Infrared Study of Weakly Bound Hydrogen Bonds in Crystalline Sodium Sulfanilate Dihydrate

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We have studied the infrared spectra of the O−H(D) hydrogen bonds from the water and N−H(D) bonds from the NH_2 group in the title compound as functions of deuterium concentration and temperature. Some of the vibrational stretching bands are re-assigned. The crystal contains two distinct water molecules. The two O−D bands from one HOD molecule merge together as the temperature is raised, suggesting homogenization of the environments of two O−D's due to increasing librational motion. The two O−D bands from the other HOD molecule behave as expected and do not merge over the temperature range. The two N−D bands of the HND group show the overlap or resonances between the N−D bands and combination bands. The shifts with temperature of the various stretching bands of the hydrogen-bonded atoms are in agreement with the changes expected from the changes in structure determined by previous X-ray analyses.

I. Introduction

Sodium sulfanilate dihydrate, $NH_2C_6H_4SO_3Na{\cdot}2H_2O$ (SSDH), forms a crystalline hydrate with a number of interesting features suitable for elucidating conformational dynamics. Infrared studies using deuterium substitution, the change of the spectrum with temperature, and infrared hole burning have revealed the dynamics of the amino group of amino acid salts[1] and of the water of hydration in a number of different compounds[2,3] in the crystal. Similarly, irradiation of N−H-containing compounds using a combination of ultraviolet and infrared radiation has produced observable conformational changes in molecules embedded in gas-phase clusters.[4,5]

SSDH has an uncharged NH_2, unlike the amino acid salts we have studied previously. The detailed dynamics of the NH_2 group and the effect of the dynamics on the infrared spectrum are unknown. In this paper, we present the infrared spectrum of the hydrogen-stretching region of crystalline SSDH as a function of deuterium concentration and temperature. Previous studies have included that of W. H. Evans,[6] who published an assignment that we revise. Also relevant are a number of studies of various anilines.[7−9]

SSDH crystallizes in bipyramidal plates with an orthorhombic space group P*bca* (D^{15}_{2h}, #61) and eight molecules per unit cell.[10,11] The cell parameters are $a = 23.895$, $b = 10.101$, and $c = 7.944$ Å at room temperature (RT). The X-ray studies show no evidence of a phase transition between RT and 78 K. The benzene ring is close to planar, with the sulfur and the nitrogen atoms displaced out of this plane. The amine group is significantly distorted from a simple sp^2 bonding geometry, and this distortion implies that the NH_2 bonding is intermediate between sp^2 and sp^3. There are six hydrogen bonds in crystalline SSDH: two of the form $N-H\cdots O_s$, three $O_w-H\cdots O_s$, and one $O_w-H\cdots N$, where O_s is an oxygen atom of the SO_3 group and O_w is an oxygen of water. The distances between the heavy atoms of the hydrogen bonds are 2.8−3.1 Å. These are longer than those in most hydrates and, consequently, the corresponding vibrational frequencies are higher.

We introduce a small amount of deuterium into the aqueous solution to form some HOD and HND in the resulting SSDH crystals. Since SSDH has eight molecules per unit cell, there are 8 nitrogen atoms and 16 oxygen atoms. The site symmetry of both the amine group and the water is C_1.[12] The 16 amine hydrogen atoms must then belong to two nonequivalent sets $8H_5 + 8H_6$,[13] and the 32 water hydrogen atoms belong to four nonequivalent sets $8H_7 + 8H_8 + 8H_9 + 8H_{10}$.[13] Replacing the NH_2 group and H_2O molecules in SSDH by HND and HOD results in two sets of nonequivalent HND and of HOD moieties, respectively. Since much of the broadening of the vibrational absorption bands of the water and amine group in SSDH is due to intermolecular vibrational coupling, the H (or D) bands are narrower than the D (or H) bands with dilute H (or D) in the sample.

At low temperature, the unit cell contracts, and amplitude of the librational motion diminishes. In addition, all hydrogen bonds become shorter, so the O−H(D) and N−H(D) stretching bands are expected to shift to lower frequencies.

II. Experimental Section

Samples of SSDH were recrystallized from water containing different amounts of deuterium. When deuterium is introduced into the crystal, some of the deuterium goes into the amine group to produce HND, while some goes into the water to produce HOD. H/D ratios of the samples were determined from the ratios of the corresponding O−H/N−H and O−D/N−D band areas in the infrared spectra, assuming that the integrated absorptivity of the O−H/N−H band is twice that of the corresponding O−D/N−D band. Since the N−H bands overlap the O−H bands, we compare the sum of the O−H and N−H band areas to the sum of the corresponding O−D and N−D band areas.

After the crystals precipitated, they were washed with ethanol and dried under an N_2 atmosphere. The crystals obtained were mulled with mineral oil or Fluorolube, and then the mull was put either between two CaF_2 or two KBr plates. Using

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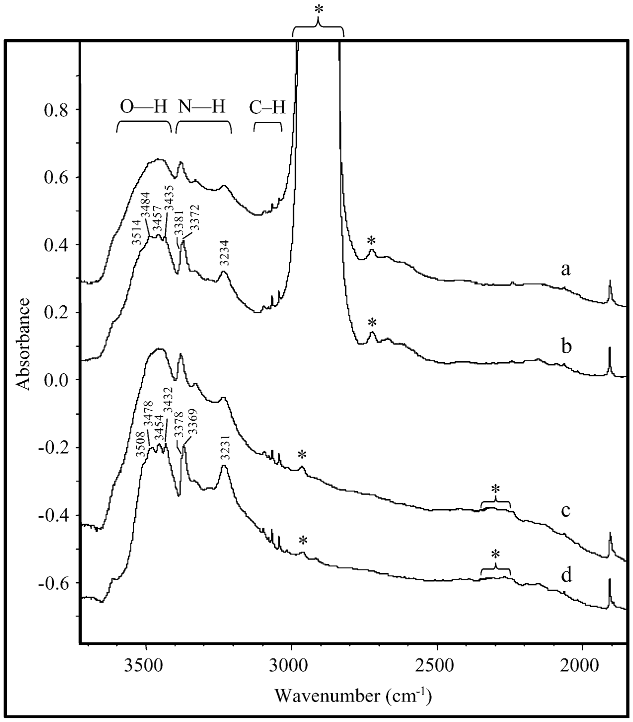

Figure 1. Infrared absorption spectra of sodium sulfanilate dihydrate in mineral oil at (a) RT and (b) 78 K; infrared spectra in Fluorolube at (c) RT and (d) 78 K. Bands marked with an asterisk (*) are from the mulling agents. The C—H bands due to the mineral oil go off scale. See also Figures 3A-a, 3B-a and 4A-a, 4B-a.

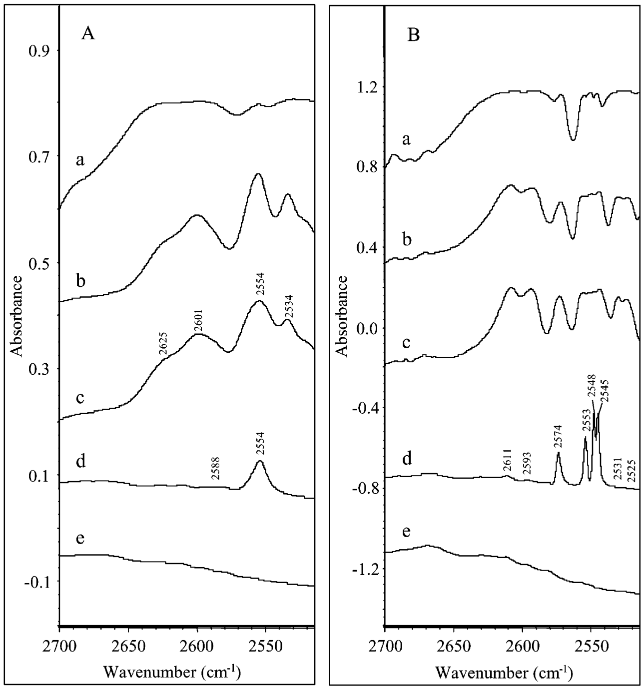

Figure 2. The O—D stretching band region of the infrared absorption spectra of sodium sulfanilate dihydrate (A) at RT and (B) at 10 K, except spectrum B-e at 78 K, as a function of deuterium concentration: (a) 89%; (b) 60%; (c) 44%; (d) 2%; (e) 0%.

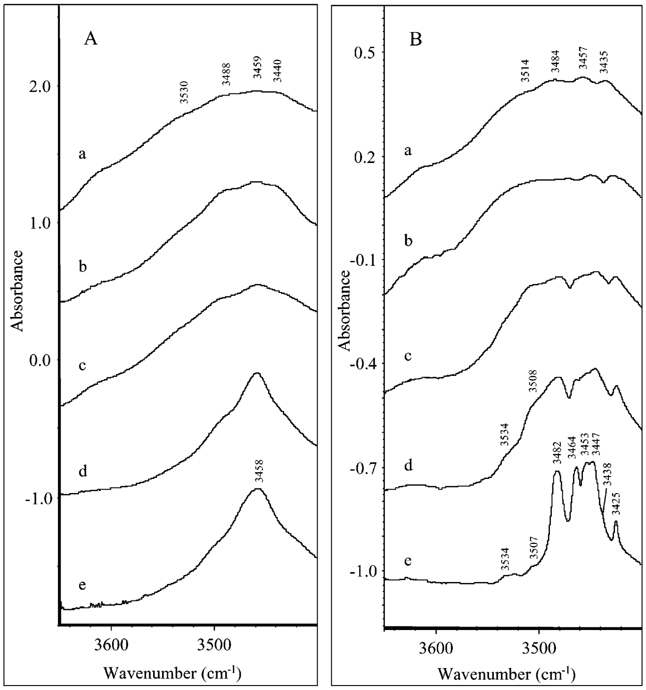

Figure 3. The O—H stretching band region of the infrared absorption spectra of sodium sulfanilate dihydrate (A) at RT and (B) at 10 K, except spectrum B-a at 78 K, as a function of hydrogen concentration: (a) 100%; (b) 98%; (c) 56%; (d) 40%; (e) 11%.

Fluorolube as a mulling agent causes asymmetric distortion of absorption band shapes in the spectrum. We could avoid this distortion by using mineral oil, but the mineral oil has huge absorption bands in the 2800−3000 cm^{-1} region that disturb the baseline of the N—H bands used for getting a correct H/D ratio. We obtained the approximate band shapes by comparing the spectrum of the sample in Fluorolube with those in mineral oil.

Infrared spectra at 1-cm^{-1} resolution were observed at liquid-nitrogen temperature in the 4000−400 cm^{-1} region using a Nicolet 550 Fourier transform infrared spectrophotometer with an MCT detector with the sample in a cryostat (Janis Research Co., Inc. ST-100). Infrared spectra were measured at lower temperatures in the 4000−2000 cm^{-1} region using a Nicolet 850 FT-IR with an InSb detector with the sample loaded into a closed-cycle helium cryostat (CTI-Cryogenics SC 21). The details of this setup have been described previously.[14] Line shifts and widths were obtained using second derivative, peak finder, and Fourier self-deconvolution programs.[15]

III. Results and Discussion

A. Assignments. The infrared spectra of the undeuterated sample in mineral oil and in Fluorolube at room temperature (RT) and 78 K are displayed in Figure 1. These spectra are normalized to the 1905 cm^{-1} band at RT (1906 cm^{-1} at 78 K). This band is relatively insensitive to the environment, and it probably arises from a combination of the C—H bending mode of the phenyl ring, by analogy with the various combination bands seen in the anilines[7,8] and crystalline *p*-chloroaniline.[9]

For our assignments, we concentrate on the spectra of SSDH in mineral oil, which show symmetric bands, and start with the spectra at RT. The broad bands at 3440−3650 cm^{-1} belong to the O—H bands of water, and those at 3230−3380 cm^{-1} belong to the N—H bands of the NH_2 group. The bands at 3010−3100 cm^{-1} are the C—H stretching modes of the phenyl ring.[6,7] As the temperature goes down, most of the bands become sharper. The N—H band at 3380 cm^{-1} at RT (Figure 1a) splits into two at 3372 and 3381 (shoulder) cm^{-1} in the spectrum at 78 K (Figure 1b). This is more obvious in Figure 4B-a, which shows the N—H band region on an expanded scale. This splitting also occurs in the spectrum with Fluorolube (Figure 1d), showing that this phenomenon is not due to the mulling agent. The peak

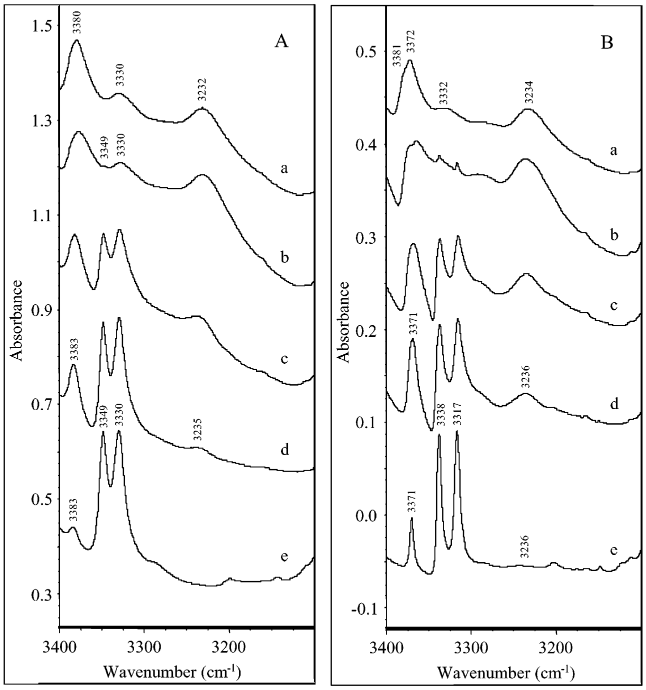

Figure 4. The N—H stretching band region of the infrared absorption spectra of sodium sulfanilate dihydrate (A) at RT and (B) at 10 K, except spectrum B-a at 78 K, as a function of hydrogen concentration: (a) 100%; (b) 98%; (c) 56%; (d) 40%; (e) 11%.

TABLE 1: Assignment of Selected Vibrational Stretching Bands in Sodium Sulfanilate Dihydrate at 10 K

frequency (cm^{-1})[a]	assignment	frequency (cm^{-1})[b]	assignment
3534	H_2O ν_{as}	2611	D_2O ν_{as}
3507	H_2O ν_{as}	2593	D_2O ν_{as}
3482	ν_{O-H} of HOD	2574	ν_{O-D} of HOD
3464	ν_{O-H} of HOD	2553	ν_{O-D} of HOD
3453	ν_{O-H} of HOD	2548	ν_{O-D} of HOD
3447	ν_{O-H} of HOD	2545	ν_{O-D} of HOD
3438	H_2O ν_s	2531	D_2O ν_s
3425	H_2O ν_s	2525	D_2O ν_s
3371	NH_2 ν_{as}	2509	ND_2 ν_{as}
3338	ν_{N-H} of HND	2457	ν_{N-D} of HND
3317	ν_{N-H} of HND	2442	ν_{N-D} of HND
3236	NH_2 ν_s	2396	ND_2 ν_s

[a] The frequencies are from the 89%-D_2O spectrum. [b] The frequencies are from the 2%-D_2O spectrum.

TABLE 2: The Ratio of ν (X—H) to ν (X—D) in Sodium Sulfanilate Dihydrate at 10 K

band no.	X—H (cm^{-1})	X—D (cm^{-1})	ν (X—H)/ν (X—D)
N—H(D) I	3317	2442	1.358
N—H(D) II	3338	2457	1.359
O—H(D) I[a]	3447	2545	1.354
O—H(D) II	3453	2548	1.355
O—H(D) III	3464	2553	1.357
O—H(D) IV	3482	2574	1.353

[a] The O—H bands are from the 89%-D_2O spectrum, and the O—D bands are from the 2%-D_2O spectrum.

TABLE 3: Assignment of Hydrogen Bonds X—H—O in Sodium Sulfanilate Dihydrate

		78 K[a]	
band no.	X—H—O[a]	X—O distance (Å)	X—H—O angle (°)
N—H(D) I	N′—H(6)′···O(1)	3.056	173
N—H(D) II	N″—H(5)″···O(1)	3.086	164
O—H(D) I	O(4)—H(7)···O(1)	2.823	172
O—H(D) II	O(4)′—H(8)′···O(3)	2.872	163
O—H(D) III	O(5)′—H(10)′···O(2)	2.925	176
O—H(D) IV	O(5)″—H(9)″···N	3.034	151

[a] X-ray data from ref 11.

positions of the vibrational stretching fundamentals shift as the temperature changes. The O—D bands are sharper and better resolved than the O—H bands, and so we assign the O—D bands first, and then discuss the O—H bands.

A-1. The O—D and O—H Stretching Bands. Figures 2 and 3 show the O—D and O—H stretching bands in the infrared spectra of samples with different deuterium concentrations at RT, 78 K, and 10 K. The spectra in Figure 2A are taken at RT and the spectra in Figure 2B are taken at 10 K, except the spectrum of the undeuterated sample (Figure 2B-e), which is taken at 78 K. As we mentioned before, the bands are sharper and better resolved with dilute deuterium and at low temperature. In Figure 2B-d, the bands at 2525 and 2531 cm^{-1} are the symmetric D_2O stretching modes (D_2O ν_s), and those at 2593 and 2611 cm^{-1} are the asymmetric modes (D_2O ν_{as}). The four O—D stretching bands from HOD are at 2545, 2548, 2553, and 2574 cm^{-1}. As the hydrogen bonding becomes stronger, the O—D stretching bands are expected to drop in frequency and gain in intensity. This correlation accounts for the asymmetric nature of the HOD bands in Figure 2B-d, which shows that the lower frequency bands are stronger than the high-frequency ones. Our assignments are listed in Table 1.

The O—H stretching bands are similar to the O—D bands; the H_2O stretching bands are broad and unresolved at high hydrogen concentration, but they become sharper and simpler to interpret at low concentration. In the undeuterated SSDH at 78 K (Figure 3B-a), the two bands at 3435 and 3457 cm^{-1} are assigned as the H_2O symmetric stretching modes (H_2O ν_s), and the two bands at 3484 and 3514 cm^{-1} are assigned as the H_2O asymmetric modes (H_2O ν_{as}).

The highest concentration of deuterium yields the O—H stretching bands of HOD and minimizes contributions from H_2O molecules and HOD—HOD nearest-neighbor pairs (Figure 3B-e). There are four O—H stretching bands of HOD at 3447, 3453, 3464, and 3482 cm^{-1}. The ratio of the frequencies of the corresponding stretching bands, ν(O—H) to ν (O—D) is 1.36 for gas-phase HOD[16] and varies systematically with the hydrogen-bond heavy atom distances.[17] Our assignments yield between 1.35 and 1.36 as listed in Table 2 and are in agreement with the values expected for the observed heavy atom distances as indicated in Table 3.

A-2. The N—H and N—D Stretching Bands. Figures 4 and 5 display the N—H and N—D stretching bands in the infrared spectra with different deuterium concentrations at RT, 78 K, and 10 K. In the undeuterated SSDH at RT (Figure 4A-a), there are three bands in the N—H band region at 3232, 3330, and 3380 cm^{-1}. Evans[6] assigned these three bands as an overtone of the NH_2 bending mode, an NH_2 symmetric stretch (NH_2 ν_s), and an NH_2 asymmetric stretch (NH_2 ν_{as}), respectively. However, the band at 3232 cm^{-1} should not be assigned as the overtone of the bending mode, but as the NH_2 ν_s, in agreement with the assignments in crystalline aniline[8] and *p*-chloroaniline,[9] which each have a band between NH_2 ν_{as} and NH_2 ν_s assigned as a combination of a C—H stretching and a lower-frequency ring mode. We assign the band at 3330 cm^{-1} to such a combination, and list the rest of our assignments of the fundamentals in Table 1.

As the deuterium concentration increases, the two N—H stretching bands of HND show up at 3330 and 3349 cm^{-1}. At low hydrogen concentrations (Figure 4A-e), the bands are very

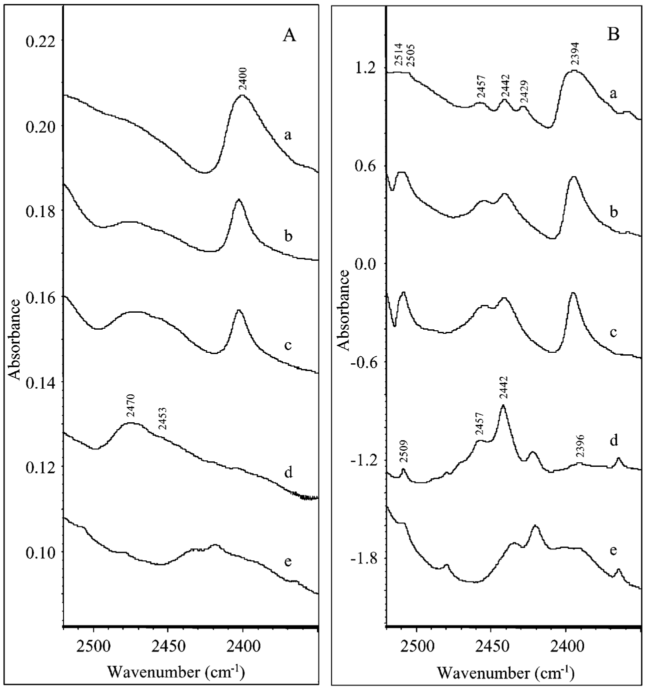

Figure 5. The N—D stretching band region of the infrared absorption spectra of sodium sulfanilate dihydrate (A) at RT and (B) at 10 K, except spectrum B-e at 78 K, as a function of deuterium concentration: (a) 89%; (b) 60%; (c) 44%; (d) 2%; (e) 0%.

strong and almost the same intensity. However, at high hydrogen concentrations (Figure 4A-b), the concentration of HND becomes very small, and, consequently, the two N—H bands of HND become very weak. Thus, the contribution from the C—H combination to the band at 3330 cm^{-1} is more obvious, and the apparent intensity of the band at 3330 cm^{-1} is stronger than that of the band at 3349 cm^{-1}.

As the temperature decreases, the N—H bands become sharper and shift their positions. We now consider the 10 K spectrum by itself and will discuss the thermal behavior of each stretching band in more detail later. The low-hydrogen concentration spectrum (Figure 4B-e) consists of two N—H bands from HND of equal intensity, with a separation of about 20 cm^{-1} at 10 K. At high hydrogen concentrations (Figures 4B-a and b), the NH_2 ν_{as} band splits into two at 3372 and 3381 (shoulder) cm^{-1} (78 K), and at 3365 and 3374 cm^{-1} (10 K), but the splitting disappears as the hydrogen concentration decreases (Figures 4B-d and e). This implies that the splitting is due to coupling between the nearest neighbors of the NH_2 groups in SSDH at the high-hydrogen concentration, possibly between the N—H_5 bond of one NH_2 group and the N—H_6 bond of the adjacent NH_2 group. These two H atoms are hydrogen bonded to the same SO_3^- oxygen atom.

The bands in the N—D region are complicated due to resonance with the ring modes. In the N—D band region, one band (2400 cm^{-1}) shows up in the high-deuterium concentration spectrum (Figure 5A-a) at RT. As the deuterium concentration decreases, overlapping bands appear at 2453 and 2470 cm^{-1} in Figures 5A-b, c, and d. As the temperature decreases, these bands become sharper. There are four bands at 2396, 2442, 2457, and 2509 cm^{-1} in the low-deuterium concentration spectrum at 10 K (Figure 5B-d). We assign these as the ND_2 symmetric stretch (ND_2 ν_s), two N—D stretching modes from HND, and the ND_2 asymmetric stretch (ND_2 ν_{as}), respectively. The ND_2 ν_{as} splits into two at 2505 and 2514 cm^{-1} in the high-deuterium concentration spectrum as does the corresponding N—H band (Figures 5B-a and b). The band at 2429 cm^{-1} in Figure 5B-a could be a combination between a ND_2 bending mode and a C—N stretching mode between the phenyl ring and the ND_2 group by analogy with deuterated aniline.[7] The assignment of each band is listed in Table 1 and the ratios of the N—H/N—D in Table 2. Once again the heavy atom lengths suggest weak hydrogen bonds and a ratio of about 1.36, which is what is observed.

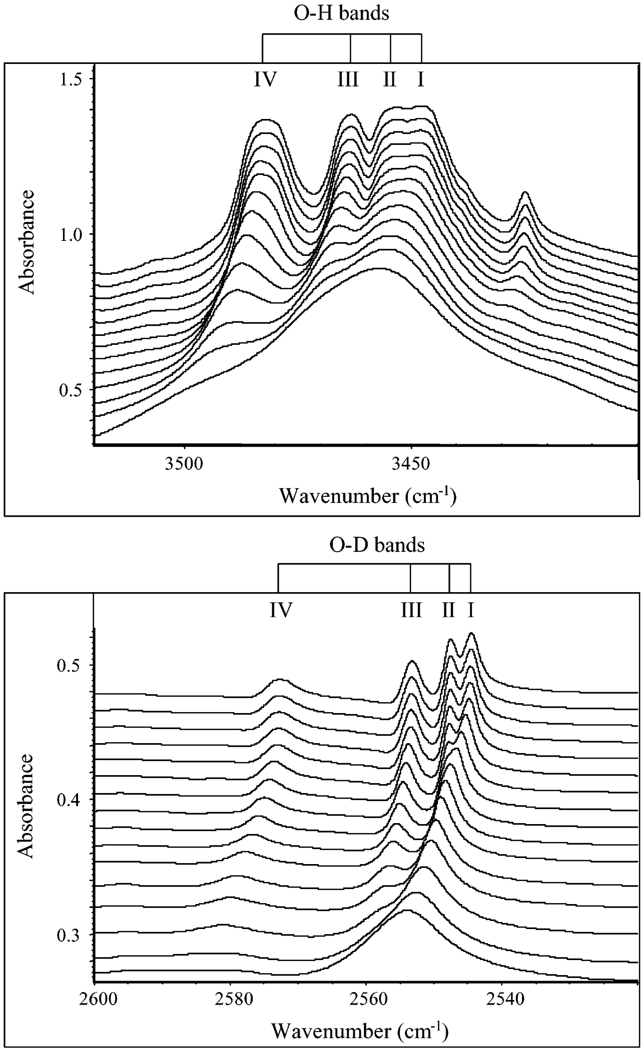

Figure 6. (upper panel) The four O—H stretching bands in the 89%-deuterium concentration spectra of sodium sulfanilate dihydrate as a function of temperature: 10, 25, 50, 75, 80, 100, 125, 150, 175, 200, 225, 250, and 300 K (top → bottom). (lower panel) The four O—D bands in the 2%-deuterium concentration spectra as a function of temperature: 10, 20, 30, 40, 50, 70, 90, 110, 130, 150, 175, 200, 225, 250, 275, and 300 K (top → bottom).

B. Temperature Dependence. As the temperature decreases, the bonds distances change, resulting in the shift of each vibrational frequency. These shifts are on the order of 10 wavenumbers for the hydrogen stretches directly associated with a hydrogen bond. For those hydrogen stretches not directly involved in hydrogen bonding such as the C—H stretch of the phenyl ring, the shift is an order of magnitude smaller. All the N—H···O and O—H···O bands shift to lower frequencies, while the two C—H stretching bands at about 3050 cm^{-1} move in opposite directions.

B-1. The O—H and O—D Stretching Bands. The upper panel of Figure 6 shows the variation with temperature of the four O—H stretching bands from HOD in the spectra of the 89% D_2O sample. The bottom panel displays the four O—D stretching

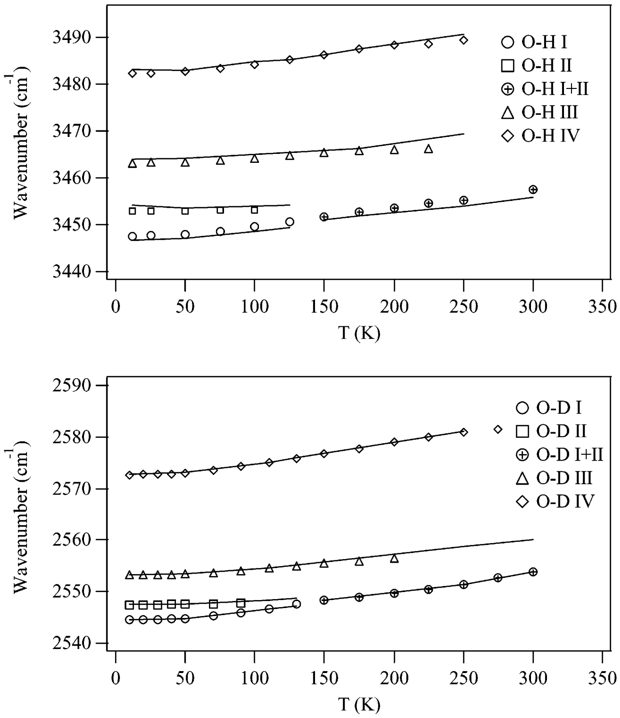

Figure 7. A plot of the O—H (upper panel) and the O—D (lower panel) stretching band frequencies of HOD as a function of temperature for sodium sulfanilate dihydrate. Solid lines are the peak positions of the deconvoluted bands, and the symbols mark the undeconvoluted positions. Note that on the scale of the figure that the differences between these are small.

bands from dilute HOD (2% D$_2$O). The O—H and O—D bands behave similarly as a function of temperature. The four O—H and O—D bands are sharp and separate at low temperatures, but they broaden with increasing temperature.

To identify the position of each band, the observed O—H(D) bands were deconvoluted. The deconvolution yields slightly different band positions and for instance, the separation of two peaks from the deconvoluted O—H I and II bands at 50 K become 7 cm^{-1}, instead of the 5 cm^{-1} for the bands in the observed spectrum. The bands O—H(D) I and II belong to the same water molecule, and they broaden and merge as the temperature rises (Figure 7). On the other hand, O—H(D) III and IV which belong to the other water molecule do not merge throughout the temperature range (Figure 7). The numbering of the bands, the bond lengths, and bond angles are listed in Tables 2 and 3. All the O—H(D) bands shift to higher frequencies with increasing temperature. The frequencies of the O—H hydrogen bands change with the O—O distances, in agreement with the general correlation that predicts a change of a bit less than 1000 cm^{-1}/Å. The O—O distances decrease about 0.03 Å between RT and 78 K,[10,11] and the observed shifts are about 10 cm^{-1} to lower wavenumbers.

The peak intensities of the O—H (D) bands do not change with temperature up to about 100–150 K, but then decrease dramatically in the higher-temperature range. The bandwidths (fwhh) of O—D I, II, and III are 3.13, 2.41, and 2.65 cm^{-1} in the spectrum at 10 K, respectively, and they become 3.38 cm^{-1} for O—D I/II and 2.89 cm^{-1} for O—D III at 150 K. The combined fwhh of O—D I and II decreases up to 150 K, while O—D III increases a little bit. However, above 150 K, these three bands broaden further, becoming 10.6 cm^{-1} wide at 250 K and 13.0 cm^{-1} wide at RT. O—D IV broadens and decreases its peak intensity as well, and becomes indistinct above 275 K.

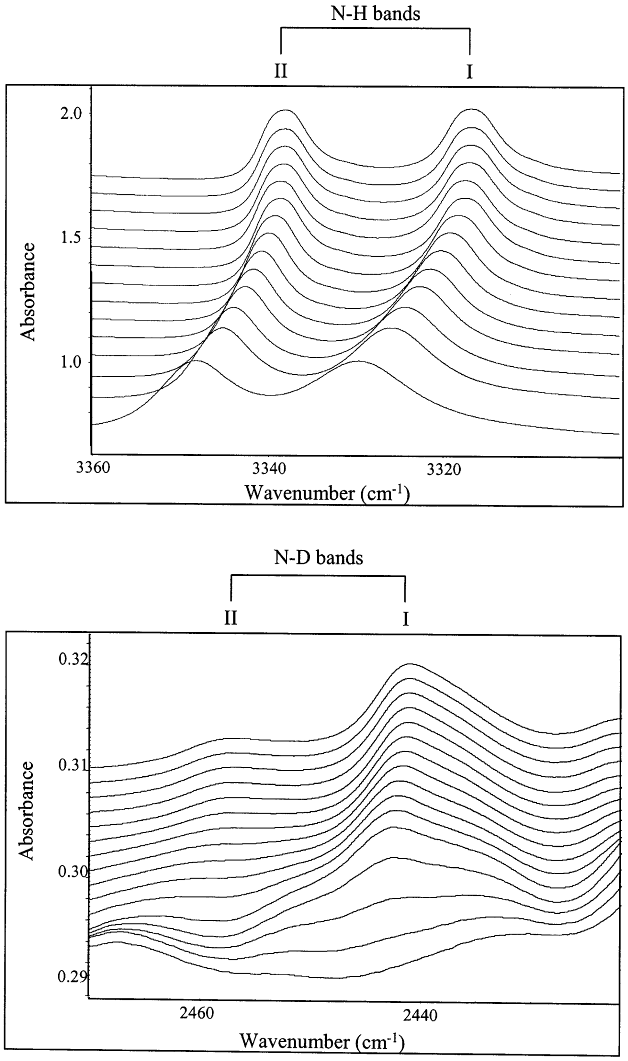

Figure 8. (upper panel) The two N—H stretching bands in the 89%-deuterium concentration spectra of sodium sulfanilate dihydrate as a function of temperature: 10, 20, 30, 40, 50, 75, 100, 125, 150, 175, 200, 225, 250, and 300 K (top → bottom). (lower panel) The two N—D bands in the 2%-deuterium concentration spectra as a function of temperature: The temperatures are the same as those in the lower panel of Figure 6.

Although the O—H bands are broader than the O—D bands, they behave similarly.

The O—H (D) I and II bands belong to one water molecule, and the infrared spectrum shows that O—H (D) I is stronger than O—H (D) II at 10 K. The merging of O—H(D) I and II with increasing temperature indicates that there is an interchange between the O—H and the O—D positions due to the increasing librational motion and probably direct interchange of the two hydrogens at high temperatures. This motion is similar to that analyzed in the sodium perchlorate crystal.[2]

The O—H (D) III and IV bands belong to the other water molecule. O—H(D) IV is hydrogen bonded to the lone pair on the nitrogen atom of the NH$_2$ group, and O—H(D) III is hydrogen bonded to the SO$_3^-$ oxygen atom, and the hydrogen bond distance of O—H(D) IV is longer than O—H(D) III. This is consistent with the X-ray studies[10,11] which show that O—H(D) IV is longer and more bent than the other hydrogen bonds, suggesting this bond is weaker than the others.

B-2. The N—H and N—D Stretching Bands. The upper panel of Figure 8 shows the two N—H stretching bands in the spectra of the 89% D_2O sample with temperature. The bottom panel is for the two N—D stretchings at the 2%-D_2O concentration. The two N—H(D) bands remain separated from each other through the temperature range and shift about 10 cm^{-1} to high frequency with temperature.

The intensity of N—D I in the 2%-D_2O spectra is greater than that of N—D II at 10 K (the bottom panel of Figure 8), while the two N—H bands have almost the same intensity both in 2% and 89% deuterium concentrations in Figure 4B-b and the upper panel of Figure 8, respectively. The relative intensities of N—D bands in the 2%-D_2O spectrum switch above 150 K. The two N—D bands overlap with the vibrational resonances and combination bands from the ring modes, yielding the asymmetric and complicated band shapes observed.

IV. Summary and Conclusion

Two of each H_2O (D_2O) ν_{as} and H_2O (D_2O) ν_s bands show up in the low-temperature spectra of the isotopically dilute samples and these have been assigned. Furthermore, there are four O—H(D) stretching bands from the HOD molecules in the infrared spectra and these have been assigned as well. One of the water molecules has two distinctly different O—H (D) hydrogen bonds. Conversely, the other water molecule has two rather similar bonds and the hydrogen-bond absorption bands merge at high-temperature. This merging is due to large-amplitude librational motion with the probable interchange of the O—H and the O—D positions of the HOD molecule at the highest temperatures.

Two N—H (D) bands of the HND group appear in all of the spectra, regardless of the deuterium concentration, with a separation of 21 cm^{-1} for the N—H bands and 15 cm^{-1} for the N—D bands at 10 K. In the low-deuterium concentration spectrum, complicated asymmetric-appearing bands show up, due to the overlap between these bands and the vibrational resonances and combination bands from the ring modes. The NH_2 (ND_2) ν_{as} band doubles in the high-hydrogen (deuterium) concentration spectrum due to the interaction between the nearest neighbors. The temperature shifts of bands of the hydrogen-bonded groups are in agreement with the known correlations of frequency with bond distance.

Details of the large amplitude motion of the one water molecule should become clearer on further investigation by infrared hole burning or neutron diffraction. The interaction of the N—H and N—D fundamental bands with lower frequency modes and the interaction of these modes with similar modes on neighboring molecules seem to be typical of N—H modes in amino acids and other molecules and a detailed explanation of these phenomena also awaits further experiments.

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