Evidence of Quantum Correlation Effects of Protons and Deuterons in the Raman Spectra of Liquid H_2O-D_2O

C. A. Chatzidimitriou-Dreismann,* U. K. Krieger, A. Möller, and M. Stern
I. N. Stranski-Institute for Physical and Theoretical Chemistry, Technical University of Berlin, Str. d. 17. Juni 112, D-10623 Berlin, Germany

(Received 2 March 1994)

Measurements of the intrinsic Raman scattering activity of the stretching vibrational regime of H_2O, D_2O, and their mixtures at room temperature reveal an "anomalous" behavior. The data are analyzed in connection with neutron scattering results and analytical and numerical quantum mechanical studies, which showed the constancy of the microstructure of water with respect to H/D substitution. The Raman scattering results are unequivocally in conflict with at least one of the assumptions: (i) validity of the Born-Oppenheimer approximation, (ii) classical character of H and D nuclei.

PACS numbers: 78.30.Cp, 33.90.+h, 67.20.+k

Proton quantum tunneling and H-bond quantum dynamics in condensed systems are indispensable for the understanding of many important physical, chemical, and biological processes; e.g., quantum tunneling is known to be responsible for the high conductance of H^+ in water and ice [1,2], H bonding in liquid water was very recently described with the aid of *ab initio* quantum molecular dynamics [3], and it was suggested that protonic quantum effects may play some role in the H-bond stability of DNA base pairs [4,5]. All thus far existing spectroscopic investigations of water (and other condensed systems) at room temperature, however, did not reveal any clear evidence of a nonclassical character of protons, cf. Ref. [3]. Motivated by recent predictions [6], we searched for an "anomalous" component in the intrinsic Raman scattering activity of the OH and OD stretching vibrational bands of H_2O-D_2O mixtures. As is well known, the considerable width of these bands is caused by the H- and D-bond networks. In the following we will show that the presented data, in connection with extensive neutron scattering results [7,8], provide for the first time strong evidence for the existence of (short-lived [6]) protonic quantum correlations in liquid water.

For the assessment of the Raman data presented below, the knowledge of the existing most precise neutron scattering (or diffraction) results [7,8] on the same systems is indispensable. In analyzing these data, it is assumed that either the microscopic structures of liquid H_2O and D_2O are equal [7] or the scattering data are considered to be caused by the weighted average (given by the H/D mole fraction) of light and heavy water structures [8]. In any case, however, all data are fully consistent with the usual (see below) expectation that the microstructures of light, heavy water, as well as their mixtures are almost equal. Possible differences—due to the quantum character of H and D—are considered to be below measuring accuracies associated with all pair-correlation functions and/or partial structure factors [3,7–9]. This is furthermore supported by a certain quantum mechanical study [10], which showed that the nuclear quantum corrections to the structure of water, due to isotropic H/D substitution, are very small indeed; cf. also Refs. [3,9]. (In Ref. [10], however, intramolecular degrees of freedom have not been considered.) This finding is consistent with the well-known Born-Oppenheimer (BO) approximation, which we assume here to be valid (in agreement with Refs. [3,7–10] as well as "common belief").

Furthermore, it is crucial to stress the following two alternative points concerning H/D substitution: (A) If all molecules (i.e., H_2O, D_2O, and HDO) behave classically, then it follows easily that all pair-correlation functions $g_{XX}(r)$ and $g_{XO}(r)$ ($X =$ H,D) remain unchanged. (B) If the molecules behave quantum mechanically [10], then these equations do not hold strictly; however, the above neutron experiments imply that $g_{HH}(r) \approx g_{DD}(r) \approx g_{HD}(r)$ and $g_{HO}(r) \approx g_{DO}(r)$, where the sign "$\approx$" means "equal within measuring accuracy." Thus, in both cases we observe a "constancy of the microstructure" of water. According to the BO approximation we are then forced to conclude that H/D substitution leaves the electron density distribution in liquid water (and/or the wave function of different clusters of water molecules [3]) essentially unchanged. Therefore, the same holds for all possible intramolecular and intermolecular interactions (e.g., dipole-dipole). This conclusion is confirmed by the most recent infrared [11] and dielectric relaxation [12] experiments on H_2O-D_2O, too. These physical considerations imply that the total Raman intensities of the OH and OD Stretching spectral regions (cf. Fig. 1) must be strictly proportional to the number of the scattering OH and OD oscillators in the H_2O-D_2O mixtures. Surprisingly, however, the Raman data presented in the following are in clear contrast to this proportionality.

Our experiment consists simply in the determination of the integral Raman scattering cross sections of the OH and OD stretching vibrational bands of H_2O-D_2O mixtures and their comparison with the corresponding cross sections of pure H_2O and pure D_2O. The experimental method used is as follows: Samples were prepared under a dry N_2 atmosphere using purified water (obtained from a Millipore purification system, $\rho > 18$ MΩ cm) and D_2O (Sigma

0031-9007/95/75(16)/3008(4)$06.00

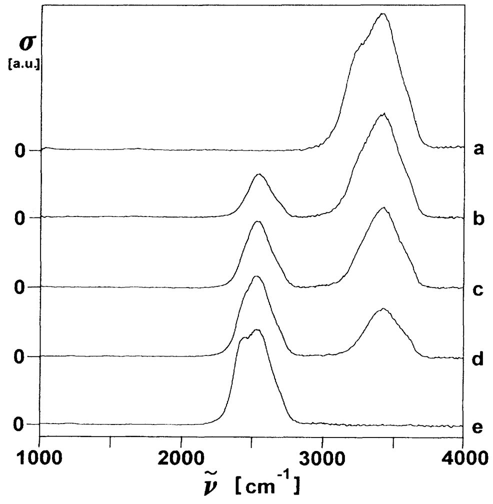

FIG. 1. Some typical Raman scattering cross sections ($T = 20\,°C$) vs Stokes frequency shift for (a) pure water, (e) pure heavy water, and H_2O-D_2O mixtures with the following H:D atom compositions: (b) H:D = 7:3, (c) H:D = 5:5, and (d) H:D = 3:7. Cross sections are in arbitrary units; same ordinate scale is used for all spectra. For convenience, spectra are parallel shifted along the ordinate, and the zeros mark the positions of their baselines. Spectra are presented as measured, i.e., without any smoothing and/or base-line corrections.

Chemical, D content >99.9%). All probes were filtered twice through a Millipore filter (pore diameter 0.2 μm). Spectra were recorded in a $X(Z, X + Z)Y$ orientation with the collection angle at 90° to the laser beam (being in the X direction), using a 50 cm collection achromat. A stabilized Ar^+ laser operating at 514.5 nm and a spectragraph in a Czerny-Turner configuration (focal length $f = 32$ cm, aperture $f/4.2$, grating 300 grooves/mm, entrance slid width 260 μm) with an optical-multichannel-analyzer (OMA) detection system (SIT-Vidikon) allowed the simultaneous measurement of the complete spectrum from 1000 to 4000 cm^{-1}. The count rate was typically 13 000 counts/(sec channel) in the OH stretching region of water. The laser intensity was monitored continuously by a separate photon counting system. The spectra shown were accumulated over 64 s, corrected for dark counts, a constant offset inherent to the detection system, and the spectral response of the spectrograph and photocathode. Frequency reduction was performed in the standard way, i.e., by multiplying the measured intensity $I(\nu)$ by the factor $\nu(1 - \exp[-h\nu/kT])/(\nu_L - \nu)^4$, where ν_L is the frequency of the laser light and ν is the frequency difference of the scattered light (i.e., the Raman shift); compare, e.g., Refs. [13,14]. This transformation is necessary in order to obtain the intrinsic molar scattering activity or, equivalently, the scattering cross section for a Raman process. The temperature was about 20 °C.

Some examples of the measured, individual Raman spectra are shown in Fig. 1. These graphs also demonstrate one important advantage—for our purposes—of the Raman effect as compared with the infrared absorption [11]: the OH- and OD-spectral domains are well separated, and the bending (around 1600 cm^{-1} for water) and the combination vibration (around 2100 cm^{-1} for water) bands are extremely weak; cf. also Refs. [13–15]. As a consequence, our results are completely free of any data fitting and/or deconvolution procedure. Furthermore, our apparatus measures the complete spectral region of interest simultaneously, thus increasing the precision of the intensity measurements considerably.

The first feature of our effect is presented in Fig. 2. The quotient $Q = \sigma^{\mathrm{H}}/\sigma^{\mathrm{D}}$ gives the ratio between the integral Raman scattering cross sections of the OH stretching and that of the OD stretching vibration. Repeated measurements of the corresponding cross sections of pure H_2O and pure D_2O gave for Q the value $Q_{\text{pure}} = 1.96$ (maximal error ± 0.02), as represented by the straight line in Fig. 2. The Q values for different H_2O-D_2O mixtures—as described by the D atom fraction X_{D}—are given by the points, representing four independent experimental series. The determination of Q for the mixtures is independent from that of Q_{pure}. The unexpected "anomaly" is represented here by the large difference between Q_{pure} and the Q values of all mixtures. Note also that Q varies with H/D composition of the mixture. Our data for pure H_2O and pure D_2O are in agreement with those of Scherer, Go, and Kint [14]. (The comparison is based on Crawford's intensity sum rule [16]; a paper is in preparation.)

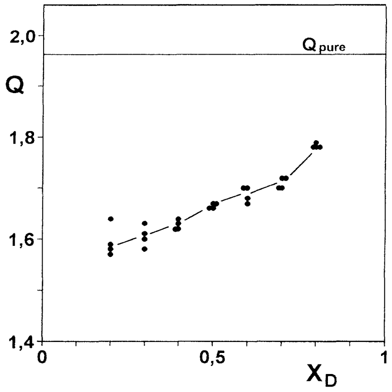

FIG. 2. The quotient $Q = \sigma^{\mathrm{H}}/\sigma^{\mathrm{D}}$ of the integral Raman scattering cross sections of the OH stretching and that of the OD stretching vibration vs the mole fraction X_{D} of deuterium. σ^{H} is integrated between 2810 and 3780 cm^{-1}; σ^{D} is integrated between 2110 and 2810 cm^{-1}. The typical number of photoelectron counts associated with each value of σ^{H} and σ^{D} is about 4×10^8. Overlapping Q data points of the mixtures are slightly shifted along the abscissa to make them visible. The straight lines connecting the points are guides to the eye. $Q_{\text{pure}} = 1.96$ (maximal error ± 0.02) is the quotient Q defined above for pure H_2O and pure D_2O, and its magnitude is marked by the horizontal line. Note the large differences between Q_{pure} and the Q values of all mixtures, which are related with the anomalous effect under consideration.

The second feature of our effect, presented in Fig. 3, throws more light on this effect. Let $\Delta\sigma^{\mathrm{H}} = (\sigma^{\mathrm{H}}_{\mathrm{mix}} - \sigma^{\mathrm{H}}_{\mathrm{pure}})/\sigma^{\mathrm{H}}_{\mathrm{pure}}$ represent the relative deviation of the considered OH-vibronic integral cross section for a mixture, $\sigma^{\mathrm{H}}_{\mathrm{mix}}$, from that of pure water, $\sigma^{\mathrm{H}}_{\mathrm{pure}}$. $\Delta\sigma^{\mathrm{D}}$ is defined analogously. The deviation $\Delta\sigma^{\mathrm{H}}$ decreases with decreasing protonic concentration [H], i.e., with increasing X_{D}, whereas, on the contrary, $\Delta\sigma^{\mathrm{D}}$ increases with decreasing concentration [D]. This is the most surprising feature of the considered anomalous effect. Note also the substantial differences in magnitude and shape of the functions $\Delta\sigma^{\mathrm{H}}$ and $\Delta\sigma^{\mathrm{D}}$.

The revealed anomaly is given by the facts that the Raman integral intensities exhibit a large deviation from the expected proportionality to the number of the existing OH and OD "particles" and—at the same time—that $\Delta\sigma^{\mathrm{H}}$ and $\Delta\sigma^{\mathrm{D}}$ have different signs. One should also emphasize the striking differences in the Raman scattering behavior of the mixtures having the same HDO, but different H_2O and D_2O concentrations (e.g., those with $X_{\mathrm{D}} = 0.3$ and $X_{\mathrm{D}} = 0.7$). Therefore one cannot extract "individual" spectra (or well-defined Raman cross sections) of the "components" H_2O, D_2O, and HDO from the measured spectra of the mixtures. This result is qualitatively in contrast to all known conventional expectations; cf. Refs. [11,15].

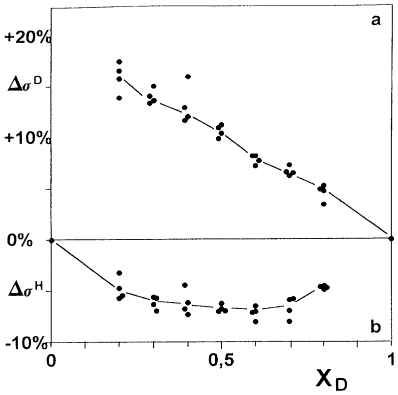

FIG. 3. (a) Relative deviation of the OD-vibronic integral cross section of the mixtures from that of pure D_2O, i.e., $\Delta\sigma^{\mathrm{D}} = (\sigma^{\mathrm{D}}_{\mathrm{mix}} - \sigma^{\mathrm{D}}_{\mathrm{pure}})/\sigma^{\mathrm{D}}_{\mathrm{pure}}$ vs the D atom mole fraction of the mixtures. (b) Relative deviation of the OH-vibronic integral cross section of the mixtures from that of pure H_2O, i.e., $\Delta\sigma^{\mathrm{H}} = (\sigma^{\mathrm{H}}_{\mathrm{mix}} - \sigma^{\mathrm{H}}_{\mathrm{pure}})/\sigma^{\mathrm{H}}_{\mathrm{pure}}$ vs the D atom mole fraction of the mixtures. Overlapping data points are slightly shifted along the abscissa to make them visible. The straight lines are guides to the eye. These deviations represent the most significant features of the effect under consideration, since, e.g., they show that the considered Raman scattering intensities are not strictly proportional to the number of fermionic OH and bosonic OD oscillators. Note that $\Delta\sigma^{\mathrm{H}}$ decreases with decreasing protonic concentration [H], whereas, on the contrary, $\Delta\sigma^{\mathrm{D}}$ increases with decreasing concentration [D].

From first sight, one could think that possible intermolecular couplings between OH and (and OD) oscillators may explain the observed effect. (This thought may be motivated by the attenuation of the low-frequency shoulders of both OH and OD stretching vibrational bands in the mixtures, which are conventionally attributed to the symmetric vibrational modes; cf. Fig. 1.) This possibility, however, can be easily ruled out: In a mixture with $X_{\mathrm{D}} = 0.5$, the OH and OD oscillatory modes are decoupled to the same degree. This may explain the finding $\Delta\sigma^{\mathrm{H}} < 0$, since one naturally may assume that coupling between different OH oscillators is tantamount to an increased cross section σ^{H}. Exactly the same argument, however, implies $\Delta\sigma^{\mathrm{D}} < 0$ too, which completely contradicts the experimental result.

Summarizing the above considerations, let us stress that if the BO approximation is valid and the constancy of the microstructure of water holds, then one should have (A) $\Delta\sigma^{\mathrm{H}} \approx \Delta\sigma^{\mathrm{D}} \approx 0$ in the (crude) approximation of "independent oscillators," or (B) $\Delta\sigma^{\mathrm{H}} \approx \Delta\sigma^{\mathrm{D}} < 0$ due to the decoupling of the oscillators in the mixtures, for all X_{D}. Thus the existence of intermolecular couplings between OH and (and OD) vibrational modes—in connection with the BO approximation—cannot explain the *different* signs of $\Delta\sigma^{\mathrm{H}}$ and $\Delta\sigma^{\mathrm{D}}$. These remarks conclusively demonstrate that even a qualitative explanation of the revealed effect is hardly conceivable in the frame of conventional theories.

The present experiment has been motivated by recent theoretical [6] and experimental investigations concerning short-lived and spatially restricted quantum correlated domains of protons in water [17], which have no classical analog. In this context, an anomalous light scattering component was predicted [6]. The lifetime of such quantum correlations is often called decoherence time [18].

A quantal model (being conceptually related with the general theory [6]) may now give corroborating evidence for the quantum nature of the above effects. This model concerns the (short-time [6]) quantum correlations (or interference) of *pairs* of oscillators. For every pair of fermionic OH oscillators (spin = 1/2) one simply finds three antisymmetric (odd-parity) $\Phi^{\mathrm{H}}_{-}(r_1, r_2)$ and one symmetric (even-parity) $\Phi^{\mathrm{H}}_{+}(r_1, r_2)$ linearly independent *spatial* wave functions [19] (since the total wave function is antisymmetric). Correspondingly, for a pair of bosonic OD oscillators (spin = 1) one has three antisymmetric $\Phi^{\mathrm{D}}_{-}(r_1, r_2)$ and six symmetric $\Phi^{\mathrm{D}}_{+}(r_1, r_2)$ functions [19]. r_1 and r_2 may represent the center-of-gravity coordinates.

The crucial point now is that *only the odd parity* Φ_{-}'s may contribute to the scattering cross sections, whereas there are vanishing contributions from the Φ_{+}.'s To show this, let us remark that the quantum state of the pair after Stokes excitation may be naturally represented by the uncorrelated product function $\phi^{\mathrm{ex}}(r_1)\phi^{\mathrm{gr}}(r_2)$; i.e., the vibronic excitation energy is well localized in one of the oscillators. The parity of the ϕ's with respect to the coordinates shown is even. (r_1 and r_2 can be interchanged. The upper indices denote vibronic excited and ground states.) Note that the standard interaction Hamiltonian $H_I = -(\partial\alpha/\partial r^{\mathrm{vibr}}) r^{\mathrm{vibr}} E(t) E(t)$ which effectuates the Raman process [20] depends only on the internal vibrational coordinates r^{vibr} of the OH and OD oscillators (not explicitly shown in the above wave functions). As is well known, the parities of ϕ^{ex} and ϕ^{gr} with respect to r^{vibr} are -1 and $+1$, respectively; Φ_- and Φ_+ have r^{vibr} parity equal to $+1$, since they are associated with vibrational ground states. The further reasoning uses a well-known "symmetry" argument (regarding spectroscopic transitions): The cross sections under consideration depend on the matrix elements $M = \langle \Phi_\pm | H_I | \phi^{\mathrm{ex}} \phi^{\mathrm{gr}} \rangle$. Let us now consider the inversion of all relevant coordinates appearing in M: $r_{1,2} \rightarrow -r_{1,2}$ and $r^{\mathrm{vibr}} \rightarrow -r^{\mathrm{vibr}}$. According to the parities mentioned above and the explicit form of H_I, the complete parity of the expression in M is equal to $+1$ for Φ_- (and thus also $M \neq 0$), and equal to -1 for Φ_+ (and thus $M = 0$). This concludes the proof.

Let us now apply quantitatively the model to the case of pure H_2O (and D_2O) and the mixture with $X_D = 0.5$. Let p_{qc} be the part of quantum correlated OH and OD oscillators in the pure substances. In the mixture, the above quantum correlations are to a large extent removed due to the spin and mass superselection rules concerning protons and deuterons [6,17]. For simplicity of the calculation [21] let us assume now that all these quantum correlations are broken, and thus that $\sigma^{\mathrm{H}}_{\mathrm{mix}}(0.5)$ is due only to "classical" single OH oscillators with scattering cross section $\sigma^{\mathrm{H}}_{\mathrm{clas}}$. The cross section of a proton participating to a quantum correlated OH pair may be then represented by $F_{\mathrm{qc}}\sigma^{\mathrm{H}}_{\mathrm{clas}}$, where F_{qc} is some amplifying factor (> 1). (Since oscillator pairs are considered, one intuitively expects that $F_{\mathrm{qc}} \approx 2$.) Furthermore, Fig. 3 tells us that $\sigma^{\mathrm{H}}_{\mathrm{pure}} \approx (1 + 0.075)\sigma^{\mathrm{H}}_{\mathrm{mix}}(0.5)$. Thus we obtain straightforwardly the following equation: $\sigma^{\mathrm{H}}_{\mathrm{clas}}[(1 - p_{\mathrm{qc}}) + p_{\mathrm{qc}}(3/4)F_{\mathrm{qc}}] = 1.075\sigma^{\mathrm{H}}_{\mathrm{clas}}$. The first term on the left-hand side, $\sigma^{\mathrm{H}}_{\mathrm{clas}}(1 - p_{\mathrm{qc}})$, represents the contribution of the uncorrelated (or classical) OH oscillators to the measured scattering cross section. The second term, $\sigma^{\mathrm{H}}_{\mathrm{clas}} p_{\mathrm{qc}}(3/4)F_{\mathrm{qc}}$, represents the contribution due to the quantum correlated pairs with an odd-parity spatial wave function. (Remember that only these can contribute to the measured cross section; see above.) In the case of D_2O and the mixture, Fig. 3 tells us that $\sigma^{\mathrm{D}}_{\mathrm{pure}} \approx (1 - 0.10)\sigma^{\mathrm{D}}_{\mathrm{mix}}(0.5)$ and thus, with similar notation, we obtain analogously $\sigma^{\mathrm{D}}_{\mathrm{clas}}[(1 - p_{\mathrm{qc}}) + p_{\mathrm{qc}}(3/9)F_{\mathrm{qc}}] = 0.90\sigma^{\mathrm{D}}_{\mathrm{clas}}$. [In both cases we have assumed the same amplifying factor F_{qc}, since the external field $E(t)$ couples with the "electronic clouds" of the oscillators.]

From these two linear equations one easily derives with some algebra $F_{\mathrm{qc}} \approx 1.75$ (which lies near the intuitively expected value of 2), and $p_{\mathrm{qc}} \approx 0.24$. In other words, the model yields the remarkable results that about 24% of the OH (or OD) oscillators appear to be quantum correlated [6,17] in pure H_2O (or pure D_2O). (Of course, due to the thermal motion one cannot expect that all oscillators may be quantum correlated.) The crucial point is, however, that the "perplexing" experimental findings $\Delta\sigma^{\mathrm{H}} < 0$ and $\Delta\sigma^{\mathrm{D}} > 0$ are naturally explained on the same footing and from first quantum mechanical principles. Further work is in progress.

C. A. C.-D. wishes to thank Professor Erik Karlsson (Uppsala) for helpful discussions. This work was supported in part by the Fonds der Chemischen Industrie (Frankfurt am Main).

---

*To whom correspondence should be addressed.

[1] M. Eigen and L. de Maeyer, Proc. R. Soc. London A **247**, 505 (1958).

[2] M. Eigen, Angew. Chem. Int. Ed. Engl. **3**, 1 (1964).

[3] K. Laasonen, M. Sprik, M. Parrinello, and R. Car, J. Chem. Phys. **99**, 9080 (1993).

[4] Y. S. Kong, M. S. Jhon, and P.-O. Löwdin, Int. J. Quantum Chem. Quantum Biol. Symp. **14**, 189 (1987).

[5] C. A. Chatzidmitriou-Dreismann, Helv. Chim. Acta **75**, 2252 (1992).

[6] C. A. Chatzidmitriou-Dreismann, Adv. Chem. Phys. **80**, 201 (1991); Int. J. Quantum Chem. **23**, 153 (1989).

[7] W. E. Thiessen and A. H. Narten, J. Chem. Phys. **77**, 2656 (1982).

[8] A. K. Soper and M. G. Phillips, Chem. Phys. **107**, 47 (1986).

[9] A. K. Soper and J. Turner, Int. J. Mod. Phys. B **7**, 3049 (1993).

[10] R. A. Kuharski and P. J. Rossky, J. Chem. Phys. **82**, 5164 (1985).

[11] Y. Maréchal, J. Chem. Phys. **95**, 5565 (1991).

[12] U. Kaatze, Chem. Phys. Lett. **203**, 1 (1993).

[13] M. H. Brooker, G. Hancock, B. C. Rice, and J. Shapter, J. Raman Spectrosc. **20**, 683 (1989).

[14] J. R. Scherer, M. K. Go, and S. Kint, J. Phys. Chem. **78**, 1304 (1974); **77**, 2108 (1973).

[15] G. E. Walrafen, in *Water—A comprehensive Treatise,* edited by F. Franks (Plenum Press, New York, 1972), Vol. 1, pp. 151–214.

[16] B. Crawford, J. Chem. Phys. **20**, 977 (1952).

[17] H. Weingärtner and C. A. Chatzidimitriou-Dreismann, Nature (London) **346**, 548 (1990).

[18] W. H. Zurek, Phys. Today **44**, 36 (1991); W. H. Zurek and J. P. Paz, Phys. Rev. Lett. **72**, 2508 (1994); M. Gell-Mann and J. B. Hartle, Phys. Rev. D **47**, 3345 (1993); R. Omnès, Rev. Mod. Phys. **64**, 339 (1992).

[19] R. P. Feynman, R. B. Beighton, and M. Sands, *Lectures on Physics* (Addison-Wesley, Reading, 1966), Vol. III.

[20] A. Yariv, *Quantum Electronics* (Wiley, New York, 1989).

[21] An "improved" model, which takes into account the chemical H/D equilibrium in the mixtures, does not alter essentially the following conclusions..