(iii) B_4H_{10} and B_5H_{11} in $S(CH_3)_2$. A 0.542-mmol sample of B_4H_{10} and a 0.534-mmol sample of B_5H_{11} were placed in a 10 mm o.d. Pyrex tube and were dissolved in 1.5 mL of $S(CH_3)_2$ at –80 °C. At this temperature the solution gave the signals of $B_3H_7{\cdot}S(CH_3)_2$, $B_4H_8{\cdot}S(CH_3)_2$, and $BH_3{\cdot}S(CH_3)_2$. As the tube was allowed to warm to +20 °C, the B_5H_9 and $BH_3{\cdot}S(CH_3)_2$ signals grew rapidly at the expense of the $B_3H_7{\cdot}S(CH_3)_2$ and $B_4H_8{\cdot}S(CH_3)_2$ signals. Seventeen hours later, the signals of $B_3H_7{\cdot}S(CH_3)_2$ were not detectable and weak signals of $B_4H_8{\cdot}S(CH_3)_2$ were seen. The solution remained clear and colorless all the time, and no hydrogen gas was found in the reaction tube. Eleven days later, the spectrum consisted of the signals of B_5H_9 (strong), $BH_3{\cdot}S(CH_3)_2$ (strong), $B_4H_8{\cdot}S(CH_3)_2$ (very weak), and others (faint and unidentified). The solution was clear and colorless.

5. B_4H_{10} in Diethyl Ether. A mixture of B_4H_{10} and diethyl ether in a 1:3.5 molar ratio was prepared at –80 °C in a 5 mm o.d. NMR sample tube, and its ^{11}B NMR spectra were recorded. Below –10 °C, the spectra contained only the signals of B_4H_{10}. At –10 °C, the B_2H_6 signal began to appear slowly. As the temperature was raised to 15 °C, weak signals of B_5H_9 became discernible. No signals of $B_3H_7{\cdot}O(C_2H_5)_2$ could be detected. The solution was clear and colorless.

6. Reaction of $B_3H_7{\cdot}S(CH_3)_2$ with $B_2H_4{\cdot}2N(CH_3)_3$. A sample of $B_3H_7{\cdot}S(CH_3)_2$ was prepared from 0.481 mmol of B_4H_{10} in a 10 mm o.d. Pyrex tube that was equipped with a Teflon valve. The sample was dissolved in ca. 2 mL of CH_2Cl_2 in the tube, and the solution was frozen at –197 °C. Then, a 0.291-mmol sample of $B_2H_4{\cdot}2N(CH_3)_3$ was introduced into the tube under an atmosphere of nitrogen gas. The tube was allowed to warm to 0 °C, the contents were mixed well, and the ^{11}B spectra of the resulting solution were recorded. At 0 °C, the signals of $B_4H_8{\cdot}N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ were seen in addition to those of the initial reactants. The change, however, was very slow. As the temperature was raised to +20 °C, $B_2H_4{\cdot}2N(CH_3)_3$ disappeared in 10 min, the signals of $B_3H_7{\cdot}S(CH_3)_2$ became weaker, and those of $B_4H_8{\cdot}N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ became stronger. Weak signals of $B_3H_7{\cdot}N(CH_3)_3$ and $B_3H_8^-$ were detectable. The solution was clear and colorless.

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Single-Crystal Polarized Spectra in the Near-Infrared Region: A Local-Mode Analysis of the Spectra of $BaCl_2{\cdot}2H_2O$

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The near-infrared (near-IR) spectra of single crystals of $BaCl_2{\cdot}2H_2O$ and its partially deuterated analogue have been recorded at 10 K in polarized light. Two crystallographically independent water molecules are present in these crystals. Each water gives rise to numerous, often well-resolved overtone and combination features. The bands in the first and second stretch overtone regions were analyzed by using local-mode theory. The local-mode anharmonicity, X, and harmonic frequency, ω, were evaluated for each of the oscillators on the two water molecules, as well as the two local-mode coupling constants, λ. The local-mode parameters so obtained are substantially altered from the values reported for gas-phase water. This is a consequence of hydrogen-bond formation in the crystal.

Introduction

In several recent articles we have shown that the near-infrared (near-IR) spectra of water in crystals are distinctive and that they are strongly influenced by the chemical environment in which the water is located.[1-3] In some of the cases that we have considered up to now the water molecules are highly oriented with respect to the crystal axes. The bands are strongly polarized in such circumstances, and from the polarization and energy of the bands we were able to clarify the nature of some librational modes that could not be assigned on the basis of the fundamental spectra.[2]

Crystals in which the water molecules are less well oriented with respect to the crystal axes are more common. In this article we examine the polarized near-IR spectra of $BaCl_2{\cdot}2H_2O$ at 10 K. This solid belongs to space group $P2_1/c$ (C_{2h}^5, $Z = 4$).[4] Sheets of $BaCl_2{\cdot}2H_2O$ units form a layered arrangement overlying each other along the crystal b axis. The positions of all atoms have been determined by neutron diffraction.[5] The two water molecules, which we shall henceforth call water(I) and water(II), are on C_1 sites and are not related by crystal symmetry. The angles and distances characterizing the hydrogen bonds in this substance have been codified by Brink[6] and are shown in Figure 1; we use his numbering system in this paper. Both O–H bonds of water(I) engage in normal hydrogen bonds to chloride ions. One O–H bond of water(II) forms a normal hydrogen bond, while the other engages in relatively weak, bifurcated hydrogen bonds to two neighboring chloride ions at different distances. There are thus four different O–H oscillators in $BaCl_2{\cdot}2H_2O$, and each has distinctive hydrogen-bond properties.

It has been amply shown over the last decade that local-mode theory is most convenient for describing the higher energy vibrational spectra of gas-phase water. In this article we extend the local-mode theory developed for C_{2v} symmetry[7-9] to cases such as $BaCl_2{\cdot}2H_2O$, in which the local oscillators are not related to one another by symmetry. We also show that the local-mode theory can give a good account of the fundamental spectra of water in low-symmetry sites.

Experimental Section

Reagent grade $BaCl_2{\cdot}2H_2O$ was slowly recrystallized from water to yield crystals suitable for optical spectroscopy. Partially deuterated crystals were prepared by slow evaporation of an H_2O/D_2O solution of $BaCl_2{\cdot}2H_2O$ over concentrated H_2SO_4 in a desiccator. The crystals form as large rectangular plates showing the [010] face.[10]

The crystals were mounted in a Displex cryogenic refrigerator, and near-IR spectra were recorded on a Varian 2300 spectrophotometer at 290 and 10 K. Light in both sample and reference beams was polarized by using a pair of Glan–Thompson prisms. The light beam was parallel to the crystal b axis (C_2) and was polarized with its electric vector along

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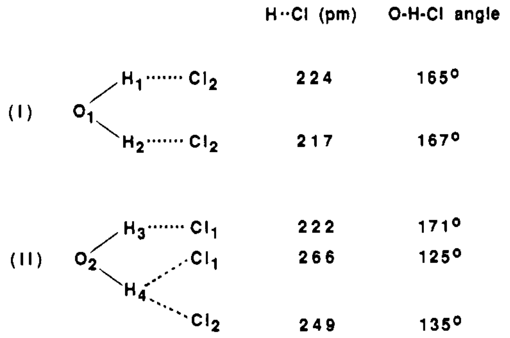

Figure 1. Structural parameters for the waters in $BaCl_2 \cdot 2H_2O$. Data are from ref 6.

the crystal extinction directions. One of these lies in the *ac* plane ([010] face) about 8° from the *a* axis. Accordingly, the two orthogonal polarizations are both perpendicular to C_2. Since the water molecules lie nearly in the *ac* plane, the two orthogonal spectra contain various mixtures of absorptions parallel and perpendicular to the O–H bonds. This is confirmed by the fact that most bands in the near-IR spectra appear in both polarizations at nearly the same energy but with varying intensities. We have used the average values as the observed absorptions listed in Table I. Because of the crystal habit, no spectrum with $E \| b$ could be recorded.

Results and Discussion

Fundamental Vibrations. The fundamental vibrational bands of $BaCl_2 \cdot 2H_2O$ and its deutero analogue have been studied by several authors.[11-13] The most extensive compilation is that of Lutz et al.[13] These latter data will be used in our subsequent discussion, since they appear to be of exceptionally high quality and include both the Raman and infrared (IR) spectra at 295 and 95 K. A detailed low-temperature study of partially deuterated $BaCl_2 \cdot 2H_2O$ was carried out by Brink,[6] who assigned the observed fundamentals to the oscillators shown in Figure 1. The band assignments of these two authors are in good agreement but differ somewhat from our assignment, as will be seen below. Since the crystal is centrosymmetric, IR and Raman spectra are not expected to be coincident, and indeed factor-group splittings can be seen for many bands.

Near-IR Spectra. The near-IR spectra of $BaCl_2 \cdot 2H_2O$ are very rich in detail. This is expected from the fact that there are eight waters per unit cell in this crystal and the waters are of two distinct types. For each of the two types of water there are six fundamentals, namely, two stretches (ν), one bend (δ), and three librations (ρ). If each water is considered in isolation there can be 21 binary and 56 ternary combinations and overtones. Of these, 11 binary and 40 ternary combinations lie in our range of observation (3690–10400 cm^{-1}). If one considers the possibility of coupling of two symmetry-related waters in the unit cell and combines the Raman and IR fundamentals to yield *ungerade* combinations, then each of the two distinct types of water can show 36 binary and 182 ternary combinations in the infrared spectrum. Of these, 20 binary and 133 ternary combinations are calculated to lie in our range of observation. The use of polarized crystal spectroscopy allows one to estimate the size of these factor-group splittings. In the present case measurement of spectra along the extinction axes gives spectra close to those expected for $E \| a$ and $E \| c$. The bands in each (both B_u in C_{2h}) will be slightly different in energy due to factor-group splitting.

In most cases we do not have enough information to make detailed assignments of the individual features. The sum of the fundamentals does, however, give a good estimate of the energy of the various band types. In addition, binary combinations are in general considerably more intense than ternary combinations. These facts allow us to determine the general nature of the various band clusters and to distinguish features, such as 2ν and $\nu + 2\delta$, which fall in a single cluster.

Figure 2 shows the polarized crystal spectra of $BaCl_2 \cdot 2H_2O$ at 10 K. The spectra are presented in parts, since they were measured on several crystals of varying thickness (up to 3.2 mm). The strongest observable features are about 25000 times as intense as the weakest. No other features were observed at energies higher than those reported here. On the spectra we indicate the nature of the various band clusters.

By far the most intense features are the combination bands involving one quantum of stretch (ν) plus one quantum of libration (ρ) or bend (δ) (Figure 2a). The bands near 4000 cm^{-1} are associated with $\nu + \rho$ combinations. For each of the two types of water six such combinations are possible, even in the absence of factor-group splitting. Because of this large number and because

Table I. Calculated and Observed Energies of $BaCl_2 \cdot 2H_2O$

	energy, cm^{-1}			assgnt[d]	
band[a]	obs[b]	calc[c]	diff[c]	H_2O(I)	H_2O(II)
1	1600	1592.47	7.53		δ
2	1641	1636.20	4.80	δ	
3*	3305	3306.20	−1.20		$\|10\rangle$
4	3305[e]	3312.67	−7.67		$\|10\rangle$(uncpled)
5	3320[e]	3339.40	−19.40	$\|01\rangle$(uncpled)	
6*	3324	3320.70	3.30	$\|01\rangle(+\|10\rangle)$	
7	3356[e]	3364.25	−8.25	$\|10\rangle$(uncpled)	
8*	3374	3382.94	−8.94	$\|10\rangle(+\|01\rangle)$	
9*	3459	3456.12	2.88		$\|01\rangle$
10	3460[e]	3449.65	10.35		$\|01\rangle$(uncpled)
11	4902.2	4897.47	4.73		$\|10\rangle+\delta$
12	4946.8	4960.20	−13.40	$\|01\rangle(+\|10\rangle)+\delta$	
13	5036.2	5010.20	26.00	$\|10\rangle(+\|01\rangle)+\delta$	
14	5078.6	5051.47	27.13		$\|01\rangle+\delta$
15	5800.7[f]	5804[g]	−3.30	$\|1_D 1_H\rangle$	
16	5814.2[f]	5814[g]	0.20	$\|1_H 1_D\rangle$	
17	5879.7[f]	5860[g]	19.70		$\|1_D 1_H\rangle$
18	5922.5[f]	5908[g]	14.50		$\|1_H 1_D\rangle$
19*	6294.7	6286.70	8.00		$\|20\rangle$
20*	6348.6	6346.03	2.57	$\|02\rangle$	
21*	6418.4	6410.78	7.62	$\|20\rangle$	
22*	6688.3	6683.99	4.31		$\|02\rangle(+\|11\rangle)$
23*	6712.2	6713.59	−1.39	$\|11\rangle$	
24*	6792.6	6788.60	4.00		$\|11\rangle(+\|02\rangle)$
25	7855.4	7887.17	−31.77		$\|20\rangle+\delta$
26	7974.6	7984.80	−10.20	$\|02\rangle+\delta$	
27	8066.4	8054.60	11.80	$\|20\rangle+\delta$	
28	8286.2	8280.77	5.43		$\|02\rangle(+\|11\rangle)+\delta$
29	8329.4	8348.40	−19.00	$\|11\rangle+\delta$	
30	8372.0	8385.07	−13.07		$\|11\rangle(+\|02\rangle)+\delta$
31*	8929.8	8930.45	−0.65		$\|30\rangle$
32*	9030.7	9030.93	−0.23	$\|03\rangle$	
33*	9148.0	9150.78	−2.78	$\|30\rangle$	
34*	9674.3	9678.81	−4.51	$\|12\rangle(+\|21\rangle)$	
35*	9720.4	9727.40	−7.00		$\|21\rangle$
36*	9765.0	9763.72	1.28		$\|03\rangle$
37*	9802.8	9799.26	3.54	$\|21\rangle(+\|12\rangle)$	
38*	10036.6	10041.66	−5.06		$\|12\rangle$

Parameters Used in Best Fit[c,h]

$\omega_1 = 3676.88\ (11.47)$	$X_1 = -156.32\ (3.17)$
$\omega_2 = 3667.27\ (11.22)$	$X_2 = -163.94\ (3.10)$
$\omega_3 = 3647.36\ (9.75)$	$X_3 = -167.35\ (2.75)$
$\omega_4 = 3642.62\ (9.84)$	$X_4 = -96.49\ (2.85)$
$\lambda_{12} = 28.53\ (2.34)$	$\lambda_{34} = 30.46\ (2.90)$
$\delta_1 = 1641$	$\delta_2 = 1600$

Root-Mean-Square (Rms) Deviation 11.60 cm^{-1}

[a] Eighteen bands marked with asterisks have rms deviation 4.61 cm^{-1}. [b] Observed bands below 4000 cm^{-1} from ref 13. [c] Results of computer calculations are listed to two decimals; because of estimated standard deviations some decimals cannot be regarded as significant. [d] The numbers in the kets refer to oscillators 1 and 2 (water(I)) or 3 and 4 (water(II)) (see Figure 1). [e] From HOD spectra.[13] [f] Observed in partially deuterated spectra. [g] Sums of data from ref 13. OD stretches are as follows (data in cm^{-1}). Water(I): 2458, $|10\rangle$, 2484, $|01\rangle$. Water(II): 2448, $|10\rangle$, 2555, $|01\rangle$. [h] Standard deviations in parentheses; all data in cm^{-1}.

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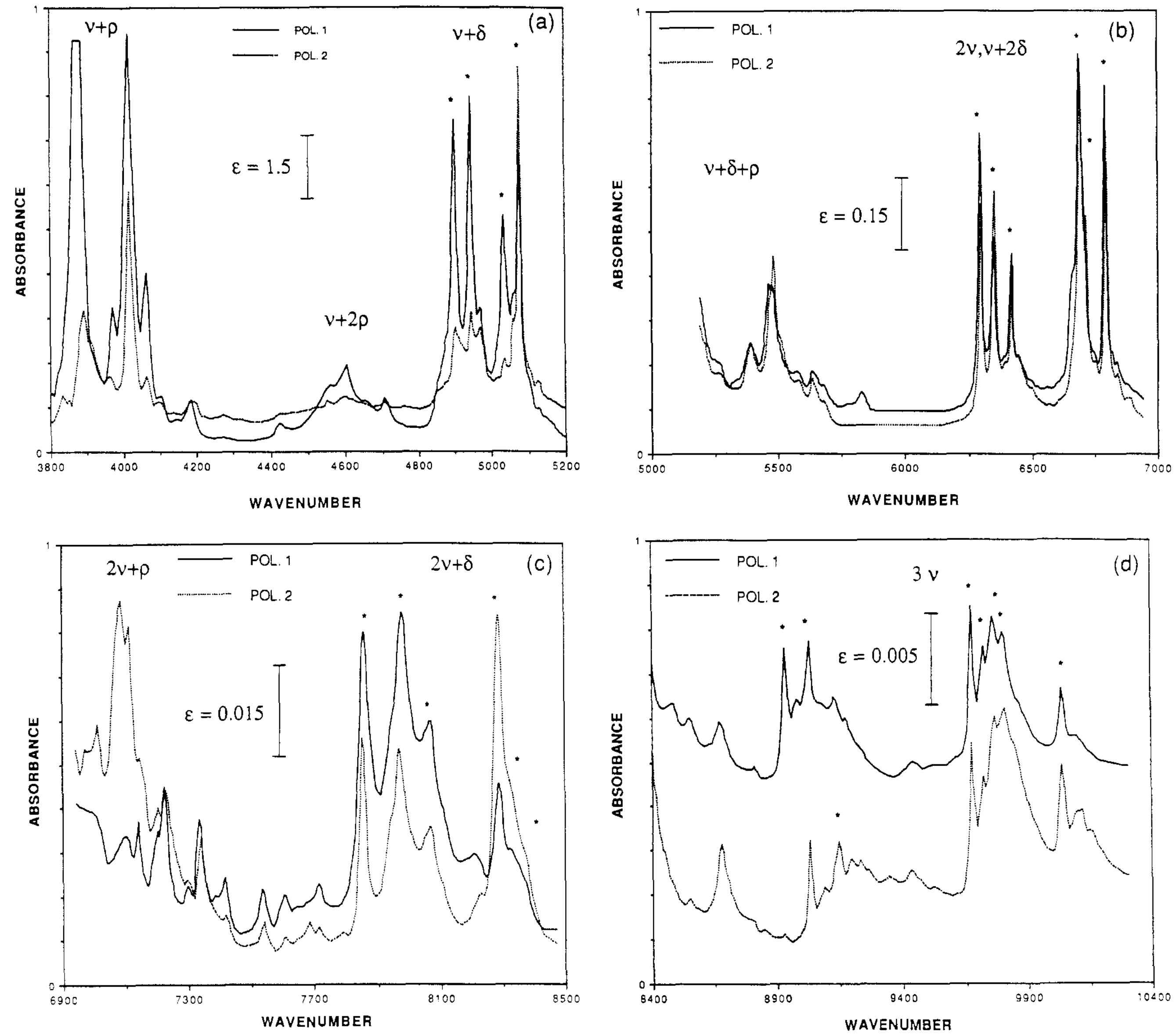

Figure 2. Polarized crystal spectra of $BaCl_2{\cdot}2H_2O$ at 10 K. Note different values of ϵ for the various spectra. Bands marked with asterisks were used in the fitting procedure.

of the uncertainty in the assignment of the fundamental librations, we have not been able to make any firm assignments in this region. Similar comments apply to the $2\nu + \rho$ region around 7100 cm^{-1}.

Four bands of moderate intensity near 5000 cm^{-1} are associated with $\nu + \delta$ combinations. In isolated water (C_{2v} symmetry) two features are expected in this region. In our experience only the $\nu_a + \delta$ combination can be observed. When the symmetry is lowered, the distinction between symmetric and antisymmetric stretch is blurred and both combinations might be expected to be observable. This was the case in low-symmetry water in $K_2SnCl_4{\cdot}H_2O$.[2] Therefore, the occurrence of four strong peaks is not surprising, since here there are two different water molecules of low symmetry.

Of the numerous near-IR bands the O–H stretch overtone regions (Figure 2b,d) contain the information that is chemically most interesting. The 2ν bands appear as a series of rather weak absorptions between 6200 and 6800 cm^{-1}. Interspersed between these binary features are very weak features, which on energy grounds are assigned to $\nu + 2\delta$ absorptions.

The 3ν bands are extremely weak and, under the conditions of our experiments, lie near the limit of detection. It may be of interest to note that the relative intensities of the strongest bands in the $\nu + \delta$, 2ν, $2\nu + \delta$, and 3ν band groups are approximately 1000:80:6:1.

The use of local-mode theory will allow us to assign in detail the bands associated with these overtones and combinations.

Local-Mode Theory. The theory for the stretching vibrations in isolated water has been considered in detail by Child and Halonen[7] and Mills and Robiette.[8] A general overview of local-mode parameters in water and other simple molecules has recently appeared.[9]

The wave function for a pair of anharmonic oscillators that make up a water molecule may be written as $|v_i,v_j\rangle$, where v_i and v_j are the vibrational quantum numbers of the two oscillators. The vibrational Hamiltonian consists of two types of terms, those that characterize the oscillators in isolation from one another (local-mode terms) and those that couple the oscillators together. The local-mode terms are predominant for the O–H stretch. The diagonal elements of the Hamiltonian for isolated (C_{2v}) water may be written

$$\langle v_i,v_j|H|v_i,v_j\rangle = \omega \sum_{k=i,j} (v_k + \tfrac{1}{2}) + X \sum_{k=i,j} (v_k + \tfrac{1}{2})^2 \qquad (1)$$

where ω is the harmonic frequency and X is the local-mode anharmonicity constant. Since the two oscillators in isolated water are related by symmetry, there is one common value of ω and X. When water is on a C_1 site, each oscillator can experience a different chemical environment. The diagonal matrix elements in this case must be written

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

so that in general each water has two harmonic frequencies and

Table II. Secular Equations for the Stretch Overtones

First overtones

$$\begin{vmatrix} 2\omega_i + 6X_i - E & 2^{1/2}\lambda & 0 \\ 2^{1/2}\lambda & \omega_i + \omega_j + 2X_i + 2X_j - E & 2^{1/2}\lambda \\ 0 & 2^{1/2}\lambda & 2\omega_j + 6X_j - E \end{vmatrix} = 0$$

Second overtones

$$\begin{vmatrix} 3\omega_i + 12X_i - E & 3^{1/2}\lambda & 0 & 0 \\ 3^{1/2}\lambda & 2\omega_i + \omega_j + 6X_i + 2X_j - E & 2\lambda & 0 \\ 0 & 2\lambda & \omega_i + 2\omega_j + 2X_i + 6X_j - E & 3^{1/2}\lambda \\ 0 & 0 & 3^{1/2}\lambda & 3\omega_j + 12X_j - E \end{vmatrix} = 0$$

two local-mode anharmonicity constants. The coupling constant, λ, between the local modes arises from the off-diagonal elements:

$$\langle v_{i+1},v_{j-1}|H|v_i,v_j\rangle = \lambda[(v_i + 1)v_j]^{1/2} \qquad (3)$$

We consider only coupling between states of the same total vibrational excitation, V, where $V = v_i + v_j$. The reader is referred to the literature[7-9] for a fuller description of the theory.

Fundamental Bands. In isolated water of high symmetry the transition energies for the symmetric stretch (E_s) and antisymmetric stretch (E_a) are given by

$$E_s = \omega + 2X + \lambda \qquad E_a = \omega + 2X - \lambda \qquad (4)$$

The separation between the two observed IR features is just 2λ, and provided resolution is good, this parameter may be measured for many hydrogen-bonded crystals. For water on general sites the two eigenstates of the system must be found from the secular equation:

$$\begin{vmatrix} \omega_i + 2X_i - E & \lambda \\ \lambda & \omega_j + 2X_j - E \end{vmatrix} = 0 \qquad (5)$$

This means that the splitting of the fundamentals is dependent on λ as well as on the difference between the local-mode parameters ω and X for the two oscillators. As the diagonal terms become increasingly different, the λ-coupling has a smaller effect on the transition energies. So, as a general rule, the splitting of the fundamental bands cannot be meaningfully interpreted without an exact knowledge of the local symmetry of water in condensed phases.

The eigenstates of an HOD molecule in low symmetry follow naturally from eq 5. Since the difference between the diagonal energies is very large in HOD (ca. 1000 cm^{-1}), the off-diagonal terms in λ contribute very little to the final eignestates (ca. 1 cm^{-1}). It follows that we may to a good approximation write for the stretch frequencies

$$\nu_{OH} = \omega_{OH} + 2X_{OH} \qquad \nu_{OD} = \omega_{OD} + 2X_{OD} \qquad (6)$$

When HOD is on a C_{2v} site, only one feature is predicted to occur in the O–H stretch region. This is nicely confirmed in $CuCl_2 \cdot 2H_2O$ and $K_2CuCl_4 \cdot 2H_2O$, where the water is on high-symmetry sites.[3] Water in $BaBr_2 \cdot 2H_2O$ lies on general sites, although the crystal structure is not the same as that for the chloride.[14] There is, however, only one measurable O–H frequency in partially deuterated crystals of the bromide.[15] We may conclude that it is possible in some cases for two oscillators on general sites to have very similar local mode ω and X values.

Stretch Overtone Regions. The stretch overtones of water on a general site may be found by solving the secular equations shown in Table II. There are three first overtones and four second overtones for each water. In the limit of small values of λ, we may identify the three states for the first group as $|11\rangle$, the local mode combination, and the two overtones, $|20\rangle$ and $|02\rangle$. These latter will, as we have seen, have different diagonal energies. The $|11\rangle$ will occur at higher energy than either of the overtone states, since it is less dependent on X, which is large and negative. It is expected to occur at energies close to the sum of the two possible O–H fundamentals in HOD, but pushed to higher energy due to interaction with the overtone states. When X_i and X_j are large and about the same size, the overtone states will occur close together, and if the λ term were absent, they would be degenerate in high-symmetry water. Since there are two low-symmetry waters, six binary features are expected in the first overtone region. Similar reasoning indicates that eight features are expected in the second overtone region. The stretch overtones for HDO follow directly from the secular equation in Table II. Since ν_{OH} and ν_{OD} differ so widely in energy, the coupling constant λ has little effect on the calculated energies.

Choice of Observed Bands. The four fundamentals were taken as the IR bands observed at 95 K (bands 3, 6, 8, and 9 in Table I).[13] The uncoupled ν_{OH} (bands 4, 5, 7, and 10 in Table I) were taken from the spectra of partially deuterated crystals.[13] In these crystals four different HOD molecules are possible, and the four distinct bands in the O–H stretch region[13] correspond to O–H oscillators on each of the four possible crystal sites. There are four corresponding bands in the O–D stretching region as well, and these have an analogous interpretation. They are listed in the footnotes of Table I and were used to calculate the energies of the $|1_H 1_D\rangle$ and $|1_D 1_H\rangle$ states for the two waters.

Five of the six expected 2ν bands are clearly seen in our spectra. The sixth band could be either the strong shoulder at 6660 cm^{-1} (see especially polarization 1) or the resolved shoulder at 6712 cm^{-1} (see especially polarization 2). The former vanishes in the partially deuterated samples, while the latter remains strong. So the latter was taken as the sixth observed band. It is quite likely that one of the weak $\nu + 2\delta$ bands in this region undergoes Fermi resonance with a 2ν band, leading to enhancement of the ternary combination. This is a probable reason for the appearance of seven reasonably intense absorptions in this region instead of the expected six.

The four expected $\nu + \delta$ bands were assigned to the very prominent features in the 4800–5200-cm^{-1} region. The choice of the six $2\nu + \delta$ bands is less sure, and those bands were chosen that gave the best fit. The choice of the eight 3ν bands also involves some uncertainty. The best fit was observed when the eight strongest features between 8900 and 10040 cm^{-1} were used. Other selections gave poorer fits, and in particular the choice of the strong feature at 8674 cm^{-1} as one of the eight bands gave a much poorer fit.

Fitting the Spectra. In using the local-mode model to fit the spectra, we set up the matrices for the pertinent states and, with a reasonable estimate of parameter values, determined the eigenvalues for the states. The sum of the squares of differences between calculated and observed values was obtained. An iteration process based on the Newton–Raphson method altered the parameters systematically to minimize this sum. When successive iterations produced no further improvement, the process was stopped. The resulting eigenvalues represent a "best fit". Because of the large number of parameters, the process could stop at various minima. Repeated application of the process with various starting parameters yielded a small set of minima. We report the fit that gave the smallest rms deviation but note that some slightly better fit is not excluded. It seems that the rms deviation surface is rather flat in the region of the global minimum, and so the program can often reach a local minimum in this region. It should be noted that in this fitting procedure no prior assumptions were made as to which observables correspond to water(I) or (II). Indeed, we tried many fits with various assumptions as to band identity and in each case the rms was considerably larger than the best fit.

The local-mode parameters needed for the present case are a stretching frequency (ω) and anharmonicity (X) for each O–H bond and one coupling constant (λ) for each water. The resulting

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ten parameters permit an exact fit of the calculated energies to those observed for the four stretch fundamentals and six 2ν bands. These parameters provide a first estimate for the fit which now includes the eight 3ν absorptions. The resulting best fit for these 18 bands (marked with asterisks) is shown in Table I; the rms deviation was 4.61 cm^{-1}.

Using the parameters and assignments for this fit, we calculated the best fit for the two δ, four $\nu + \delta$, and six $2\nu + \delta$ bands by varying the value of δ for each water separately. The values for the four uncoupled ν_{OH} frequencies were also calculated with the same ω and X parameters and were compared with the observed values reported by Lutz et al.[13] Finally, the values of the four OH–OD stretch combinations were calculated from the data of Lutz et al.[13] and were compared with the bands we observed in the 5800-cm^{-1} region in partially deuterated samples. The final fit for the 38 bands is given in Table I; the rms deviation has a value of 11.60 cm^{-1}. The identity of the bands, such as $|01\rangle$ or $|11\rangle$, was determined from the eigenvectors of the matrix after minimization was achieved. Coupled states are indicated only for coefficients of the eigenvectors equal to or greater than 0.40.

The local-mode parameters that give the best fit as well as their estimated standard deviations are also listed in Table I. The standard deviations were calculated by the method outlined by Cowan.[16]

Although the parameters ω_1, X_1 and ω_2, X_2 refer to water(I), they cannot with certainty be assigned directly to O_1–H_1 and O_1–H_2 in Figure 1. Since these two parameter sets are so similar, the assignments could readily be reversed. For water(II) the assignments of ω_3, X_3 and ω_4, X_4 to O_2–H_3 and O_2–H_4 is considerably firmer due to the great difference in the type of hydrogen bonds that are formed (see Figure 1). It should also be noted that the sign of λ cannot be determined from these calculations in low-symmetry cases.

In all the minimizations the identity of the fundamentals differed somewhat from the assignments of Brink[6] and Lutz et al.[13] Specifically, we found the lowest and highest of the four fundamentals on the same water. This we interpret to be water(II) (see Figure 1), since it seems quite certain that the bifurcated hydrogen bond will be the weakest of all and will accordingly have the highest frequency. The other three O–H···Cl bonds are quite similar in length and bond angle. Even though O_2–H_3···Cl is not the shortest of the three, it forms the most nearly linear hydrogen bond, and it seems that this feature might make it the strongest of the hydrogen bonds. If one assumes the assignment of Brink[6] for the four fundamentals and makes the best assignments for the 2ν and 3ν bands, the rms deviation for the 18 bands is 5.07 cm^{-1}. This is somewhat larger than the fit we report, and while it does not invalidate his assignments, it lends some support to our method.

The values of ω are very similar for the four O–H bonds. They are 5–6% lower than the value for isolated water (3876.2 cm^{-1}).[7] It is expected that this parameter will be somewhat smaller in hydrogen-bonded environments.[17] The anharmonicity values show more correlation with hydrogen-bond strength. One value (−96.5 cm^{-1}) is quite different from the other three. This must be the bifurcated hydrogen bond. It is the weakest, shows the smallest anharmonicity, and lies nearest the value reported for isolated water (−84.4 cm^{-1}).[7] The λ values for the two waters are quite similar and are considerably reduced (about 40%) from the value found for gas-phase water (−49.5 cm^{-1}).[7] This decrease is probably a consequence of hydrogen bonding, but further speculation is not warranted at present.

In the fitting of bands containing one or more bends, the best fit is had if the assignment of Lutz et al.[13] is reversed; water(I) has the higher bending frequency. The HOH bending frequency has been observed to increase with the strength of the hydrogen bonds formed.[18] From the calculated anharmonicities it appears that the hydrogen bonds formed by water(I) are on the average stronger than those formed by water(II). The higher value of δ for water(I) is in agreement with this. Since we have assumed no $\nu + \delta$ coupling, we could not separately minimize the values of bend frequency and bend anharmonicity.

Conclusions. We have applied local-mode theory to the vibrational spectra of $BaCl_2 \cdot 2H_2O$, and our calculations confirm in essence the local-mode nature of the vibrational states in this low-symmetry system. A local-mode description of water vibrations will in general be the preferred one in most crystals at all vibrational levels. As research in this field progresses, we hope to acquire a body of local-mode parameters that can be correlated with bond distances and the hydrogen-bond strengths of water in various environments.

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Registry No. $BaCl_2 \cdot 2H_2O$, 10326-27-9; D_2, 7782-39-0.

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