The diffusion of H_2 in hexagonal ice at low temperatures

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The properties of H_2 in water ice are of relevance to questions in fields as diverse as astronomy,^{1,2} and -- as a prototypical hydrophobic solute -- to biology. The diffusion of hydrogen molecules in hexagonal D_2O ice (Ih) in the temperature range of 25 - 60 K was investigated by quasielastic neutron scattering. The observed spectra consist of a narrow elastic peak and a broad quasielastic component. A single-particle diffusion coefficient for H_2 in D_2O ice was obtained and is remarkably high, comparable to the diffusion constant of H_2 in liquid H_2 . The H_2 must move through the channels in the hexagonal ice, in contrast to its motion in the hydrogen-bonded fluctuating network in water.

The solubility of H_2 in water at 25°C is about 7.5×10^{-4} M and goes up to about 9.4×10^{-4} M at 0°C.³ H_2 is not usually thought to form stable solutions with ice at the pressures we consider.^{4,5} However, small amounts of H_2 (and He) -- amounts comparable to that in liquid water -- may dissolve in ice.^{6,7} We make H_2/D_2O ice by dissolving H_2 in heavy water and then freezing

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the ice *in situ*, and the resulting H_2 /ice solid is stable at low temperature, at least for the time of our experiments. Because of the large neutron incoherent scattering cross section of H (about 80 barns for thermal neutrons), the amount of H_2 in the ice is sufficient to provide a good neutron scattering signal. D_2O is used to achieve a good contrast for the H scattering, since the scattering cross section of deuterium is more than 10 times smaller than that of hydrogen and is mostly coherent. We study the diffusive motion of H_2 in D_2O ice by measuring the quasielastic scattering and estimating the single-particle diffusion coefficient of H_2 . Analysis of the elastic part of the neutron scattering shows that our ice is hexagonal (Ih) (Fig. 1).

The Raman spectra obtained previously^{11,12} show $J=0 \rightarrow J=2$, $1 \rightarrow 3$, $2 \rightarrow 4$, and $3 \rightarrow 5$ rotational transitions. The hydrogen molecules in water at room temperature and in ice near $0^\circ C$ thus rotate in a quantized fashion and the rotation is relatively free. Our neutron spectra all show the $0 \rightarrow 1$ and $1 \rightarrow 0$ transitions (except that, for an incident energy of 3.6 meV, the $0 \rightarrow 1$ transition is not observable because of the low incident neutron energy). This shows that the H_2 still retains its quantized rotation, even in 25 K ice. However, this rotational neutron scattering data has not yet been analyzed in detail.

The neutron scattering from the H_2/D_2O system consists of scattering from the H_2 , from the D_2O ice, and from the interference between the H_2 and D_2O . Since the solubility of H_2 in water/ice is small, the interference term is negligibly small,

and we obtained the neutron spectra of H_2 by subtracting off the corresponding D_2O reference spectra, which were normalized to account for the different D_2O filling of various H_2/D_2O runs. The corrected scattering, in terms of the scattering function S , was then plotted against the neutron energy transfer, $E = E_0 - E_1$ (where E_0 and E_1 are the neutron incident and final energies, respectively) at constant wavevector Q . The scattering function in general consists of components due to the vibrational, rotational and translation motions of the hydrogen molecules, and for the 3.6 meV spectra the vibrational part (the Debye-Waller factor) over the observed Q range is essentially constant. The observed spectra show quasielastic scattering due to rotational and translational diffusion. Since H_2 molecules are quantized rotors with large zero-point energy, the H_2 rotational and translational motions are decoupled and we treat the quasielastic spectra as due to "single-particle" diffusion. This gives a scattering function composed of a sharp elastic incoherent scattering factor, EISF, and a broadened Lorentzian function characterized by a line width Γ .

The observed scattering functions for the 3.6 meV runs were fit to the sum of a Gaussian whose width was resolution limited and a Lorentzian of adjustable width. The fit of all the spectra to this model is satisfactory, as shown in the example of Fig. 2. The widths of the Lorentzian were then plotted vs. Q^2 (Fig. 3). The values of the diffusion coefficients, obtained from a fit of $\Gamma = DQ^2$, are given in Table I. These coefficients are remarkably

high. Fitting the coefficients to the standard Arrhenius form, $D = D_0 e^{-E_{\text{act}}/kT}$, yields an activation energy, E_{act} , of about 90 ± 30 K or 0.75 ± 0.25 kJ/mole. The error is mostly due to the uncertainty in accounting for the temperature variation over the large sample cell.

The values of D and E_{act} are compared to the results of other measurements in Table I. The H-atoms were produced in crystalline ice by electron irradiation, and although they diffuse with the ubiquitous coefficient of about 10^{-5} cm²/sec, they do so near 273 K.¹⁷ The activation energy is an order of magnitude larger than that we observed for H₂, and consequently the diffusion coefficient for H is thought to be very low at cryogenic temperatures. The low T limit of the H diffusion is likely due to tunneling from site to site.¹⁷

Liquid H₂ has a somewhat higher diffusion coefficient than H₂ in ice.¹⁸ In Table I, we show the values for D extrapolated to 25 K, and at that temperature D for the liquid H₂ is one order of magnitude higher than for H₂ in ice. The activation energy for liquid H₂ is the same order of magnitude as that for the H₂ in ice. We also include the diffusion for H₂ (gas) at a pressure approximately that of our sample (~138 bar).¹⁹ The gas values are a bit higher than the liquid values and for a hard-sphere ideal gas should go up as the square root of the temperature.

The diffusion of H₂ in NaA zeolite²⁰ is much slower than the diffusion in ice and shows a considerably higher activation

energy. The zeolite framework consists of cages linked in a three-dimensional array.²¹ The cages and the openings in them are bigger than those in ice. However, the diffusion seems to be liquid-like with both intra-cage and inter-cage jumps.²⁰ The relatively slow diffusion and the high activation energy is presumably due to the much stronger interaction of the H_2 with the charged zeolite framework than with the neutral ice framework.

The activation energy of H in ice has been modeled using an atom-atom potential and the structure of ice Ih.²² The model yields an energy barrier of about 100 meV (9.6 kJ/mole) for a one-dimensional motion of H_2 along the c-axis. The atom moves from one cavity to another through a bottleneck at the position of the barrier. The hydrogen molecule has about the same polarizability (0.79 Å) as the free hydrogen atom (0.67 Å) and the molecule is surely no smaller than the atom. According to a simple model using atom-atom potentials and ignoring rotational diffusion, we would expect the hydrogen molecule to have an activation energy for cavity-to-cavity motion that is no smaller than that for the atoms. Our result is quite contrary to this expectation: the hydrogen molecules move remarkably freely through the ice structure. Probably the stronger interaction of the H atoms with the ice is due to the interactions possible for this open-shell atom (valence-type interaction with the non-bonded electrons of the oxygen), which are not possible for the closed-shell H_2 molecule. The isolated atom polarizability is not, apparently, a valid measure of the strength of its

interactions. We note, however, that the details of even ice Ih structure, particularly the arrangements and dynamics of the hydrogen bonds, are still uncertain.²³

The vibrational spectrum of H_2 in ice has been reported from an astronomical infrared source.² This ice is presumably amorphous and may contain other solutes. The interstellar ice seems to be in the same temperature range as we have investigated, and laboratory studies² suggest that the H_2 -amorphous ice system is stable below about 70 K. Amorphous ice is thought to possess a high surface area and the H_2 may be mainly on the surface or in micropores.^{1,2,24} The H_2 is adsorbed at cracks or other potential energy low points, and diffusion may be controlled more by the topology of these than by the motion through the channels that occur in crystalline ice.

Table I. Diffusion Coefficients

<u>T (K)</u>	<u>D (cm²/sec)</u>	<u>E_{act} (kJ/mole)</u>	<u>Reference</u>
H ₂ in D ₂ O ice			This work
25	1.3 × 10 ⁻⁵	0.75 ± 0.25	
43	7.9 × 10 ⁻⁵		
60	9.5 × 10 ⁻⁵		
H in H ₂ O			17
273	1.9 × 10 ⁻⁵	13	
20	~10 ⁻¹⁶	From tunneling model	
H ₂ in H ₂ liquid			18
17	6.2 × 10 ⁻⁵	0.36	
25	1.4 × 10 ⁻⁵	Extrapolated	
H ₂ in H ₂ (gas)			19
40	30 × 10 ⁻⁵		
60	60 × 10 ⁻⁵		
H ₂ in NaA Zeolite			20
100	5 × 10 ⁻⁵	2	

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Figure Captions

Fig. 1. The low-resolution neutron diffraction pattern of D_2O ice obtained by extracting the elastic scattering of a 30 meV neutron scattering run by integrating the energy transfers from -4 to +4 meV. The background scattering due to the aluminum cell has been subtracted. The tick marks indicate the positions of the Bragg reflections for hexagonal ice Ih. At low pressures, ice can only form ice Ih (the triple point ice I - ice II - ice III is at about 2000 bar⁸, much higher than the pressures reached here) or vitreous (amorphous) ice.^{1,8,9} Cubic ice⁸ is also a possibility, but it is formed from vitreous ice and is unlikely to occur in our experiments. The observed diffraction pattern matches that of ice Ih. In particular, we see discrete peaks up to the (310) reflection (with an atomic spacing $d = 1.08 \text{ \AA}$). In contrast, vitreous ice shows very broad peaks at $3.71 \text{ \AA}$ and $d = 2.15$.⁹ It is more difficult to prove that we have no cubic ice. Cubic ice¹⁰ has an x-ray line at $d = 1.59 \text{ \AA}$, which is not seen for ice-Ih and is not in our diffraction patterns. Our conclusion is that we do have hexagonal ice. The water (D_2O) was held in a sample cell made of 7075-T6, heat-treated aluminum. The aluminum flat block (15 cm x 10 cm x 1 cm) was drilled out to form space for the water while leaving aluminum posts of sufficient strength. The cell was mounted to the cold block of a closed cycle helium refrigerator and filled with water. Then H_2 gas was bubbled through under tank pressure (nominally 2000 psi

or 138 bar) until enough H_2 dissolved. The valving was similar to that we used for our previous experiments on the Raman spectroscopy of H_2 in water and ice,^{11,12} except that the H_2 gas was simply passed through once without recirculation. The water was frozen slowly while still under H_2 pressure.

Fig. 2. The spectrum of H_2 in D_2O ice at 25 K with a mean wave vector $Q = 0.74 \text{ \AA}^{-1}$. The spectrum was taken with an incident energy of 3.6 meV. The solid line corresponds to a fit of the data by the sum of resolution-limited Gaussian (dotted line), a Lorentzian (dashed line), and a linear background. The neutron scattering experiments were performed using the LRMECS chopper spectrometer at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. The sample cell was oriented at a 45° angle with the incident neutron beam (of dimension 10 cm x 5 cm) so that for all detector angles (-10° to 120°) the beam did not traverse more than 1.5 cm of material. Such a geometry minimizes multiple scattering of neutrons. Spectra were taken at 3.6, 30, 90, and 800 meV incident energies, for H_2/D_2O ice, D_2O ice (frozen under either Ar or He pressure), the empty cell, and a vanadium standard. The D_2O ice and empty cell runs were used for background correction of the spectra and the vanadium run for intensity normalization and resolution assessment. At $E_0 = 3.6 \text{ meV}$, the energy resolution (FWHM) at the elastic position, estimated from a vanadium run at room temperature, varies from 0.19 to 0.26 meV over a range of wavevectors Q from 0.3 to

2.5 $\text{\AA}^{-1}$. The slightly skewed line shape for the $E \leq 1$ meV data is due to instrumental effects.^{13,14} Although the sample temperature was controlled to within 1 K during a run, the thermocouples attached to the top and bottom of the sample cell indicated a temperature spread of up to 8 K. The temperatures (25, 43 and 60 K) given here for the 3.6 meV runs represent the mean temperature recorded by the thermocouples.

Fig. 3. The width of the quasielectric component of the neutron scattering plotted against the wave vector, Q , squared for 25 K. The slope of this plot should, in the limit of small Q^2 , give the diffusion coefficient, $D = \Gamma/Q^2$.¹⁵ At high Q^2 , the plot typically deviates from the line due to short range non-diffusive motion. Similar good fits were obtained for the 43 K ($Q^2 = 0.12 - 0.88 \text{ \AA}^{-2}$) and 60 K ($Q^2 = 0.09 - 1.2 \text{ \AA}^{-2}$) results. A possible model for the H_2 translational motion postulates diffusion in a sphere (intrasite), followed by motion between spheres (intersite). The scattering from such a system has been calculated.¹⁶ For spheres of fixed radius, r , the plot of the width vs Q^2 , the intrasite diffusion adds to the slope of the ordinary intersite diffusion for values of $Qr > \pi$. For values of $Qr < \pi$, on the other hand, the model predicts an additional constant contribution to the width vs. Q^2 plot, i.e., a resulting plot that does not go through the origin. We have $r = 1.8 \text{ \AA}$ (i.e., one-quarter of the c-spacing), so that our data is for $Qr < \pi$. Since our plots go through the origin, we have no intrasite diffusion.

Fig. 1

Fig. 2

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Fig. 3