

# Raman Spectra of D<sub>2</sub> in Water and Ice<sup>†</sup>

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Raman spectra of D<sub>2</sub> in H<sub>2</sub>O and D<sub>2</sub>O, both liquid and ice, are presented. The results are compared to previous results on H<sub>2</sub> dissolved in water and in ice. The vibration–rotation bands shift from their gas-phase frequencies. The ratios (H<sub>2</sub>/D<sub>2</sub>) for both the shifts and the widths are about  $\sqrt{2}$ , even though the shifts are in opposite directions in water and in ice, and a theoretical justification for this is given. The rotational bands of D<sub>2</sub> are more difficult to observe than the corresponding H<sub>2</sub> bands, and so a numerical procedure to extract these bands from the noise has been employed. The pure rotational bands of H<sub>2</sub> and D<sub>2</sub> are unshifted in the liquid and shifted only slightly, if at all, in the ices. The experimentally observed widths for the H<sub>2</sub> are reproduced by available simulations. The variation in the widths for D<sub>2</sub> with *J* are smaller than those for H<sub>2</sub> in both water and ice.

## Introduction

The system of hydrogen dissolved in either water or ice is of fundamental interest. Although only a small concentration of H<sub>2</sub> dissolves in water or ice at atmospheric pressure, substantial concentrations can be dissolved under pressure. We have previously investigated H<sub>2</sub> dissolved in both liquid H<sub>2</sub>O and D<sub>2</sub>O<sup>1</sup> and in the corresponding ices.<sup>2</sup> Raman spectra of H<sub>2</sub> show resolved pure rotation bands and unresolved vibration–rotation bands. We have also examined the inelastic neutron scattering for H<sub>2</sub> in D<sub>2</sub>O ice.<sup>3,4</sup> The quasi-elastic scattering provides the diffusion coefficient for the hydrogen.<sup>3</sup> At higher values of the energy transfer, the rotation bands appear.<sup>4</sup> Raman spectra of H<sub>2</sub> in liquid H<sub>2</sub>O differ from those in D<sub>2</sub>O, showing that the interactions between solute and solvent must be considered by quantum mechanics. The dynamics of water are complicated, involving both hydrogen-bonded and non-hydrogen-bonded motions, and these are the subject of continuing investigation.<sup>5</sup> Molecular hydrogen uniquely provides a chemically simple, but dynamically complicated, probe of the water, and this has led to the development of extensive models and simulations. The rotational spectra of H<sub>2</sub> in liquid are modeled in an earlier paper by Hunter et al.<sup>6</sup> and then in a more sophisticated treatment by Xiao and Coker.<sup>7</sup> The diffusion in water and both the rotation and translation in ice are considered in later papers.<sup>8,9</sup>

In this paper, we present the results for the rotation and rotation–vibration Raman spectra of D<sub>2</sub> in both water and ice. We expect to observe differences between the H<sub>2</sub> and the D<sub>2</sub> spectra, since even the change from H<sub>2</sub>/H<sub>2</sub>O to H<sub>2</sub>/D<sub>2</sub>O makes an observable difference. The decrease in the rotational constant in going from H<sub>2</sub> to D<sub>2</sub> changes the correlation times, which in turn may make the rotational spectrum “collapse” into its classical form.<sup>10</sup> A useful comparison is obtained by noting that the rotational constant of H<sub>2</sub> is 61 cm<sup>−1</sup>, while that for D<sub>2</sub> is 31 cm<sup>−1</sup>. For H<sub>2</sub>O, the A constant is 28 cm<sup>−1</sup>, while for D<sub>2</sub>O, it is

15 cm<sup>−1</sup>. Thus for D<sub>2</sub>/H<sub>2</sub>O, the rotational constants match, but they do not match for the other combinations. The values of the rotational constants lead us to expect that the motions of deuterium and ordinary water are the most strongly coupled.

The small spacing of the D<sub>2</sub> bands makes the spectra more difficult to resolve and raises questions as to the accuracy of our data. Consequently, we tried numerical methods for resolving the spectra and improving the signal-to-noise ratio. We show that we can get accurate results for the parameters of the spectra in a relatively short time and are able to check the parameters we obtain.

## Experimental Section

At room temperature and atmospheric pressure, the solubility of H<sub>2</sub> in water<sup>11</sup> is about 10<sup>−3</sup> M. To obtain spectra, we worked at about 2000 psi (136 atm) for H<sub>2</sub> and at about 1700 psi (116 atm) for D<sub>2</sub>. This yields solutions of about 0.1 M. The Raman cell was the same as previously described<sup>1</sup> and incorporated a gaslift pump to mix the gas and the water. To obtain D<sub>2</sub> in ice, D<sub>2</sub> was dissolved in water in the cell. The cell was then cooled by passing a refrigerant through coils surrounding the cell. The cooling had to be done slowly to prevent bubbles or cracks from forming. A stream of dry nitrogen was passed over the cell windows to prevent condensation of atmospheric moisture. The transparent ice sample can be examined through the cell windows. The freezing point of D<sub>2</sub>O is 4 °C, making D<sub>2</sub>O ice a bit easier to obtain than H<sub>2</sub>O ice. The spectrometer, the Reticon detector, and the light source were the same as in ref 1 but with a more modern computer.

Obtaining the spectrum of D<sub>2</sub> in H<sub>2</sub>O proved to be more difficult than obtaining the spectrum in D<sub>2</sub>O. We previously found that the quartz windows etch when examining H<sub>2</sub>/H<sub>2</sub>O under irradiation.<sup>12</sup> We then switched to sapphire windows, and this was satisfactory for H<sub>2</sub> in either H<sub>2</sub>O or D<sub>2</sub>O, but apparently a reaction (1/2D<sub>2</sub> + H<sub>2</sub>O = HDO + 1/2H<sub>2</sub>) occurred for D<sub>2</sub> in H<sub>2</sub>O. The entire sample cell was cleaned and rebuilt, and as before, high conductivity water was used. Satisfactory spectra of D<sub>2</sub> in H<sub>2</sub>O were then obtained.

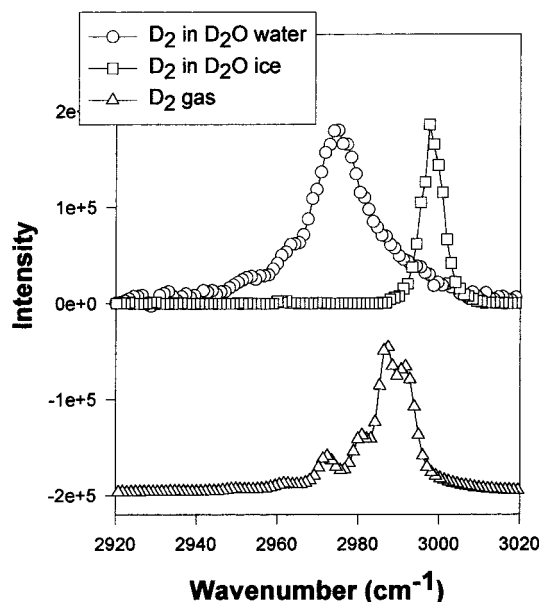
The difficulties of obtaining the spectra and of properly subtracting the spectrum of the solvent from that of the solution

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**Figure 1.** Raman Q branch of D<sub>2</sub> in the gas phase compared to the vibration-rotation band of D<sub>2</sub> in D<sub>2</sub>O water and D<sub>2</sub>O ice. The spectrometer was run with wide slits with a resolution sufficient to define the condensed phase spectra but that broadened the gas-phase spectra.

led us to try sophisticated data analysis. This analysis is reported in the Appendix and compares raw and “enhanced” rotation spectra accumulated over different lengths of time. The OMA detector was read after accumulating data for 30 s, and we call each such reading one “scan”. The result of this signal enhancement is values of the bandwidths for H<sub>2</sub> in H<sub>2</sub>O and D<sub>2</sub> in D<sub>2</sub>O that do not differ significantly from the values obtained by directly fitting the spectra to a series of Lorentzians. In directly fitting the spectra, Lorentzian, Gaussian, and Voigt functions were tried. The Lorentzian functions fit the best.

Vibration-rotation band shifts from its gas-phase position in both liquid and in ice. The absence of an observable unshifted band shows that we are looking at dissolved or intercalated H<sub>2</sub>/D<sub>2</sub> and not at hydrogen in bubbles, cracks, or dead space.

## Results and Discussion

**Vibration-Rotation Bands.** We have previously obtained the spectra of the vibration-rotation band of H<sub>2</sub> in H<sub>2</sub>O and D<sub>2</sub>O both in liquid and in ice.<sup>2</sup> The spectra of D<sub>2</sub> (Figure 1) are similar. The rotational structure of the gas-phase band is still partly resolved. The frequency of the band shifts down in water and up in ice.

The frequencies and widths of H<sub>2</sub> and D<sub>2</sub> in H<sub>2</sub>O and D<sub>2</sub>O are compared in Table 1. The ratio of the frequencies of the most intense bands for the gas is 1.39, close to the value of  $\sqrt{2}$  expected for a simple harmonic oscillator-rigid rotor. The table lists the frequency shifts from the gas-phase values<sup>13</sup> and the widths of the bands in the solutions and shows that H<sub>2</sub>/D<sub>2</sub> ratios for both the shifts and the widths are close to  $\sqrt{2}$ .

The shifts and widths for H<sub>2</sub> have been measured in other solvents<sup>14,15</sup> and calculated by various theories.<sup>15–20</sup> We present a simple theory for the shifts and the widths and compare them to the results for water/ice solvent and for other solvents.

We model the variation of the potential energy of the H<sub>2</sub>/D<sub>2</sub> with the H–H distance,  $x$ , as

$$V(x) = cx + 1/2(k + \Delta k)x^2 + 1/6Kx^3 \quad (1)$$

**TABLE 1: Vibrational Band of Hydrogen in Water and Ice**

	H <sub>2</sub> (cm <sup>-1</sup> ) <sup>a</sup>	D <sub>2</sub> (cm <sup>-1</sup> ) <sup>a</sup>	ratio H <sub>2</sub> /D <sub>2</sub>
gas-phase maximum	4155.2	2987.2	1.39
	shift (cm <sup>-1</sup> )		fwhm (cm <sup>-1</sup> )
H <sub>2</sub> in H <sub>2</sub> O(l)	-19.1 ± 0.9		18.0 ± 0.7
H <sub>2</sub> in D <sub>2</sub> O(l)	-16.3 ± 1.1		20.1 ± 0.8
D <sub>2</sub> in D <sub>2</sub> O(l)	-11.4 ± 1.3		15.6 ± 1.7
H <sub>2</sub> /D <sub>2</sub> in D <sub>2</sub> O(l); ratio	1.43 ± 0.19		1.29 ± 0.15
H <sub>2</sub> in H <sub>2</sub> O(s)	16.0 ± 0.5		11.1 ± 1.5
H <sub>2</sub> in D <sub>2</sub> O(s)	17.5 ± 1.4		12.0 ± 1.8
D <sub>2</sub> in D <sub>2</sub> O(s)	11.1 ± 0.5		8.7 ± 0.7
H <sub>2</sub> /D <sub>2</sub> in D <sub>2</sub> O(s); ratio	1.58 ± 0.15		1.38 ± 0.23

<sup>a</sup> For H<sub>2</sub>, the position is that of the Q(1) band. For D<sub>2</sub>, this is the Q(2) band.

Here  $k$  and  $K$  are the isolated-molecule quadratic and cubic potential constants, respectively, and  $c$  and  $\Delta k$  represent the effect of the solvent. The linear term shifts the minimum in  $x$ . Taking the derivative, we find  $0 = c + (k + \Delta k)x + 1/2Kx^2$ , and  $x_0 = -c/(k + \Delta k)$  as the new minimum to zero order in  $K$ . Expanding the potential about  $x_0$ , we find a shifted second derivative term:

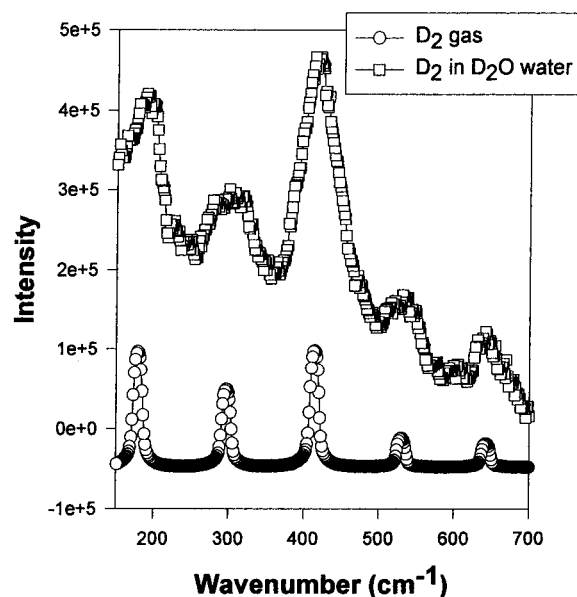
$$1/2[\partial^2 V / \partial x^2] = 1/2(k + \Delta k) - 1/2[Kc/(k + \Delta k)] \quad (2)$$

The frequency of the oscillator is then

$$\omega^2 = \omega_0^2 + \frac{1}{\mu}[\Delta k - Kc/(k + \Delta k)] \quad (3)$$

where  $\omega_0^2 = k/\mu$ , and  $\mu$  is the reduced mass. Thus, both the unperturbed frequency  $\omega_0$  and the shift in frequency vary as  $\mu^{-1/2}$ ; indeed, scaling as  $1/\sqrt{\mu}$  will occur for any model in which the solvent affects the potential energy only. The vibrational band in liquid water shifts down in frequency (red shift) as is typical for most solvent shifts (Table 1). The ratio of the H<sub>2</sub> to the D<sub>2</sub> shift is  $1.43 \pm 0.10$ , in agreement with the predicted  $\sqrt{2} = 1.41$ . For H<sub>2</sub>/D<sub>2</sub> in ice, the shift is to higher frequencies (blue shift). A red shift is usually attributed to the action of attractive forces, and a blue shift is usually attributed to repulsive forces in liquid solvents.<sup>21</sup> However, here we compare liquid to a less dense solid. In ice, the hydrogen is held in channels but is not necessarily centered. The measured isotope ratio, 1.58, indicates that the description of the interaction of hydrogen with ice is more complicated and may involve kinetic energy effects, such as the oscillation of hydrogen within the ice cavities found by a MD simulation.<sup>9</sup>

The width of the bands can be found by using the same model for the frequency with additional consideration of the solvent motion. Water and ice can relax through a combination of reorientation and hydrogen bond shifts, and the various processes are characterized by times ranging from a few tenths of a picosecond to about 10 ps.<sup>5,22,23</sup> The spectra (Figure 1 and ref 2) show that the rotational structure is completely obliterated in the liquid and in the ice, and so the width is due mostly to vibrational relaxation. The solvent motions are relatively slow as compared to the vibrational times, and we consider the vibrational broadening to give a Gaussian time dependence of the form  $1/\tau^2 = \mu[(x_{11} - x_{00})/\hbar]^2[(\Delta\omega)^2]$ , where the  $x_{ii}$  are the diagonal matrix elements for  $x$  (the vibrational coordinate) and  $\Delta\omega$  is the shift in the frequency.<sup>17</sup> The  $\Delta\omega^2$  terms scale with  $1/\mu$  as we have shown above. There is one more factor of  $1/\mu$  in the matrix elements of  $x^2$ ;  $1/\tau^2$  is then proportional to  $1/\mu$  and the width of the Gaussian band proportional to  $1/\sqrt{\mu}$  in rough agreement with our observations.



**Figure 2.** Rotational Raman spectrum of D<sub>2</sub> in D<sub>2</sub>O water and in the gas phase.

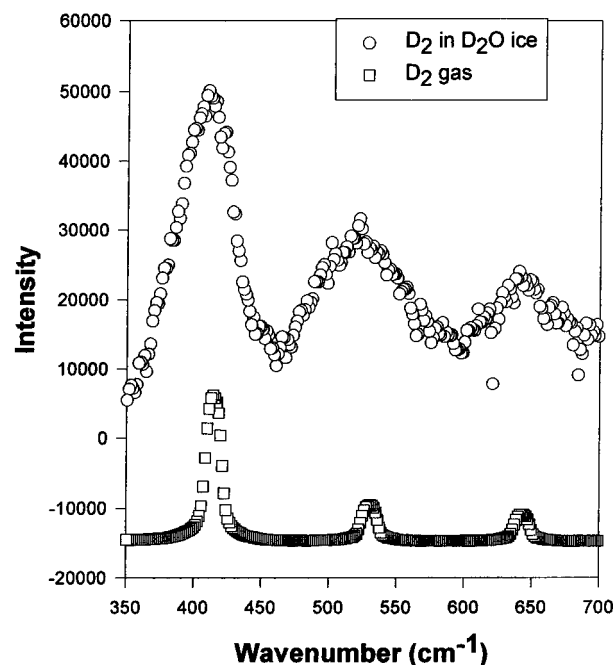
It is difficult to specify what is required to obtain this scaling—at least some models invoking short-range forces also scale with  $1/\sqrt{\mu}$ .<sup>15</sup> For H<sub>2</sub>/D<sub>2</sub> in liquid Ar and in liquid SF<sub>6</sub>, both the shifts and widths are in the approximate  $\sqrt{2}$  ratio.<sup>14</sup> Even for H<sub>2</sub>/D<sub>2</sub> attached to a sodium ion, the ratio of the observed frequency shift, 1.5, is close to  $\sqrt{2}$ .<sup>20</sup> However, the theoretical estimates for this situation can be widely off from this ratio—for example, as much as a ratio of 14 calculated for one orientation of H<sub>2</sub> and D<sub>2</sub>.<sup>20</sup>

**Rotational Spectra of D<sub>2</sub> in Water.** The rotational spectrum of D<sub>2</sub> differs from that of H<sub>2</sub>; the value of the rotational constant B is about 30 cm<sup>-1</sup> rather than 60 cm<sup>-1</sup>, and the spin statistics differ. For D<sub>2</sub>, the even *J* and odd *J* states have spin weights of 6 to 3 as compared to 1 to 3 for H<sub>2</sub>. As a consequence, the D<sub>2</sub> intensities vary with *J* more slowly than do the H<sub>2</sub> intensities, and in the gas, we are able to observe the first seven transitions from *J* = 0 → 2 to *J* = 6 → 8. In the liquid, we see the first five of these (Figure 2).

The positions of the rotational bands for D<sub>2</sub> in either H<sub>2</sub>O or D<sub>2</sub>O are not shifted significantly from their gas-phase positions. It is the bandwidths and their variation with *J* that indicate the nature of the interactions between the H<sub>2</sub>/D<sub>2</sub> and the water. Table 2 shows the experimental values of the various combinations of H<sub>2</sub> and D<sub>2</sub> in H<sub>2</sub>O and D<sub>2</sub>O in the liquid, and Table 3 shows these values for the ices.

The widths of the H<sub>2</sub> bands in H<sub>2</sub>O and D<sub>2</sub>O water are well reproduced by theory<sup>7</sup> as are the widths in H<sub>2</sub>O ice.<sup>9</sup> A particularly noticeable feature for H<sub>2</sub> is the variation of the widths with *J*. In ice, it is the *J* = 1 → 3 band that is the widest since this arises from the first anisotropic energy level.<sup>9</sup> In water, the bands decrease in width with increasing *J*, as the faster spinning of the molecule at the higher *J* values averages out the anisotropy. The rotational relaxation is due to a combination of the H<sub>2</sub> motion and the solvent motion as shown by comparing H<sub>2</sub>/H<sub>2</sub>O and H<sub>2</sub>/D<sub>2</sub>O. The D<sub>2</sub>O moves more slowly than the H<sub>2</sub>O, leading to smaller widths.

Turning to the D<sub>2</sub> solutions, the widths of D<sub>2</sub> in H<sub>2</sub>O decrease with increasing *J* but more slowly. However, for D<sub>2</sub> in liquid D<sub>2</sub>O, the *J* = 1 → 3 band is again the widest, and the variation with increasing *J* is the smallest. The experiments for D<sub>2</sub> in ice show that all the bands have the same width (within rather



**Figure 3.** Rotational Raman spectrum of D<sub>2</sub> in D<sub>2</sub>O ice and in the gas phase.

**TABLE 2: Rotational Bands of H<sub>2</sub> and D<sub>2</sub> in Water**

H <sub>2</sub> transition <sup>a</sup>	Half Width at Half Height (cm <sup>-1</sup> )	
	H <sub>2</sub> in H <sub>2</sub> O water	H <sub>2</sub> in D <sub>2</sub> O water
0 to 2	47.6 ± 0.6	46.7 ± 2.9
1 to 3	39.7 ± 1.1	37.8 ± 1.4
2 to 4	28.0 ± 1.4	26.0 ± 1.6
3 to 5	20.6 ± 1.5	15.8 ± 1.0
D <sub>2</sub> transition <sup>b</sup>	Half Width at Half Height (cm <sup>-1</sup> )	
	D <sub>2</sub> in H <sub>2</sub> O water	D <sub>2</sub> in D <sub>2</sub> O water
0 to 2	39.5 ± 8.7 <sup>c</sup>	35.7 ± 7.8
1 to 3	38.8 ± 2.1	39.9 ± 3.4
2 to 4	36.5 ± 1.7	34.4 ± 3.5
3 to 5	30.3 ± 7.0	30.8 ± 1.6
4 to 6	26.4 ± 0.8	27.0 ± 1.0

<sup>a</sup> From ref 1. <sup>b</sup> This work. <sup>c</sup> The error estimates quoted are at 95% confidence limits except for this value, which is at 80% confidence.

substantial error bars). The relaxation of H<sub>2</sub> in ice differs from that in water since in the ice the anisotropic fluctuations of “solvent”—hydrogen interactions are slow on the rotational time scale.<sup>8</sup> The slow motion limits the relaxation to transitions among the various *M* levels and does not lead to relaxation by changing *J*. The same should be true for D<sub>2</sub> in ice and explains the lack of variation of the widths. For H<sub>2</sub> and D<sub>2</sub> in ice, there is little difference between the widths in H<sub>2</sub>O and D<sub>2</sub>O in contrast to the situation in H<sub>2</sub>/liquid H<sub>2</sub>O and H<sub>2</sub>/liquid D<sub>2</sub>O. This is also in agreement with the simulation results of the “slow” motion. Finally, there is some indication that the rotational bands in ice are shifted (Table 3). However, the error limits are large, and we cannot say definitely whether the shifts are real.

## Conclusions

We have presented results for the vibration and rotation motion of D<sub>2</sub> in water and ice. The system hydrogen/water is unique in showing the effects of quantum coupling between this simple solute and this most important of solvents. The experiments for D<sub>2</sub> in water were checked by using a new signal enhancement technique, since the spectra are noisy and the

**TABLE 3: Rotational Bands of H<sub>2</sub> and D<sub>2</sub> in Ice**

Half Width at Half Height (cm <sup>-1</sup> )		
H <sub>2</sub> transition <sup>a</sup>	H <sub>2</sub> in H <sub>2</sub> O ice	H <sub>2</sub> in D <sub>2</sub> O ice
0 to 2	20.1 ± 2.6	20.8 ± 2.2
1 to 3	26.2 ± 1.5	28.2 ± 1.5
2 to 4	22.7 ± 2.9	17.0 ± 2.8
3 to 5	17.0 ± 2.6	19.5 ± 4.0
D <sub>2</sub> transition <sup>b</sup>	D <sub>2</sub> in H <sub>2</sub> O ice	D <sub>2</sub> in D <sub>2</sub> O ice
2 to 4	17.9 ± 2.4	19.6 ± 1.9
3 to 5	21.9 ± 5.3	21.5 ± 1.4
4 to 6	20.6 ± 6.9	19.3 ± 1.6
Band Maximum Shift (cm <sup>-1</sup> )		
H <sub>2</sub> transition <sup>a</sup>	H <sub>2</sub> in H <sub>2</sub> O ice	H <sub>2</sub> in D <sub>2</sub> O ice
0 to 2	+5.4 ± 5.7	+1.3 ± 1.9
1 to 3	+2.6 ± 2.5	+9.6 ± 2.6
2 to 4	+5.2 ± 5.4	+16.4 ± 4.6
3 to 5	+18.0 ± 0.9	-5.1 ± 2.4
D <sub>2</sub> transition <sup>b</sup>	D <sub>2</sub> in H <sub>2</sub> O ice	D <sub>2</sub> in D <sub>2</sub> O ice
2 to 4	+0.2 ± 5.1	-7.2 ± 2.5
3 to 5	+4.8 ± 9.1	-6.8 ± 4.3
4 to 6	+14.8 ± 5.7	+2.9 ± 5.1

<sup>a</sup> Ref 1. <sup>b</sup> This work.

values obtained for the widths of the bands are shown to be reliable.

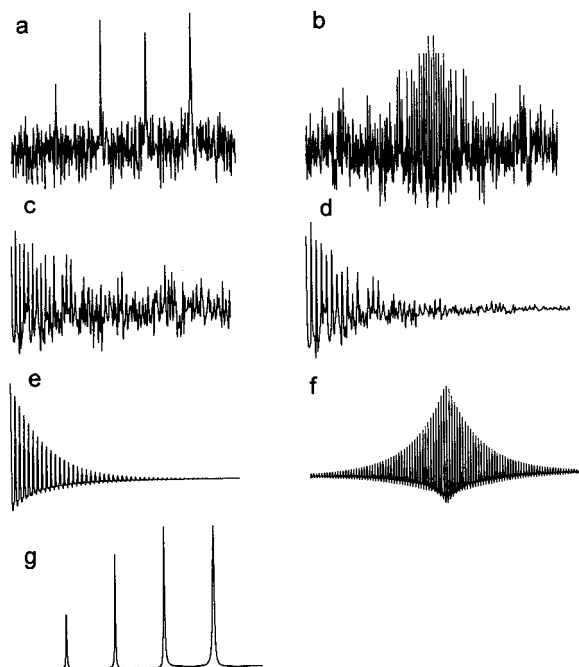
The results for D<sub>2</sub> in water and ice follow those for H<sub>2</sub> with few surprises, although specific coupling effects might have been predicted on the basis of the near match between the rotational constants of D<sub>2</sub> and H<sub>2</sub>O. The H<sub>2</sub>/D<sub>2</sub> ratio for the vibration-rotation band shift and for the bandwidths are both close to  $\sqrt{2}$  even though the band shifts in opposite directions in water and in ice. The variation of rotational bandwidths with  $J$  for D<sub>2</sub> in water are less pronounced than for H<sub>2</sub>. For D<sub>2</sub> in ice as for H<sub>2</sub> in ice, any variation in the line widths is small. The D<sub>2</sub> data provide a probe of water dynamics in a slower time scale than do the H<sub>2</sub> data and thus provide the experimental basis for further tests of dynamical theories and simulations.

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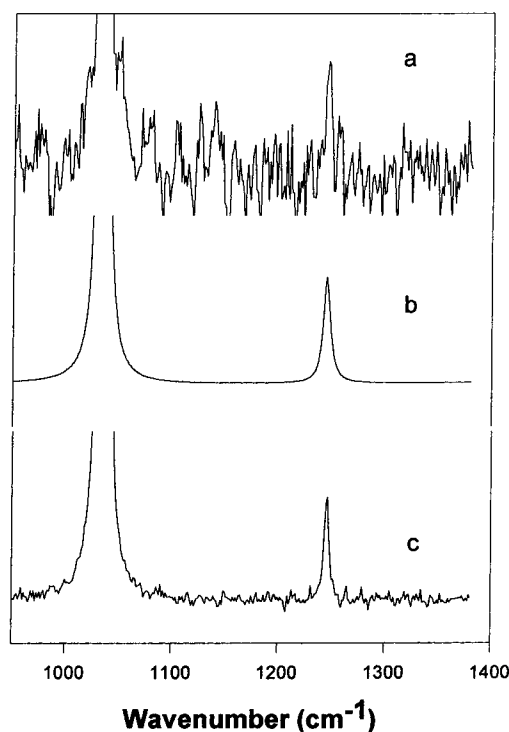
### Appendix: Signal Enhancement Techniques and the Resulting Spectra

Sophisticated signal enhancement techniques have been applied to NMR signals. These techniques can be applied in the space of the spectra themselves or to the data in the time domain. For NMR, it can often be assumed that the spectra consist of Lorentzian bands, or equivalently that the signal from a given line decays exponentially. For example, such methods have been applied to noisy free induction decays that are truncated.<sup>24</sup> Supplementing the data with information about the band shapes and constraining other parameters improve the effective signal-to-noise ratio.<sup>24-26</sup>

The gas-phase Raman rotational spectrum of H<sub>2</sub> consists of widely spaced bands of approximately Lorentzian shape. We found that we could modify the methods used in NMR to improve the Raman spectra. The first data analyzed was a computer-generated frequency scan of the Raman spectrum of gas-phase H<sub>2</sub>. The data were Fourier-transformed into the time domain. Only the positive half time ( $t \geq 0$ ) need be processed, and this was multiplied by a damping function.



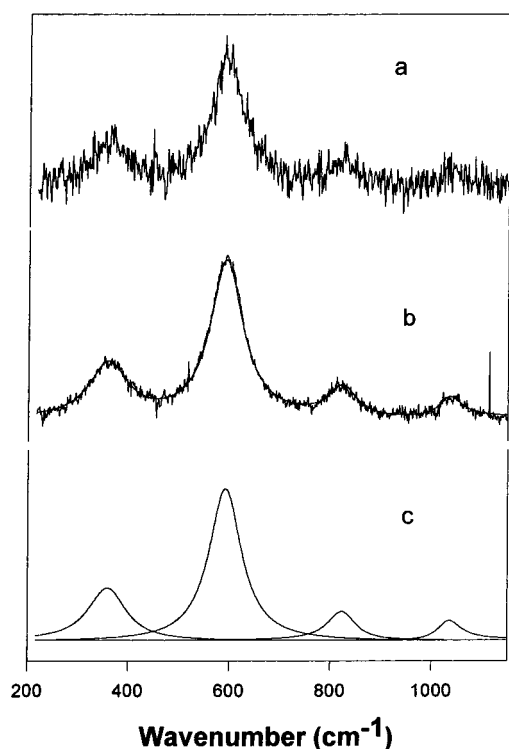
**Figure 4.** Computer-generated data illustrating the signal enhancement process: (a) Computer-generated spectral data. (b) Fourier transform of the data (the time domain). (c)  $t > 0$  part of panel b. (d) Panel c multiplied by a damping function. (e) Time domain data after optimization using the known properties of the spectrum (see text). (f) Full time dependence restored. (g) Spectrum obtained by Fourier transforming panel f.



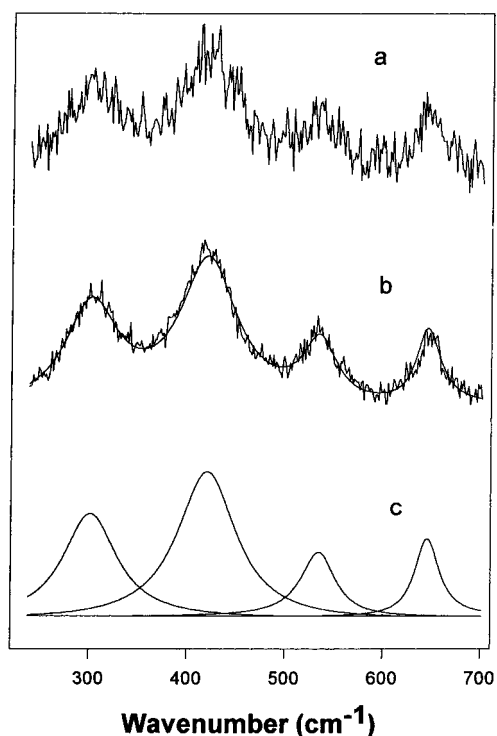
**Figure 5.** Fourth ( $J = 3 \rightarrow 5$ ) and fifth ( $J = 4 \rightarrow 6$ ) bands of the rotational Raman of gas-phase H<sub>2</sub>. (a) Experimental spectrum (an average of 20 scans). Each "scan" is data taken for 30 s. (b) Enhanced spectrum (20 scans). (c) Experimental spectrum (an average of 430 scans).

A singular value decomposition was then used on the matrix formed from the data. Since we know that there are four bands in the spectrum, the matrix is reduced to rank 4. The reduced data are projected into the space of the matrices that express





**Figure 6.** H<sub>2</sub> in H<sub>2</sub>O water. (a) Experimental spectrum (an average of 120 scans). (b) Experimental spectrum (an average of 4400 scans) with the 120-scan enhanced spectrum superimposed. (c) Enhanced spectrum (from the 120-scan spectrum).



**Figure 7.** D<sub>2</sub> in D<sub>2</sub>O water. (a) Experimental spectrum (an average of 6360 scans). (b) Experimental spectrum (an average of 60 000 scans) with the 6320-scan enhanced spectrum superimposed. (c) 6320-scan spectrum, enhanced.

the known properties of the system. For the gas-phase spectrum, the known properties are four bands of Lorentzian shape.

A new matrix is formed from the various projected matrices, and the process is iterated until convergence. Finally,

**TABLE 4: Results of Signal Enhanced Spectrum of H<sub>2</sub> in H<sub>2</sub>O Water**

		Half Width at Half Height (cm <sup>-1</sup> )			
		<i>J</i> = 0 to 2	<i>J</i> = 1 to 3	<i>J</i> = 2 to 4	<i>J</i> = 3 to 5
this work <sup>a</sup>	120 scans	48.5	39.5	31.5	24.5
	4400 scans	47.5	40.0	32.0	24.0
	previous <sup>1</sup>	47.6 ± 0.6	39.7 ± 1.1	28.0 ± 1.4	20.6 ± 1.5
		Peak Center (cm <sup>-1</sup> )			
		<i>J</i> = 0 to 2	<i>J</i> = 1 to 3	<i>J</i> = 2 to 4	<i>J</i> = 3 to 5
this work	120 scans	356	587	816	1033
	4400 scans	354	587	814	1036
	previous <sup>1</sup>	354	587	814	1035
H <sub>2</sub> gas		354	587	814	1035

<sup>a</sup> The contribution of the slit width (10 cm<sup>-1</sup>) has been deconvoluted from the widths.

**TABLE 5: Results of Signal Enhanced Spectrum of D<sub>2</sub> in D<sub>2</sub>O Water**

		Half Width at Half Height (cm <sup>-1</sup> )			
		<i>J</i> = 1 to 3	<i>J</i> = 2 to 4	<i>J</i> = 3 to 5	<i>J</i> = 4 to 6
this work <sup>a</sup>	6360 scans	39.0	35.0	29.0	24.0
	60 000 scans	41.0	34.5	31.5	27.5
	direct fit <sup>a</sup>	39.9 ± 3.4	34.4 ± 3.5	30.8 ± 1.6	27.0 ± 1.0
		Peak Center (cm <sup>-1</sup> )			
		<i>J</i> = 1 to 3	<i>J</i> = 2 to 4	<i>J</i> = 3 to 5	<i>J</i> = 4 to 6
this work	6360 scans	298	414	531	642
	60 000 scans	296	414	530	644
	direct fit	294 ± 11	417 ± 4	533 ± 9	648 ± 6
D <sub>2</sub> gas		298	415	530	643

<sup>a</sup> The contribution of the slit width (10 cm<sup>-1</sup>) has been deconvoluted from the widths.

the resulting data are Fourier-transformed back to frequency space.

The entire procedure is outlined in Figure 4, which shows the computer-generated example. Actual experimental data are shown in Figure 5. In this example, the first five bands of the gas-phase H<sub>2</sub> spectrum were obtained. Only the fourth (*J* = 3 → 5) and fifth (*J* = 4 → 6) bands are shown. The figure shows the result of 20 scans, the 20-scan enhanced spectrum, and the result of 430 scans. Note that the fifth band is about 1/25 the intensity of the fourth band. Both the enhanced 20 scan and the 430 spectra gave this value for the intensity. We repeated the numerical procedure with four different 20-scan spectra and obtained the same results each time, showing that the procedure is stable.

We then examined the spectra of H<sub>2</sub> in H<sub>2</sub>O and D<sub>2</sub> in D<sub>2</sub>O (Figures 6 and 7) and compared them to the spectra obtained by the brute force method of taking an enormous number of scans (up to 60 000). The properties assumed were Lorentzian bands not fixed in position but of the known relative integrated intensity. The intensity criterion helped fix the baseline of the experimental spectra. The result for the widths of the bands in the liquid are tabulated in Tables 4 and 5 and are in satisfactory agreement with the widths obtained by simply fitting a series of Lorentzian peaks to the spectra. The values of the widths given have been deconvoluted to remove the effect of a spectral slit width of about 10 cm<sup>-1</sup>.

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