

## O–D(H)...S Hydrogen Bonds in Crystalline Hydrates: Survey and Correlation of Vibrational Spectroscopic and Structural Data

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### Abstract

Structural and vibrational spectroscopic data of  $O_W-D(H)...S$  H-bonds in crystalline hydrates are discussed. The compilation includes 85  $O_W-D(H)...S$  groups in 16 different compounds, for which accurate structural data (from neutron and/or X-ray diffraction measurements), as well as high quality  $\bar{\nu}_{OD}$  stretching frequency data (from low temperature Raman and/or IR measurements of isotopically dilute samples) are available. The data are discussed with respect to accuracy of neutron and X-ray data, temperature effects, different types of water molecules with approximately linear H-bonds, bifurcated H-bonds and 'free' O–D(H) groups, and reliability of assignments of frequencies to O–D(H) groups. From the correlation between  $\bar{\nu}_{OD}$  frequencies and  $R_{O...S}$  bond distances the existence of significant and systematic differences between different kinds of sulfur acceptors becomes evident. It is shown in particular that at comparable bond distances the  $\bar{\nu}_{OD}$  stretching frequencies of O–D...S H-bonds in different compounds significantly increase within the series  $S'' \ll SnS_4'''' < XCS_2'$  ( $X = RO, R_2N$ )  $\leq XS_4'''$  ( $X = P, As, Sb$ )  $< S_2O_3'' < SCN'$ , from about 2380 to 2530  $cm^{-1}$  at  $R_{O...S} = 3.3 \text{ \AA}$ . The observed differences may reasonably well be interpreted in terms of different mean net charges of the different kinds of sulfur acceptors, which systematically decrease within this series.

### 1. Introduction

Because of its fundamental importance in chemistry and biology, the water molecule holds an exceptional position within the field of hydrogen bond research. Particular interest in hydrogen bonding in crystalline hydrates results from the enormous variety of different proton acceptors, which are

found to be involved in  $O_W-H...Y$  H-bonds (for a very recent review see [1]). This provides the possibility of spectroscopically as well as structurally characterizing hydrogen bonds with similar proton donors, i.e. water molecules, but widely differing proton acceptors, and hence, of studying the role of the latter ones systematically.

Commonly accepted high potential proton acceptors, like fluorine or oxygen, are characterized by high electronegativities, while the H-bond capability of elements with low electronegativities, like iodine or sulfur, is often assumed to be rather poor. However, the existence of H-bonds involving sulfur proton acceptors has actually been known for a long time [2–4] and from several spectroscopic and calorimetric solution studies it has become apparent that the corresponding association enthalpies or stretching frequency shifts are not very different from those of H-bonds involving analogous oxygen acceptors [5–8].

Some years ago we started systematic investigations of  $W...S$  H-bonds ( $W$  denoting a water hydroxyl group) in solid hydrates. The main scope of this study was to obtain a consistent set of vibrational spectroscopic and structural data, sufficiently large and varied for a comprehensive characterization of the role of sulfur acting as proton acceptor and for a comparison with other more common acceptors. Crystallographic data of  $W...S$  H-bonds in some compounds have already been reported in the literature [9–13], but there is an almost total lack of corresponding  $\bar{\nu}_{OD(H)}$  stretching frequency data, which are most commonly used for a characterization of H-bond strengths in solids. When dealing with crystalline hydrates in particular, 'uncoupled'  $\bar{\nu}_{OD(H)}$  frequencies obtained from isotopically dilute samples should preferably be considered for a meaningful discussion of spectroscopic–structural relations. Within the last years several appropriately selected compounds have been investigated and the number of data available now seems to be large enough for the intended summarizing characteriza-

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tion of W...S H-bonds in hydrates. These data were already included in a recent survey of W...Y H-bonds (Y = N, O, S, Se, Cl, Br, J) in crystalline hydrates [14], but they shall be analyzed in greater detail in the present paper. Firstly, the spectroscopic and structural data will be surveyed. Secondly, the data will be discussed on the basis of the frequency–distance correlation and an approach for a qualitative interpretation of the significant differences observed for different kinds of sulfur acceptors will be made.

## 2. Experimental Data

Sixteen compounds containing W...S H-bonds, for which structural data as well as vibrational spectroscopic data of isotopically dilute samples are available, are summarized in Table 1, which gives references to original work and contains information about the numbers of different kinds of H-bonds within the compounds.

### 2.1. Spectroscopic Data

Among the different water fundamentals, the stretching vibrations are the main point of interest with respect to a characterization of H-bonds and will exclusively be dealt with in this paper. It is well

known that the stretching frequencies decrease with hydrogen bonding, and the shifts relative to the frequencies of the free molecules most commonly even serve as a synonym for H-bond strengths. For a discussion of the effects of hydrogen bonding on water bending vibrations and librational modes in hydrates the reader is referred to refs. 1, 27 and 28.

Only high quality spectroscopic data obtained from isotopically dilute samples at liquid nitrogen temperature are considered in this study. The technique of isotopic dilution (dilute HDO in H<sub>2</sub>O or D<sub>2</sub>O), which largely excludes intra- and intermolecular vibrational coupling effects as well as Fermi resonance effects, has become a well established method for the investigation of water (cf. refs. 29 and 30). When dealing with hydrates in particular the well known sharp line spectra of ‘uncoupled’ O–D(H) oscillators result, with halfwidths typically less than 10 cm<sup>-1</sup> at liquid nitrogen temperature. Even with rather complex compounds containing a larger number of different hydrate water molecules satisfactorily resolved spectra are usually obtained, with the number of lines being equal or only slightly less than the number of different O–D(H) groups. For an example see Fig. 1, which also demonstrates that, when dealing with complex hydrates, low temperature measurements are actually necessary to obtain sufficiently resolved spectra.

TABLE 1. Compounds included in the survey: references to original diffraction and spectroscopic studies; numbers of different kinds of W...Y H-bonds

Compound	Reference		Numbers of crystallographic independent H-bonds			
	diffr.	spectr.	W...S	W...O <sub>W</sub>	W...Y <sup>a</sup>	W...S,S
Category 1 (neutron data)						
BaS <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	12	15	1	1		
MgS <sub>2</sub> O <sub>3</sub> ·6H <sub>2</sub> O	16	14	2	1	3(O)	
Na(CH <sub>2</sub> ) <sub>4</sub> NCS <sub>2</sub> ·2H <sub>2</sub> O	17	18	4			
Na <sub>2</sub> S·9H <sub>2</sub> O	19	19	7	3		
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	13	15	4	2	4(O)	
Na <sub>3</sub> AsS <sub>4</sub> ·8H <sub>2</sub> O	20	21	13	1		1
Na <sub>3</sub> SbS <sub>4</sub> ·9H <sub>2</sub> O	22	21	4	1		1
Category 2 (X-ray data, special refinement)						
Na(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCS <sub>2</sub> ·3H <sub>2</sub> O	18	18	5	1		
α-NaSCN·2H <sub>2</sub> O	23	23	2	1		1
β-NaSCN·2H <sub>2</sub> O	23	23	4		2(N)	
Na <sub>2</sub> S·5H <sub>2</sub> O	24	24	4			
α-Na <sub>3</sub> PS <sub>4</sub> ·8H <sub>2</sub> O	25	25	13	1		1
Category 3 (X-ray data)						
C <sub>4</sub> H <sub>4</sub> N <sub>4</sub> S·H <sub>2</sub> O	10	14	1		1(N)	
NaC <sub>2</sub> H <sub>5</sub> OCS <sub>2</sub> ·2H <sub>2</sub> O	9	14	8			
Na(CH <sub>3</sub> ) <sub>2</sub> NCS <sub>2</sub> ·2H <sub>2</sub> O	26	18	4			
Na <sub>4</sub> SnS <sub>4</sub> ·14H <sub>2</sub> O	11	14	11	2		

<sup>a</sup>Proton acceptors are given in parentheses.

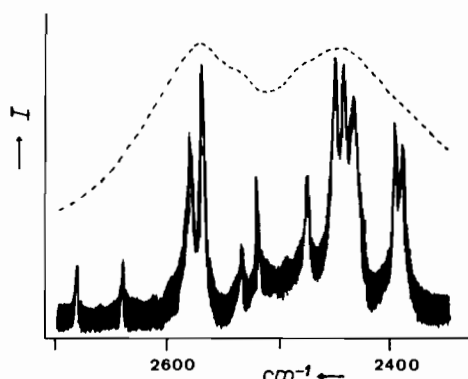


Fig. 1. Survey Raman spectra of  $\text{Na}_4\text{SnS}_4 \cdot 14\text{H}_2\text{O}$  at 295 (dotted line) and 75 (full line) K: isotopically dilute sample (5%  $\text{D}_2\text{O}$  + 95%  $\text{H}_2\text{O}$ ); range of  $\bar{\nu}_{\text{OD}}$  frequencies.

The uncoupled  $\bar{\nu}_{\text{OD(H)}}$  frequencies may be obtained from either IR or Raman measurements of samples containing about 5%  $\text{D}_2\text{O}$  + 95%  $\text{H}_2\text{O}$  (or vice versa). The discussion will be restricted to the more frequently used  $\bar{\nu}_{\text{OD}}$  frequencies, because the uncoupled  $\bar{\nu}_{\text{OD}}$  and  $\bar{\nu}_{\text{OH}}$  frequencies are known to give an excellent correlation [14] and almost identical results are obtained for either of them. Basically, O–D(H) stretching vibrations quite generally give rise to strong IR bands, but only weak Raman lines. Therefore, IR measurements are usually much simpler than Raman measurements, which may be rather difficult or even impossible, e.g. because of an annoying luminescence or scattering background. On the other hand, however, the common IR powder techniques may give rise to, possibly undetected, changes of the sample material, such as phase transitions or partial dehydration. Therefore, Raman measurements are in general more reliable and very often the only alternative, as was for instance the case with the sulfides or the thiocyanates of Table 1.

## 2.2. Structural Data

The atomic parameters of the non-hydrogen atoms of all compounds listed in Table 1 are known with accuracies of 0.01 Å or better. With respect to hydrogen atoms it is appropriate to divide the compounds into three categories. For the compounds of the first category neutron data are available providing hydrogen positions with accuracies comparable to those of the heavier atoms [31]. For the remaining compounds only X-ray data were available which, without special precautions, provide hydrogen positions with an accuracy of at least one order of magnitude less than those of the remaining atoms, owing to the comparatively small X-ray scattering power of D(H) [31]. Even more important than the limited accuracy is the systematic difference of about 0.1 to 0.2 Å between the neutron diffraction determined nuclear hydrogen positions and the X-ray diffraction determined centres of the electron clouds

of bonded hydrogen. In order to derive ‘nuclear’ hydrogen positions from X-ray diffraction data a special constrained structure refinement technique was applied to the compounds of category two. This technique uses rigid  $\text{H}_2\text{O}$  molecules with fixed H–O–H angles and separate nuclear and electron cloud centres of hydrogen. The philosophy behind this method is that the geometry of water molecules in hydrates is known to vary little, a few degrees in the H–O–H angles and a few hundredths parts of Å in the  $r_{\text{OH}}$  distances [32]. In those cases where both X-ray and neutron diffraction data were available (compounds of the first category) comparisons show, that hydrogen positions derived from X-ray data in the described way deviate on the average by only 0.03 Å ( $\sigma = 0.03$  Å) from the more accurate neutron diffraction results.

While the relevant part of vibrational spectroscopic data was determined at liquid nitrogen temperature the bulk of the available structural data is from room temperature measurements and only seven compounds have been studied at low temperatures ranging from 27 to 175 K. Since temperature affects interatomic distances only moderately in most cases, if phase transitions can be excluded, which was checked by vibrational spectroscopy in each case, it was considered best to base spectroscopy–structure correlations on room temperature structure data. From a comparison of room and low temperature bond lengths in five compounds of Table 1 it can be estimated that room temperature  $R_{\text{O} \dots \text{S}}$  distances have to be corrected by  $-0.02$  Å on average if extrapolated to 75 K. This value is in good agreement with the  $-0.022$  Å on average recently derived from a larger set of data [14] including different kinds of proton acceptors.

A typical example of a water molecule involved in  $\text{W} \dots \text{S}$  H-bonds is shown in Fig. 2a, in which the molecule is bonded to two sodium atoms, donates two approximately linear H-bonds to the sulfur atoms and thus adopts a tetrahedral coordination. Twenty-six out of 55 different water molecules of the 13 sodium compounds belong to this basic coordination type, which can be modified in several ways: (i) by replacing one sulfur atom by a water oxygen atom (10 cases), (ii) by substituting one sodium by one H-bond donating water molecule (6 cases), or (iii) by a combination of both (2 cases). Four water molecules are not engaged in  $\text{W} \dots \text{S}$  H-bonds, but form two  $\text{W} \dots \text{O}$  or two  $\text{W} \dots \text{N}$  H-bonds. The remaining seven water molecules exhibit some special features and will be discussed below. Histograms of  $R_{\text{O} \dots \text{S}}$  distances and O–H  $\dots$  S angles of the  $\text{W} \dots \text{S}$  H-bonds (including those in the three non-sodium compounds; excluding two orientationally disordered groups) are given in Fig. 3a and b. The ranges and mean values are in good agreement with those given in previous papers [32, 33].

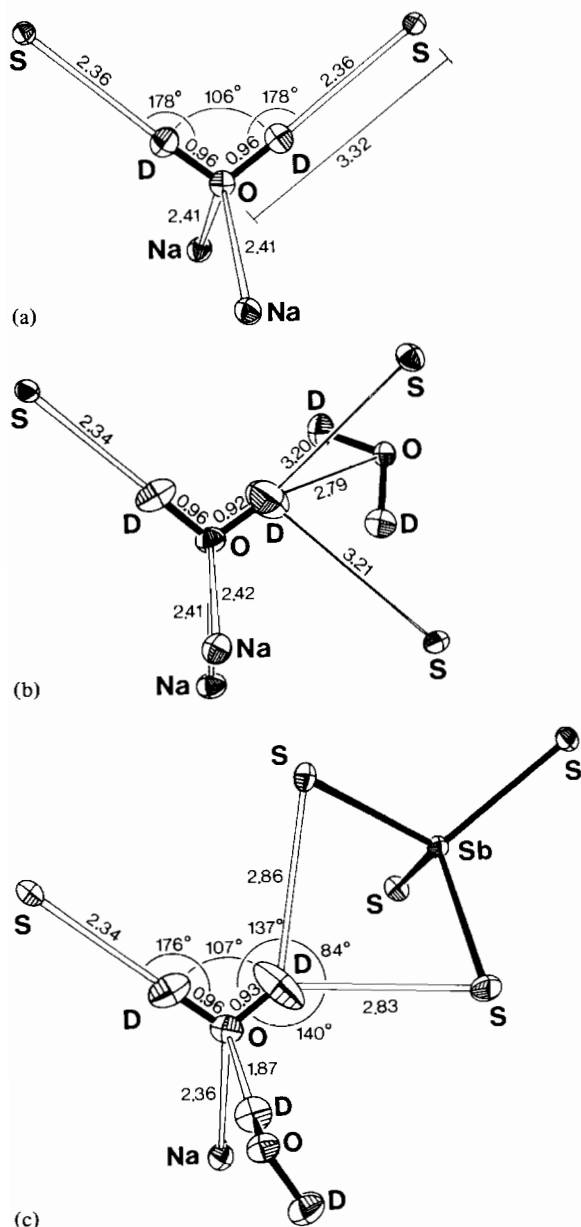


Fig. 2. Coordination of water molecules engaged in W...S H-bonds (numbers with two decimal places are distances in Å): (a) typical case (from  $\text{Na}_2\text{S}\cdot 9\text{D}_2\text{O}$ ); (b) with one bifurcated bond (from  $\text{Na}_3\text{SbS}_4\cdot 9\text{D}_2\text{O}$ ); (c) with a 'free' O-D group (from  $\text{Na}_3\text{AsS}_4\cdot 8\text{D}_2\text{O}$ ).

Besides the great majority of water O-D(H) groups that form normal W...Y (Y = S, O, N) H-bonds, i.e. a clearcut interaction with only one distinct proton acceptor, two somewhat special types of O-D(H) groups are also found in the compounds of Table 1. In Fig. 2b a water molecule of  $\text{Na}_3\text{SbS}_4\cdot 9\text{H}_2\text{O}$  is shown displaying, besides one normal W...S H-bond, a bifurcated, almost symmetrically branched O-D(H)...S,S interaction. Other

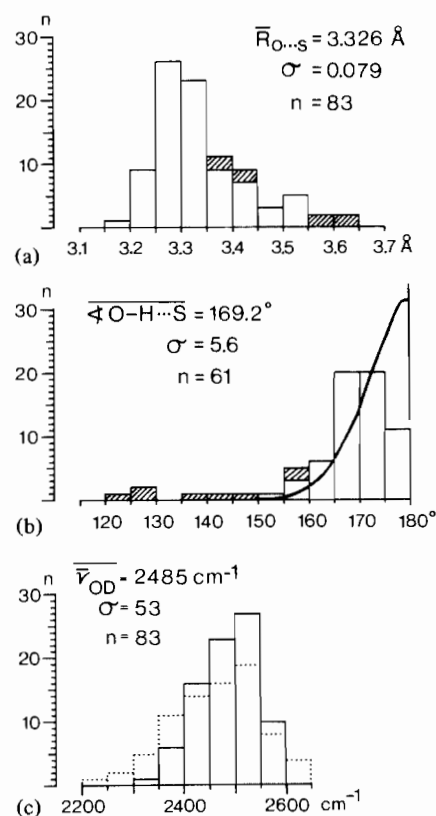


Fig. 3. Histograms for structural and spectroscopic data of W...S H-bonds. (a)  $R_{\text{O}\dots\text{S}}$  distances; hatched areas represent bifurcated bonds, which are not included in the statistics. (b) O-H...S angles for compounds of category 1 and 2 (see Table 1); hatched areas represent bifurcated bonds, which are not included in the statistics; full line shows the distribution after normalization to unit solid angle. (c)  $\bar{\nu}_{\text{OD}}$  Frequencies without bifurcated bonds; broken line represents W...O H-bonds (see text).

examples for bifurcation are found in  $\text{Na}_3\text{AsS}_4\cdot 8\text{H}_2\text{O}$ ,  $\alpha\text{-Na}_3\text{PS}_4\cdot 8\text{H}_2\text{O}$  and  $\alpha\text{-NaSCN}\cdot 2\text{H}_2\text{O}$ , all of them being less symmetric with respect to branching than that of Fig. 2b. A comparison with the data of Chiari and Ferraris [32] indicates bifurcated bonds with sulfur acceptors to be more abundant than with oxygen acceptors. Another unusual situation observed for a water molecule in  $\text{Na}_3\text{AsS}_4\cdot 8\text{H}_2\text{O}$  and in the isostructural  $\alpha\text{-Na}_3\text{PS}_4\cdot 8\text{H}_2\text{O}$  is shown in Fig. 2c. In both compounds an O-D(H) group is directed into a 'cavity' bordered by one oxygen and two sulfurs, which are located at distances from the hydrogen atom far outside the usual hydrogen bond range. A similar situation is encountered for a water molecule in  $\text{Na}_4\text{SnS}_4\cdot 14\text{H}_2\text{O}$ . Although these 'free' O-D(H) groups do not show H-bond interactions from a geometrical point of view, vibrational spectroscopy indicates some electrostatic influence of the nearer neighbors.

### 2.3. Assignments

The assignments of the observed  $\bar{\nu}_{OD}$  frequencies to the different O–D(H) groups were based on the consequent application of some common assumptions and plausible approximations, which were previously given and discussed [14, 21]. For the normal W...S H-bonds, the order of frequencies was assumed to be the order of bond distances  $R_{O...S}$  or  $R_{D(H)...S}$ , which implies that within a given compound there should exist a rigorous correlation between frequencies and bond distances. Although it is not possible to check the validity of this assumption in each single case, there are good reasons for considering the assignments to be correct within some reasonable limit. As it has recently been shown for W...Y H-bonds in hydrates, the scatter of points in a frequency–distance correlation plot is fairly small and the standard deviations are less than about  $20\text{ cm}^{-1}$ , if the plot is restricted to very similar proton acceptors [14], as it usually applies to the acceptors in a given compound.

In those cases where, besides W..S H-bonds, W...Y H-bonds with proton acceptors other than sulfur exist within a given compound (see Table 1) additional approximations are necessary to obtain assignments. For W...O<sub>w</sub> H-bonds between water molecules, as they are frequently encountered in hydrates, the data from the different modifications of ice [34] have been used to estimate the corresponding  $\bar{\nu}_{OD}$  frequencies. Special assumptions were made to obtain assignments for the thiosulfates and the thiocyanates, which possibly make them less reliable.

In Fig. 3c a histogram is shown for the  $\bar{\nu}_{OD}$  frequencies of the W...S H-bonds included in this survey and, for comparison also for the  $\bar{\nu}_{OD}$  frequencies of W...O H-bonds using the data of ref. 14. As can be seen, the maxima of the frequency distributions are rather similar, in the range from 2450 to 2500  $\text{cm}^{-1}$  in both cases, while the total frequency range is somewhat larger for W...O than for W...S H-bonds, at both, the high and the low  $\bar{\nu}_{OD}$  frequency tail.

In the spectra of the three compounds, where ‘free’ OH groups with no potential proton acceptor

TABLE 2. Highest  $\bar{\nu}_{OD}$  frequencies observed with solid hydrates

Compound	$\bar{\nu}_{OD}$ ( $\text{cm}^{-1}$ )
$\text{Na}_4\text{SnS}_4 \cdot 14\text{H}_2\text{O}$	2679
$\alpha\text{-Na}_3\text{PS}_4 \cdot 8\text{H}_2\text{O}$	2665
$\text{Na}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$	2664
$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ [29]	2654
$\text{SrFe}(\text{CN})_5\text{NO} \cdot 4\text{H}_2\text{O}$ [35]	2650

within a distance range qualified for H-bonding were found, corresponding high frequency lines were observed and the assignments are certainly straightforward. To our knowledge these  $\bar{\nu}_{OD}$  frequencies are the highest ones observed so far with crystalline hydrates (Table 2). Moreover, it may be noticed, that the stretching frequencies of these lines exhibit negative temperature dependencies, as is characteristic of very weak and highly bent H-bonds [36]. Bifurcated H-bonds, as found in four compounds (Table 1), should likewise also exhibit negative temperature coefficients [36]. However, in spite of careful measurements in the temperature range 300–75 K, we could not find negative temperature coefficients, except for the high frequency lines mentioned above. This finding is in agreement with a recent work [37], which claims, that Falk’s concept has to be modified in the way that it only applies to strongly asymmetric bifurcated H-bonds, but not to essentially symmetric ones.

### 3. Discussion

In Fig. 4a a frequency–distance correlation plot is shown for the W...S H-bonds of the compounds of Table 1, which will serve as a basis for the follow-

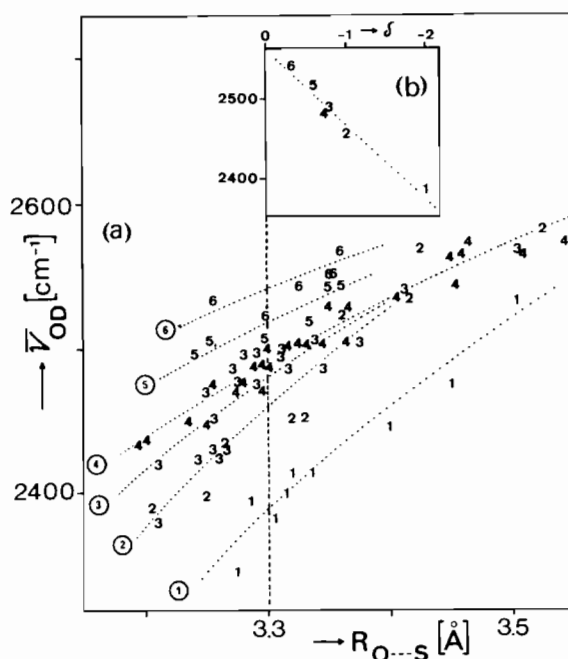


Fig. 4. (a)  $\bar{\nu}_{OD}$  Frequency vs.  $R_{O...S}$  distance of W...S H-bonds and individual correlation curves for different groups of similar sulfur acceptors (1: S'', 2:  $\text{SnS}_4^{4-}$ , 3:  $\text{XCS}_2'$ , 4:  $\text{XS}_4^{3-}$ , 5:  $\text{S}_2\text{O}_3^{2-}$ , 6:  $\text{SCN}'$ ). (b)  $\bar{\nu}_{OD}$  Frequency at  $R_{O...S} = 3.3\text{ \AA}$  vs. mean partial charge ( $\delta$ ) for the different groups of sulfur acceptors (according to ref. 39).

ing discussion. For the reasons given in Section 2.2, low temperature spectroscopic data have been used along with room temperature structural data with the exception of the thiocyanates, for which only a 130 K X-ray study is available. As already noted above, room temperature  $R_{O\dots S}$  distances are typically about 0.02 Å larger than the corresponding liquid nitrogen temperature distances, which is, however, too small to affect the following discussion.

In the course of our investigations significant differences between the various kinds of sulfur acceptors became apparent. In particular it was found that at comparable bond distances the  $\bar{\nu}_{OD}$  frequencies of the sulfides are smaller than those of other compounds by about  $100\text{ cm}^{-1}$  [15, 21]. These differences were somewhat unexpected at first, since similar effects had not been established before from other W...Y systems, such as W...O or W...Cl H-bonds. However, the existence of significant and also systematic anion effects in the W...S system could be confirmed and extended by the subsequent investigations of appropriately selected compounds. Moreover, it has recently been shown, that analogous effects can be observed with W...Se H-bonds [14]. In Fig. 4a these systematic effects become evident from the individual correlation curves, which were calculated for six groups of sulfur acceptors (details of the correlation functions are given in Table 3). The main findings are: (i) at comparable bond distances the  $\bar{\nu}_{OD}$  frequencies increase within the sequence  $S'' \ll \text{SnS}_4'''' < \text{XCS}_2' (X = \text{RO}, \text{R}_2\text{N}) \ll \text{XS}_4'''' (X = \text{P}, \text{As}, \text{Sb}) < \text{S}_2\text{O}_3'' < \text{SCN}'$ , or, which is fully equivalent, for H-bonds with comparable  $\bar{\nu}_{OD}$  the  $R_{O\dots S}$  distances decrease within this series; (ii) the differences are more pronounced at shorter bond distances, since there is a distinct trend for the correlation curves to become flatter within the same sequence.

The above sequence suggests to correlate the observed differences with the charge distributions at the sulfur acceptors, which result from the different chemical bonding situations they are involved in, and some kind of partial charges can be chosen to represent these differences [39]. One may for instance refer to Pauling's method of estimating bond

TABLE 3. Regression parameters of the correlation curves of Fig. 4a (correlation functions:  $\bar{\nu}_{OD} = 2727 - A \times \exp\{-B \times R_{O\dots S}\}$  [38])

Acceptor type	A	B
$S''$	$7.20 \times 10^5$	2.32
$\text{SnS}_4''''$	$5.70 \times 10^6$	3.02
$\text{XCS}_2' (X = \text{RO}, \text{R}_2\text{N})$	$4.28 \times 10^5$	2.26
$\text{XS}_4'''' (X = \text{P}, \text{As}, \text{Sb})$	$2.22 \times 10^5$	2.07
$\text{S}_2\text{O}_3''$	$4.64 \times 10^4$	1.63
$\text{SCN}'$	$5.05 \times 10^4$	1.69

orders from bond distances and in ref. 40 the necessary parameters have been given to determine free bond valences for the different sulfur acceptors, which may be used as partial charges. In Fig. 4b mean values of these partial charges for the six groups of sulfur acceptors are plotted against the  $\bar{\nu}_{OD}$  frequencies, which were taken from the corresponding individual correlation curves at a bond distance of  $R_{O\dots S} = 3.30\text{ Å}$ . The resulting correlation is certainly highly satisfying, although no realistic physical significance should be given to the functional approximately linear relationship. Basically, partial charges obtained in this or any other way should represent correct trends, but may become questionable when using them as absolute quantities. Apart from this, the partial charges are certainly well suited to represent the systematic differences observed in Fig. 4a and will be used as a basis in the following attempts for a qualitative interpretation of the findings.

Let us first consider a possible direct influence of charge differences on the  $\bar{\nu}_{OD}$  frequencies or H-bond strengths. Such a direct influence would not be unexpected, since weak to moderately strong H-bonds are known to be primarily of electrostatic nature and a number of experimental results and characteristic properties may be interpreted within simple electrostatic models. A very simple model by which the dependence of  $\bar{\nu}_{OD}$  frequencies on partial charges can be simulated, is the interaction of a water molecule with a negative point charge,  $q$ , and some results of corresponding model calculations are given in Fig. 5. Figure 5a showing the dependence of the stretching frequency on the  $R_{O\dots q}$  distance

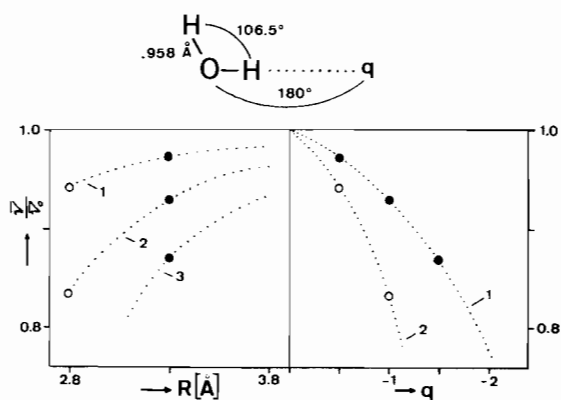


Fig. 5. Interaction of a water molecule with a negative point charge ( $q$ ) from *ab initio* calculations (basis set: (8s, 4p/4s)  $\rightarrow$  [5S, 3P/3S] according to ref. 41 with fixed parameters  $r_{OH} = 0.958\text{ Å}$ ,  $\angle\text{H-O-H} = 106.5^\circ$ ,  $\angle\text{O-H}\dots q = 180^\circ$ : (a) relative  $\bar{\nu}_{OH}$  frequency vs.  $R_{O\dots q}$  distance for constant charges (1:  $q = -0.5$ , 2:  $q = -1.0$ ; 3:  $q = -1.5$ ); (b) relative  $\bar{\nu}_{OH}$  frequency vs. charge at constant  $R_{O\dots q}$  distances (1:  $R = 3.3$ , 2:  $R = 2.8\text{ Å}$ ). (Common points are indicated by open and full circles.)

for constant charges corresponds to Fig. 4a, while Fig. 5b showing the dependence on the charge at constant distances corresponds to Fig. 4b. The main findings of Fig. 4, i.e. the largely differing  $\bar{\nu}_{\text{OD}}$  frequencies at given  $R_{\text{O}\dots\text{S}}$  bond distances as well as the different steepnesses of the individual correlation curves, may therefore be reasonably well ascribed to different charges at different sulfur acceptors.

Although this first approach for an interpretation seems to be plausible for the present, another point of view exists that should also be taken into account. If for instance the correlation curves for  $\text{W}\dots\text{O}$ ,  $\text{W}\dots\text{Cl}$  and  $\text{W}\dots\text{S}$  given in ref. 14 are compared the differences are mainly due to the different ionic radii of the elements, which produce corresponding shifts with respect to the distance abscissa scale. Other specific properties of the elements are responsible for only minor differences concerning the steepnesses of the curves, which seem to increase systematically with increasing electronegativities or mean proton affinities ( $\text{W}\dots\text{S} < \text{W}\dots\text{Cl} < \text{W}\dots\text{O}$ ). In the same way one might argue that the differences between the correlation curves in Fig. 4a should also mainly be due to different ionic or contact radii of the different kinds of sulfur acceptors. Qualification for such a point of view may be claimed from the fact that the ionic or contact radius of a given element quite generally increases with increasing negative charge. Although we are not aware of experimental data about variations of sulfur contact radii with varying partial charges, some evidence about the possible differences may be obtained from model calculations. If for instance the radii of spheres containing 95% of the total electron cloud are calculated for a sulfur atom and for a sulfide ion in a CaS like lattice potential by the augmented plane wave method (APW), values of 1.52 and 1.84 Å respectively are obtained [42], which may be representative for the corresponding contact radii. Without overestimating the validity of these calculations, it is noteworthy, that the calculated difference of about 0.3 Å between divalent and neutral sulfur agrees well with the maximum difference of 0.25 Å obtained for the  $R_{\text{O}\dots\text{S}}$  distances of  $\text{W}\dots\text{S}$  H-bonds with comparable  $\bar{\nu}_{\text{OD}}$  frequencies, i.e. between  $\text{W}\dots\text{S}$  ( $\text{S}''$ ) and  $\text{W}\dots\text{S}(\text{SCN}')^+$  H-bonds. This gives some evidence, that the different locations of the individual correlation curves in Fig. 4a can actually be ascribed reasonably well to varying contact radii, which systematically increase with increasing partial charges of the sulfur acceptors.

On summarizing it may be claimed that differences between frequency–distance correlations of different kinds of  $\text{W}\dots\text{Y}$  H-bonds may be interpreted, to a first approximation, in terms of two simple quantities characteristic of the Y acceptors: (i) the contact radius, which mainly determines the position on the

distance scale, and (ii) a second quantity, possibly the proton affinity, which determines the steepness of a curve. If  $\text{W}\dots\text{Y}$  H-bonds, with Y being different chemical elements, are compared, the two quantities are simply those of the elements that are considered. If different groups of acceptors of a given element are compared, minor dependencies of both properties on the specific bonding situation of the acceptors must be considered. We have used the partial charge as a simple and easily accessible quantity, by which the different bonding situations can be reasonably well characterized. Since both contact radii and proton affinities should be directly related to any kind of partial charges, the latter seem to be well suited for a reasonable understanding of the findings of Fig. 4, the largely differing locations, as well as the differing curvatures of the correlation curves.

At last one final point should be briefly considered, which was noted already, i.e. the fact that significant and systematic differences between different proton acceptors have so far only been observed with  $\text{W}\dots\text{S}$  and  $\text{W}\dots\text{Se}$  H-bonds, but not with other acceptors. To some extent this may be due to the lack of sufficient or sufficiently systematic data, however, it can be shown that there are also some fundamental reasons. Considering for instance the most extensively studied  $\text{W}\dots\text{O}$  system, since oxide hydrates do not exist, there is no analog to the sulfide ion, which exhibits the most significant difference to the other sulfur acceptors in the  $\text{W}\dots\text{S}$  system. An evaluation of partial charges for the oxygen acceptors included in the correlation plot of ref. 14, making use of the parameters given in refs. 43 and 44, results in maximum values of only about  $|-0.7|$ , which compares with the maximum value of  $|-2|$  for the sulfur acceptors. Consequently the differences between oxygen acceptors should be clearly less pronounced than between sulfur acceptors. As far as the chlorine acceptors are concerned, which are included in the corresponding correlation plot of ref. 14, since the acceptors are exclusively monovalent chloride ions, the differences should be even negligible. In agreement with these expectations the scatters of points in the frequency–distance correlation plots, which are mainly determined by the differences between the proton acceptors, are found to decrease markedly within the series  $\text{W}\dots\text{S} < \text{W}\dots\text{O} < \text{W}\dots\text{Cl}$  [14].

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