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Raman spectra of water in the translational and librational regions

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Abstract. Raman depolarized and isotropic spectra of water at various temperatures in the 0–1600 cm⁻¹ range are discussed in terms of interaction-induced mechanisms involving the polarizabilities of an isolated molecule. The comparison between experimental and computer simulation results is also shown.

1. Introduction

A principal source of difficulty in interpreting the Raman spectrum of water is the lack of structure in its profile. Generally the observed spectral profiles are broad and have only indistinct features that are sensitive to temperature and pressure. The peculiarity of these spectral profiles together with the knowledge that the hydrogen bond (HB) interaction could, in principle, make water a unique liquid caused the study of the Raman spectrum of water to proceed independently of the studies on light scattering from simpler molecular liquids. Indeed, even recently [1–4], seemingly '*ad hoc*' decompositions of the spectral profiles into Gaussian or Lorentzian components have been performed in order to make inferences about the HB lifetime and local molecular environment in liquid water. These studies completely disregard the knowledge of the influence of interaction-induced phenomena on the Raman spectra of simple liquids, which has been placed on a sound basis in the last fifteen years [5].

After Madden's first attempt to evaluate the dipole-induced dipole (DID) contribution to the Raman spectrum of water [6], we began a systematic study of the translational and librational spectral regions [7–13]. Accurate measurements of the depolarization ratio, spectral lineshape and integrated intensity as a function of temperature have been compared with theoretical and computer simulation (CS) results. As in the case of non-hydrogen-bonded fluids [5], in our approach the terms of the multipole and polarizability series expansions [14] are considered as possible sources of the observed spectral features. Polarizability modulations directly related to the HB formation or other electronic overlap effects have been neglected. This allows us to isolate

the features actually arising from electronic disturbances brought about by HB formation and breaking, if any, in the experimental spectral profile.

2. Basic theory

According to the linear response theory, the k -independent Raman intensity is related to the Fourier transform of the time correlation function of the fluctuating macroscopic polarizability inside the scattering volume. In a molecular fluid this tensor can be expressed as the sum over the molecular sites of proper point polarizabilities, $\mathbf{P}^i(t)$, i.e. the polarizability of a molecule embedded in the field of all other molecules. The Cartesian components of $\mathbf{P}^i(t)$ in the laboratory frame are defined as

$$P_{\alpha\beta}^i(t) = \lim_{E^0 \rightarrow 0} \frac{\partial \mu_{\alpha}^i(t)}{\partial E_{\beta}^0} \quad (1)$$

where E^0 is the incident laser field and $\mu^i(t)$ is the effective dipole moment on the i th molecule. Following [14] $\mu^i(t)$ can be expanded in terms of the 'local' electric field on the i th molecule, E^i , and its gradient $(E^i)^i$, times the isolated molecule susceptibilities. As E^i is the superposition of the laser field and those generated by dipoles, quadrupoles and higher-order multipoles centred on each molecular site, we can finally write \mathbf{P}^i as the sum of the bare molecule polarizability, α^i , plus an interaction-induced contribution, Π^i , expressed in terms of isolated molecule electronic properties. Retaining only the first-order terms in the n -pole propagator, $\mathbf{T}^{(n)}(ij)$, one has

$$P_{\alpha\beta}^i = \alpha_{\alpha\beta}^i + \Pi_{\alpha\beta}^i = \alpha_{\alpha\beta}^i + \sum_{i \neq j} (\alpha_{\alpha\gamma}^i T_{\gamma\delta}^{(2)}(ij) \alpha_{\delta\beta}^j + \beta_{\alpha\beta\gamma}^i T_{\gamma\delta}^{(2)}(ij) \mu_{\delta}^j + \frac{1}{3} \alpha_{\alpha\epsilon}^i T_{\epsilon\gamma\delta}^{(3)}(ij) A_{\beta\gamma\delta}^j + \frac{1}{3} A_{\alpha\gamma\delta}^i T_{\epsilon\gamma\delta}^{(3)}(ij) \alpha_{\epsilon\beta}^j + \dots) \quad (2)$$

where β^i is the first hyperpolarizability and \mathbf{A}^i is the dipole–quadrupole polarizability.

Thus the Raman spectrum can be interpreted as the superposition of a contribution dependent on the permanent molecular polarizability alone, i.e. the allowed spectrum (AL), plus a contribution accounting for interactions between different molecules, usually referred to as 'collision-induced light scattering' (CILS). The AL spectrum is related to the single-particle translational and orientational motion through the trace of the polarizability tensor, α , and its anisotropy, δ , respectively. The most relevant CILS intensity comes from the three contributions shown in equation (2): the ' $\beta T \mu$ ', the ' $\alpha T A$ ' and the first and better known DID term. The latter can be separated into a large contribution arising from the isotropic part of the scatterer's polarizability (IDID or ' $\alpha T \alpha$ ') plus a smaller one containing the optical anisotropy (' $\delta T \delta$ ' and ' $\delta T \delta$ '). Since for the water molecule $\delta \ll \alpha$, the ' $\delta T \delta$ ' contribution can be safely neglected.

The IDID contribution, involving only a second-rank tensor, gives a depolarization ratio, $R = I_{HV}/I_{VV}$, independent of frequency and equal to 0.75, as for the AL spectrum in this spectral region. As far as the other CILS contributions are concerned, under some simplifying assumption one has [9]

$$\alpha T \delta R = 21/68 \quad \alpha T A R \geq 9/37 \quad \beta T \mu R \geq 2/11. \quad (3)$$

As a consequence the AL and IDID scatterings only contribute to the depolarized

spectrum, while the ' $\alpha T\delta$ ', ' αTA ' and ' $\beta T\mu$ ' contributions can in principle appear in both depolarized, $I_{\text{dep}} = I_{HV}$, and isotropic spectra, $I_{\text{iso}} = I_{VV} - \frac{2}{3}I_{HV}$ [15].

3. Experimental data

Polarized, I_{VV} , and depolarized, I_{HV} , Raman spectra of high purity H_2O and D_2O have been recorded in the $0\text{--}1500\text{ cm}^{-1}$ frequency range at various temperatures ranging from $-20\text{ }^\circ\text{C}$ up to $80\text{ }^\circ\text{C}$. Details concerning the experimental procedure can be found in [9], [10] and [13]. Accurate measurements of the depolarization ratio as a function of frequency are of crucial importance to our purpose and a detailed analysis of the maximum systematic error affecting our measurements is performed in [9]. The experimental depolarization ratio $R(\nu)$ stays below 0.75, even at low-frequency shifts ($\nu \approx 10\text{ cm}^{-1}$), and decreases at higher frequencies. This indicates the presence of a quite intense and broad isotropic contribution, which can arise from ' $\alpha T\delta$ ', ' αTA ' and ' $\beta T\mu$ ' terms. The isotropic spectra of water are characterized by an almost exponential low-frequency contribution (with a characteristic frequency $\nu_0 = 80\text{ cm}^{-1}$), followed by a broad band extending up to the bending mode. The temperature behaviour of this isotropic spectrum suggests [10] that it should arise from at least two distinct spectral contributions: one confined at low frequencies ($\nu \leq 800\text{ cm}^{-1}$), $^{\text{LF}}I_{\text{iso}}$, and the other centred around 1000 cm^{-1} , $^{\text{HF}}I_{\text{iso}}$. The comparison between D_2O and H_2O spectra states that the dynamical origin of $^{\text{HF}}I_{\text{iso}}$ is librational, while both translational and librational dynamics are responsible for the polarizability modulations related to $^{\text{LF}}I_{\text{iso}}$.

As far as the depolarized spectrum is concerned, the most peculiar features of these spectra are a weak band at 180 cm^{-1} and a light scattering excess (LSE) of quasi-Lorentzian shape in the $0\text{--}30\text{ cm}^{-1}$ region. These features have been widely studied in the past [1, 3, 16–22] in order to test structural models for water or extract information about the HB lifetime. However, as far as the LSE is concerned we want to stress that an accurate study of its intensity relative to the Brillouin doublet [13] contradicts the hypothesis that this feature is directly related to the HB breaking or to the allowed rotational spectrum alone.

4. Comparison with cs results and discussion

Computer simulations of the relevant depolarized and isotropic contributions to the Raman spectrum of water have been reported recently and compared with experimental data [11–12]. This study has definitively clarified the following points:

(i) The depolarized Raman spectrum is dominated by the pure IDID contribution, which shows the well known 180 cm^{-1} band. The agreement with the experimental spectra is impressive up to 300 cm^{-1} and for the absolute intensity (see figures 1 and 2); at higher frequencies a tail ascribable to the allowed spectrum plus higher-order depolarized induced contributions appears in the experimental data. Since the IDID contribution, which is related to the relative translational dynamics of molecular pairs, masks all other spectral contributions, the librational dynamics cannot be studied using only the depolarized spectra.

(ii) The LSE is also mainly due to the IDID modulation (see [12]). As in simple fluids the IDID lineshape is almost exponential, the appearance of structures in the profiles of

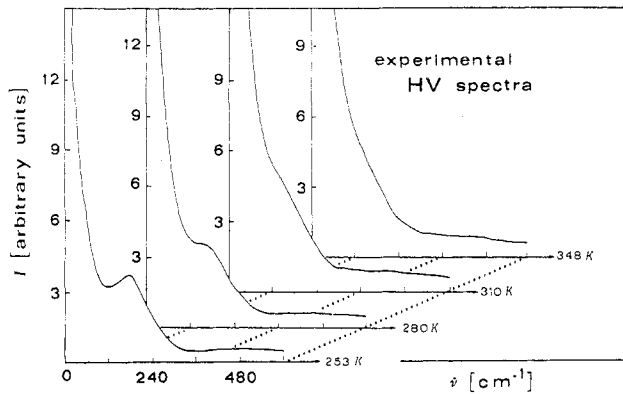


Figure 1. Experimental depolarized spectra of water.

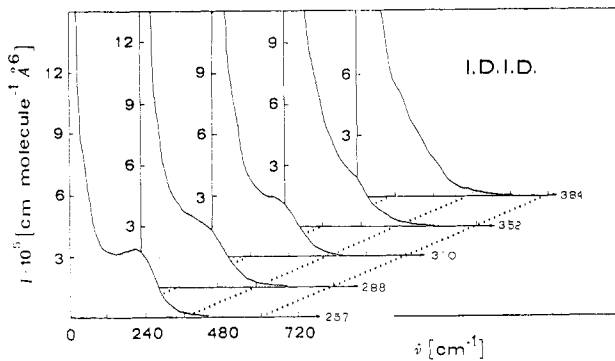


Figure 2. IDID contribution to the Raman spectra of water as evaluated by computer simulation. The labels refer to the molecular dynamics runs and are in obvious correspondence with the average run temperature in K.

water spectra gives evidence of the hindrances a molecule experiences in its translational motion, owing to the presence of HB. However, no direct information about the HB network can be derived by the observation of these structures.

(iii) The ' $\alpha T\delta$ ', ' $\beta T\mu$ ' and ' αTA ' isotropic spectra have the same profile, the latter being the most intense. Their contribution accounts well for the low-frequency component of the isotropic spectrum extracted in [10]. This confirms that accurate depolarization ratio measurements are needed, in order to study the orientational dynamics of water.

(iv) No contribution at frequencies higher than 800 cm^{-1} appears in the simulated spectra. This result together with the observation that the temperature behaviour of the zeroth moment of $I_{\text{iso}}^{\text{HF}}$ is of the Arrhenius type, suggests that this spectral contribution could arise from short-range polarizability modulations somehow related to the HB formation and breaking.

In conclusion, most of the peculiarity of the Raman spectrum of water can be interpreted as collision-induced contributions, such as in normal liquids, whereas the

relevant scattering at twice the librational frequencies, namely ${}^{\text{HF}}I_{\text{iso}}$, and probably the intensity at twice the bending frequency [23] are genuine anomalies with respect to the behaviour of non-hydrogen-bonded liquids.

References

- [1] Walrafen G E, Hokmabadi M S and Yang W H 1986 *J. Chem. Phys.* **85** 6964
- [2] Walrafen G E, Fisher M R, Hokmabadi M S and Yang W H 1986 *J. Chem. Phys.* **85** 6970
- [3] Conde O and Teixeira J 1983 *J. Physique* **44** 525
- [4] D'Arrigo G, Maisano G, Mallamace F, Migliardo P and Wanderlingh F 1981 *J. Chem. Phys.* **75** 4264
- [5] Birnbaum G (ed) 1985 *Phenomena Induced by Intermolecular Interactions* (New York: Plenum)
- [6] Madden P A and Impey R W 1986 *Chem. Phys. Lett.* **123** 502
- [7] De Santis A, Sampoli M, Mazzacurati V and Ricci M A 1987 *Chem. Phys. Lett.* **133** 381
- [8] Frattini R, Sampoli M, Ricci M A and Ruocco G 1987 *Chem. Phys. Lett.* **141** 297
- [9] De Santis A, Frattini R, Sampoli M, Mazzacurati V, Nardone M, Ricci M A and Ruocco G 1987 *Mol. Phys.* **61** 1199
- [10] Benassi P, Mazzacurati V, Nardone M, Ricci M A, Ruocco G, De Santis A, Frattini R and Sampoli M 1987 *Mol. Phys.* **62** 1467
- [11] Ricci M A, Ruocco G and Sampoli M 1989 *Mol. Phys.* **67** 19
- [12] Mazzacurati V, Ricci M A, Ruocco G and Sampoli M 1989 *Chem. Phys. Lett.* **159** 383
- [13] Mazzacurati V, Nucara A, Ricci M A, Ruocco G and Signorelli G 1990 *J. Chem. Phys.* submitted
- [14] Buckingham A D 1967 *Adv. Chem. Phys.* **12** 107
Buckingham A D and Orr B J 1967 *Q. Rev. Chem. Soc.* **21** 195
- [15] We follow the notation given by
Berne B J and Pecora R 1976 *Dynamic Light Scattering* (New York: Wiley)
- [16] Krishnamurthy S, Bansil R and Wiafe-Akenten J 1983 *J. Chem. Phys.* **79** 5863
- [17] Yeh Y, Bilgram J and Kanzig W 1982 *J. Chem. Phys.* **77** 2317
- [18] Montrose C J, Bucaro J A, Marshall-Coakley J and Litovitz T A 1974 *J. Chem. Phys.* **60** 5025
- [19] Brooker M H and Perrot M 1981 *J. Chem. Phys.* **74** 2795
- [20] Moskovitz M and Michaelian K H 1978 *J. Chem. Phys.* **69** 2306
- [21] Danninger W and Zundel G 1981 *J. Chem. Phys.* **74** 2769
- [22] Mazzacurati V and Benassi P 1987 *Chem. Phys.* **112** 147
- [23] Andreani C, Baciocco G, Postorino P and Ricci M A to be published