

Interpretation of the Raman Spectra of Aqueous Acid Solutions in Terms of the Polarizability of Hydrogen Bonds

Part 1.—Aqueous HCl Solutions

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In the Raman spectra of pure water and aqueous HCl solutions a continuous scattering is found, similar to the continuous absorption observed with the i.r. spectra of acid solutions. The continuum of energy level differences probably arises from the extremely large proton polarisability of the hydrogen bond in the H_5O_2^+ grouping, since the large polarisability causes interaction effects of these hydrogen bonds with their environment, so shifting the energy levels. Below 300 cm^{-1} an extremely strong intensity increase for the acid solution is caused by the $\text{O} \cdots \text{O}$ stretching vibration. One reason for this Raman intensity may be the large change of the hydrogen bond polarisability caused by the proton as a function of the $\text{O} \cdots \text{O}$ distance in the hydrogen bond $(\text{OH} \cdots \text{O})^+$. The intensity of the H_2O torsional vibrations at 780 and 450 cm^{-1} rises, too, with increasing acid concentration, but not as strongly. This, also, may be explained by the large proton polarisability of the H-bond.

In many different liquid systems in which $(\text{BH} \cdots \text{B})^+$ or $(\text{BH} \cdots \text{B})^-$ hydrogen bonds are present, strong continua are observed in the infra-red spectra.¹⁻⁷ With acid solutions or acidic polyelectrolytes, these continua are considered to be caused by H_5O_2^+ groupings.^{1, 4} The reason suggested for these continua is the extremely large polarisability of the hydrogen bond caused by the proton in this grouping,⁸⁻¹⁰ since the polarisability causes various strong interaction effects of the hydrogen bonds with their environment.^{1, 4, 9-12} These interactions shift and split the energy levels of the vibrations of the hydrogen-bonded systems. Hence a continuum of energy level differences is observed in the i.r. spectra. The question arises: Is this continuum also observable in the Raman spectra and are the Raman intensities influenced by the polarisability of hydrogen bonds?

EXPERIMENTAL

PREPARATION OF THE SOLUTIONS

HCl and all salts are p.a. substances supplied by Merck, Darmstadt, West Germany. All solutions except the 12 N HCl solution were degassed with a low vacuum immediately before spectral plotting, and were prepared with triple-distilled water.

All spectra were taken with Raman spectrometer Cary 82 (triple monochromator) with multipass equipment, whereby the usual Cary liquid cell was used. The excitation radiation used was at 4880 Å (Spectra Physics, argon laser, model 165). Identical results were obtained with the excitation radiation at 6471 Å (Spectra Physics krypton laser, model 165). With all spectra the following conditions were kept exactly the same: the intensity of the radiation was kept constant (100 mW, controlled at the sample). Spectral band width 1.0 cm^{-1} . Sensitivity, see legends to the figures. Pen period 20 s with acids and 10 s with salt solutions. Registration speed $0.025\text{ cm}^{-1}/\text{s}$. The spectra were plotted without zero suppression. The reproducibility of the results was checked several times.

RESULTS

In fig. 1 are plotted the Raman spectrum of pure water and the Raman spectra of aqueous HCl solutions for a range of concentrations. The Raman spectra of water and electrolyte solutions have already been investigated and discussed by various authors.¹³⁻²⁵ In table 1 is given the assignment of the Raman bands of pure water.

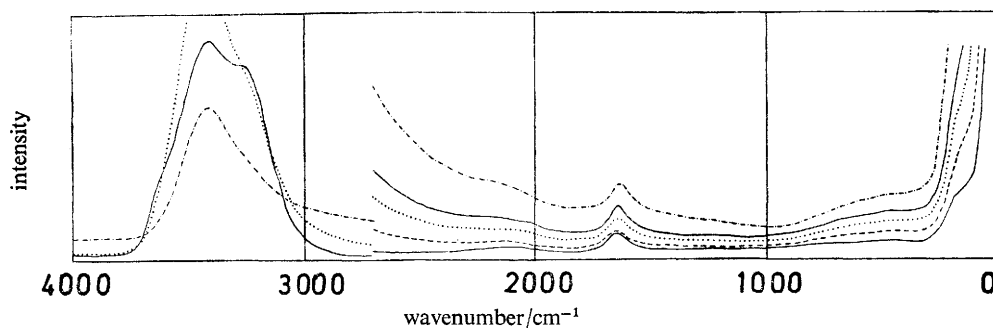


FIG. 1.—Raman spectra of aqueous HCl solutions at 20°C. Region 2700-0 cm^{-1} : counting the curves in the order of increasing background, the concentrations are 0.0; 2.0; 4.0; 6.0 and about 12 M HCl (sensitivity 10^3 c s^{-1} , f.s.d.). Region 4000-2700 cm^{-1} : — 0.0 and 4.0 M HCl (sensitivity $5 \times 10^3\text{ c s}^{-1}$, f.s.d.), - - - - 10 M HCl (sensitivity 10^4 c s^{-1} , f.s.d.)

TABLE 1.—THE RAMAN BANDS OF PURE WATER (IN cm^{-1}) (TAKEN FROM REF. (17), (19), (23))

60	see ref. (19)	
175	O...O stretching vibration	
450	torsional vibrations	
780		
1645	$\bar{\nu}_2$ H ₂ O scissor vibration	
2115	see ref. (1) p. 35	
3250	$2\bar{\nu}_2$	Fermi resonance ²⁶
3425	stretching vibration of the hydrogen-bonded OH groups	
3625	stretching vibration of the free OH groups	

On comparing the spectra of acid solutions with those of pure water, the following observations may be made:

(a) In contrast to pure water, with acid solutions a continuous scattering is observed, similar to the continuous absorption in the i.r. spectra,¹⁻⁷ which begins at the OH stretching vibration (at about 3000 cm^{-1}) and extends toward small wavenumbers. The intensity of this continuum rises with increasing acid concentration.

(b) The shoulder of the $\text{O} \cdots \text{O}$ stretching vibration which is observed in pure water at 175 cm^{-1} ¹³ becomes much stronger with increasing acid concentration, causing extremely strong scattering below 300 cm^{-1} . Hence, with the greatest HCl concentration an extremely strong broadening of the excitation line is observed.

(c) The torsional vibrations which are observed in pure water as a very weak band at 780 cm^{-1} , as well as equally weak band at about 450 cm^{-1} ,¹⁹ become more intense with increasing acid concentration. This effect is more pronounced with the band at 450 cm^{-1} .

Fig. 2 shows the Raman spectra of 4N aqueous alkali-halogenide solutions (for comparison spectra of pure water and 4N HCl).

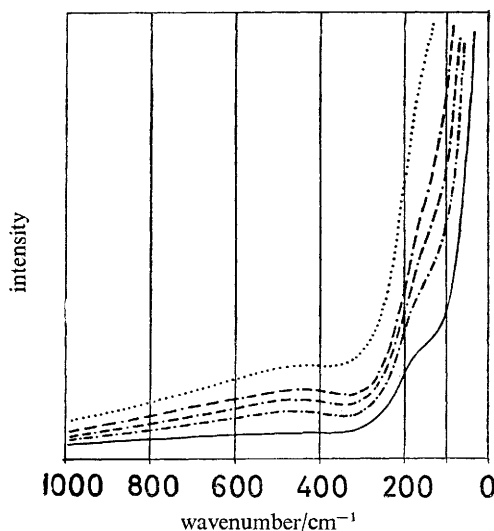


FIG. 2.—Raman spectra of pure water and 4N aqueous solutions (sensitivity 10^3 c.s.^{-1} , f.s.d.). Pure water —; LiCl - - - -; NaCl, KCl - - - - -; CsCl - - - - -; HCl (4 N)

(d) As compared with pure water a small broadening of the excitation line is also observed with the salt solutions. However, this effect is much less pronounced than with the acid solutions. The broadening of the excitation line increases from LiCl to CsCl solutions.

DISCUSSION

In fig. 3 are shown the two proton boundary structures of the H_5O_2^+ grouping with their environment.

The continuity of energy levels observed as continuum (result (a)) is likely to be caused, as in the infra-red spectrum, by the transitions of the excess proton in the hydrogen bond of the H_5O_2^+ ,^{1, 4, 9-11} whereby the coupling of these vibrations with other vibrations is of significance.^{9, 10}

The extremely strong intensity increase below 300 cm^{-1} (result (b)) can be explained as follows. Generally the Raman intensities are determined by the operator of the induced dipole moment as a function of the positions of the nuclei.²⁷ These relative transition probabilities are given by

$$A_{ij} = (\bar{\nu}_0 - \bar{\nu}_{ij})^4 \mu_{ij}^2 \quad (1)$$

whereby $\bar{\nu}_0$ is the wavenumber of the excitation line and $(\bar{\nu}_0 - \bar{\nu}_{ij})$ is the wavenumber

of the Raman line corresponding to the transition between the states i and j , μ_{ij} is the matrix element of the induced dipole moment.

In the following the induced dipole moment is considered as a linear function of the field strength.

$$\mu(q_1, q_2, \dots, q_k, E) = \alpha(q_1, q_2, \dots, q_k)E. \quad (2)$$

The normal coordinates of the vibrations are given by $q_1, q_2, \dots, q_k$; E is the amplitude of the electrical field strength of the excitation line. Only the components in bond direction are taken into account, since the polarisability in this direction is the dominating contribution. Usually $\alpha(q_1, q_2, \dots, q_k)$ is expanded in a Taylor series. In the case of small vibration amplitudes this expansion can be terminated at the linear term. Hence the usual formula for the relative transition probabilities

$$A_{ij} = (\bar{\nu}_0 - \bar{\nu}_{ij})^4 E^2 \left(\sum_{l=1}^k \left(\frac{\partial \alpha}{\partial q_l} \right)_0 \langle \psi_i | q_l | \psi_j \rangle \right)^2 \quad (3)$$

is obtained, whereby $\langle \psi_i | q_l | \psi_j \rangle$ are the transition moments between the states i and j .

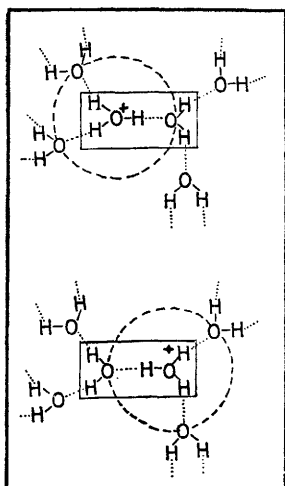


FIG. 3.—The two proton boundary structures of H_5O_2^+ with their environment.

With hydrogen bonds of the type $(\text{BH} \cdots \text{B})^+$, however, very large amplitudes may occur. The polarisability of $(\text{BH} \cdots \text{B})^+$ bonds may be two orders of magnitude larger than the usual polarisabilities of electron systems.⁸⁻¹⁰ This polarisability is caused by the proton motion in the $(\text{BH} \cdots \text{B})^+$ bond (for details see ref. (8)-(10)). Furthermore, this kind of polarisability may change very strongly with the $\text{O} \cdots \text{O}$ distance as shown by fig. 4. In this figure, the polarisability is plotted as a function of the $\text{O} \cdots \text{O}$ distance for different fields at the hydrogen bond ($0, 0.5 \times 10^7, 1.0 \times 10^7$ and $2.6 \times 10^7 \text{ V cm}^{-1}$ (data taken from ref. (10)).

When the wavenumber of the hydrogen bond stretching vibration $\bar{\nu}_{00}$ is smaller than the wavenumber of the proton fluctuation $\bar{\nu}_{\text{H}^+}$ in the hydrogen bond, μ in eqn (2) must be averaged over the proton positions in the sense of the adiabatic approximation.²⁸ In the case of H_5O_2^+ this condition

$$\bar{\nu}_{00} < \bar{\nu}_{\text{H}^+} \quad (4)$$

is fulfilled for $\text{O} \cdots \text{O}$ equilibrium distances up to about $2.6 \text{ \AA}$ in the symmetrical case, i.e., when no field is present at the hydrogen bond.¹⁰ With a rising electrical

field the wavenumber of the lowest OH transition $\bar{\nu}_{H^+}$ —in the symmetrical case the tunnelling transition—increases more and more. Thus with such fields the condition $\bar{\nu}_{00} < \bar{\nu}_{H^+}$ may be valid for larger O $\cdots$ O distances also. In fig. 4 in the region to the left of the dashed line this condition is fulfilled.¹⁰

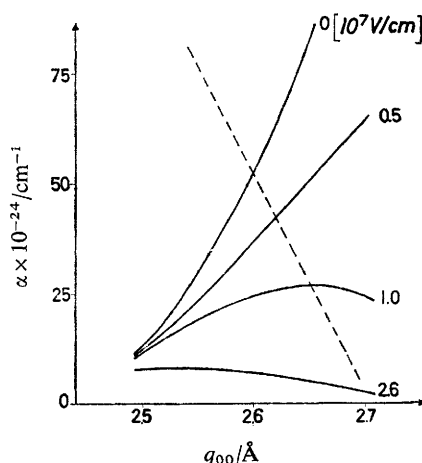


FIG. 4.—Polarisability of the hydrogen bond in $H_5O_2^+$ as a function of the O $\cdots$ O distance for different electrical field strengths (0, 0.5×10^7 , 1.0×10^7 and 2.6×10^7 V cm $^{-1}$).

In $H_5O_2^+$ isolated from its environment (fig. 3) the O $\cdots$ O stretching vibration is calculated to be 430 cm $^{-1}$.¹⁰ This value is in relatively good agreement with the value, 412 cm $^{-1}$, observed.²⁹ However, in the liquid state the $H_5O_2^+$ is not isolated, therefore the mean O $\cdots$ O bond strength in the network becomes weaker. Further, the O $\cdots$ O stretching vibration of $H_5O_2^+$ couples strongly with other O $\cdots$ O stretching vibrations in the neighbourhood. Thus the wavenumber of this O $\cdots$ O vibration of the network is lowered. Due to this lowering of the O $\cdots$ O stretching vibration the frequency condition, eqn (4), becomes more valid. Hence the polarisability caused by the proton motion might explain the high Raman intensity of the O $\cdots$ O vibration, and hence the very strong rise of the intensity in the range below 300 cm $^{-1}$ with increasing acid concentration (result (b)), because one must now substitute $\alpha = \alpha(q_{00})$ in eqn (2). Besides the polarisability of the hydrogen bonds, polarisabilities caused by rearrangement processes in the solvate structure network may also contribute to the scattering near the excitation line (see discussion on salt solutions).

The pronounced—but much less marked—intensity increase of the torsional vibrations (result (c)) may be explained similarly. The torsional vibrations of the water molecules change the potential well of the proton in the $H_5O_2^+$ and hence the polarisability of the hydrogen bond. With these wavenumber values one is, however, near the limit of validity of the wavenumber condition (eqn (4)).¹⁰ Hence the intensity of these vibrations is not as strongly increased by the proton polarisability of the hydrogen bond. The condition is more valid for the vibration at 450 cm $^{-1}$ than for the vibration at 780 cm $^{-1}$; therefore, the band at 450 cm $^{-1}$ becomes stronger.

SALT SOLUTIONS

The small broadening of the excitation line with salt solutions (fig. 2) (result (d)) may have a similar cause. The rearrangement processes in water and aqueous

solutions are connected with changes of the polarisability of these solutions. These rearrangement processes are, however, not very fast. Therefore the polarisability due to these rearrangement processes influences only very low wavenumber transitions, i.e., the transitions observed near the excitation line. Thus this broadening of the excitation line is probably strongly connected with the high frequency dielectric properties of the salt solutions.

The broadening of the excitation line increases from Li^+ to Cs^+ . Hence one should conclude that the rearrangement processes causing the polarisability are faster in the aqueous CsCl solutions than in the LiCl solutions.

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