 2 refer to oscillators 1 and 2. The f_{ij} and g_{ij} terms are the Wilson F and G matrix elements.[17] K can be shown to be

$$K = (\omega/2)(\cos\phi)m_H/(m_H + m_O) \qquad (6)$$

where ϕ is the HOH angle (104.5°). The K values calculated for $H_2O(g)$ and $D_2O(g)$ are −28.5 and −39.2 cm^{-1}. If the observed λ values are taken to be negative, as is usually assumed, the P values are −21.0 and −19.1 cm^{-1} for $H_2O(g)$ and $D_2O(g)$. The larger value of λ for $D_2O(g)$ is accordingly due mainly to the kinetic coupling. When the same calculations are made for $BaCl_2\cdot 2H_2O$ (D_2O) using the average ω values and assuming $\phi = 104.5°$, $K = -26.9$ (-36.9) cm^{-1} and $P = -2.6$ (-10.4) cm^{-1}. The smaller values of λ for the bound water compared with gaseous water are seen to be due in great part to the smaller values of the potential coupling term. This is linked to the constraints put on the movement of H (or D) in water which is hydrogen bonded to the nearby chlorine(s). The nature of the potential coupling is not well understood, but it could be angle dependent in the same way that the kinetic coupling is.

Overtone Spectra of OH Oscillators in HOD. In Figure 3 are shown the spectra in the region 5500–7000 cm^{-1} for $BaCl_2\cdot 2H_2O$ and crystals containing various H/D ratios. For $BaCl_2\cdot 2H_2O$ the bands in this region contain, in addition to $2\nu(OH)$, weaker bands that are probably due to $\nu(OH) + 2\delta(H_2O)$. With increasing deuteration, the $2\nu(OH)$ bands of H_2O should decrease in intensity, while other bands due to both $2\nu(OH)$ and $\nu(OH) + 2\delta$ of HOD will appear and then increase in intensity. The energies of these latter sets of bands are expected to differ somewhat from those of the former sets.

On progressive deuteration the $|20\rangle$ band of water(II) (6295 cm^{-1}) and the $|02\rangle$ and $|20\rangle$ bands of water(I) (6349 and 6418 cm^{-1}) become weaker, while bands 33, 15, and 24 cm^{-1}, respectively, to higher energy appear and increase in intensity. These new bands are the corresponding $|02\rangle$ or $|20\rangle$ O–H bands in the HOD molecules which replace H_2O. The $|02\rangle$ band of water(II) at 6712 cm^{-1} decreases on deuteration and seems in polarization 1 to shift a few reciprocal centimeters to higher energy in the highly deuterated sample. No clear new band forms. This band is assigned to the OH which forms the weakest hydrogen bond, and it is strongly mixed with the $|11\rangle$ band. The $|11\rangle$ band of water (I) (6688 cm^{-1}) disappears completely in the highly deuterated sample, while the $|11\rangle$ band of water(II) strongly mixed with $|02\rangle$ (6793 cm^{-1}) almost disappears in the highly deuterated

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Table V. Local-Mode Parameters for O–H Oscillators in $BaCl_2{\cdot}2X_2O$ (X = H, D)[a]

oscillator	H_2O[b] *X*	H_2O[b] *ω*	HOD *X*	HOD *ω*
1	−169	3656	−135	3626
2	−149	3659	−141	3587
3	−151	3629	−138	3596
4	−96	3650	−103	3667

[a] Data in cm^{-1}. [b] Calculated only from $v = 1$ and $v = 2$ data.

sample. This behavior is expected, since the probability of having two O–H in the same molecule will be extremely small in the 98% deuterated crystal.

It should be noted that the assignments of the bands at 6688 and 6712 cm^{-1} are the opposite of those reported previously.[2] The best fit based on a more extensive data set using the Newton–Raphson minimization gives a reverse assignment of these bands. This nicely illustrates the help that deuteration studies can give to the unambiguous assignment of bands in a complicated vibrational spectrum.

The shift of the bands to higher energy on deuteration indicates that replacement of one O–H oscillator in H_2O by O–D has a significant effect on the local-mode parameters of the remaining O–H oscillator. The extent to which these shifts on deuteration alter the local-mode parameters can be seen from the data in Table V, in which we list local-mode parameters calculated from the four OH stretches and four OH overtone bands of HOD. These are compared with the corresponding parameters calculated for $BaCl_2{\cdot}2H_2O$ by using only the 10 bands observed for the $v = 1$ and $v = 2$ data set. In going from H_2O to HOD, there is generally a decrease in ω and in the numerical magnitude of X. Oscillator 4, the bifurcated hydrogen bond, is the exception.

While the following is highly speculative, it may offer some partial explanation of these observations. Robertson's[18] extensive calculations on the system $(CH_3)_2O{\cdots}HCl$ (or DCl) predict that the O···Cl distance should be 1.8 pm longer in the DCl system. Likewise, in many hydrogen-bonded crystals the A–B distance in A–D···B is found to be slightly longer (ca. 1–4 pm) than that in A–H···B.[19] Although the distances in $BaCl_2{\cdot}2D_2O$ have not been reported, if we assume that there is an increase in the O···Cl distance on deuteration, then in a highly deuterated crystal the residual O–H oscillators would experience the longer O···Cl distance, and this would be reflected in a slight weakening of the O–H···Cl hydrogen bond and a smaller value of X. Other explanations, however, are also possible. For example, Fermi resonance between the $\nu + 2\delta$ and 2ν features of H_2O could cause the $|20\rangle$ and $|02\rangle$ bands of H_2O to be lower in energy than the corresponding bands in HOD. In the latter there would be little Fermi resonance, since the δ(HOD) vibrations are at 1410, 1427, and 1460 cm^{-1}, while the $\delta(H_2O)$ vibrations are at 1600 and 1641 cm^{-1}.[7]

Conclusions. The simplicity of the model used in this study does not permit very refined conclusions to be drawn from the data. The following statements, however, appear to be warranted. (1) The ratio ω_D/ω_H for water in BCD correlates almost exactly with that calculated from the masses of the atoms in the OD and OH bonds. Because of hydrogen bonding the values of ω_D and ω_H in BCD are both lower than in gaseous D_2O and H_2O. (2) In deuterated as well as nondeuterated BCD one X value is significantly smaller than the other three. This corresponds to the weakly hydrogen-bonded oscillator 4. (3) The λ values for coordinated D_2O (H_2O) are smaller than those for gaseous D_2O (H_2O). This is due mainly to smaller values of the potential coupling term, which is linked to constrained movement of the hydrogen-bonded H (or D) atom. (4) The value of λ for coordinated D_2O is larger than that for coordinated H_2O. This follows the trend in gas-phase water and is a consequence of the Wilson g_{ij} term. (5) The 2ν(OH) bands of HOD in deuterated crystals of BCD lie at higher energy than 2ν(OH) of H_2O. Accordingly, the local-mode parameters of HOD are perceptibly different from those of H_2O in this crystal.

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Comparative Study of Polyoxometalates and Semiconductor Metal Oxides as Catalysts. Photochemical Oxidative Degradation of Thioethers

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The photochemical degradation of thioether substrates catalyzed by representative semiconductor metal oxides and sulfides (anatase TiO_2, SnO_2, cubic WO_3, and CdS) and photoredox-active early-transition-metal polyoxometalates ($W_{10}O_{32}^{4-}$, $PMo_{12}O_{40}^{3-}$, $PW_{12}O_{40}^{3-}$, $SiMo_{12}O_{40}^{4-}$, $PV_2Mo_{10}O_{40}^{5-}$, $Cu^{II}W_{11}PO_{39}^{5-}$, and $P_2W_{18}O_{62}^{6-}$) have been examined under both anaerobic and aerobic conditions. Under anaerobic conditions, all the semiconductors are completely ineffective at photochemically oxidizing or degrading the exemplary thioether substrate tetrahydrothiophene (THT) in the oxidatively resistant solvent acetonitrile. In contrast, all the homogeneous polyoxometalate systems under the same reaction conditions, except the neutral tetra-*n*-butylammonium (Q) salt of $PW_{12}O_{40}^{3-}$, are quite effective. The latter systems generate products derived from the carbon-based radical α to the sulfur atom and not sulfoxide or sulfone, the usual products of thioether oxidation by oxometal species. The rate for the most active anaerobic system, that involving the photochemical degradation of THT by $Q_4W_{10}O_{32}$, under optically dilute conditions, is first order in $W_{10}O_{32}^{4-}$ and light intensity and variable order in THT substrate. A rate law consistent with these data is given. Upon addition of O_2, TiO_2 (with or without Pt(0)) becomes highly active, SnO_2 becomes active, but WO_3 and CdS remain inactive. Reactivity in thioether oxidation is dominated by the interactions of the semiconductors with O_2 and O_2-derived intermediates; there is no correlation between reactivity and semiconductor band gap. Upon addition of O_2, all the polyoxometalate systems become more active. Both the semiconductors and polyoxometalates under aerobic conditions oxidize thioethers further than the sulfoxides or sulfones to a range of products.

Introduction

Several of the structural, electronic, and photochemical features of many semiconductor metal oxides parallel those of some families of early-transition-metal polyoxometalates. Both classes of materials exhibit a rich photoinduced redox chemistry and can catalyze the photochemical modification of a range of organic

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