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SLOW NEUTRON SCATTERING KERNELS
FOR H₂O AT 423°K AND 550°K

H. L. McMurry

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by

H. L. McMurry

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SLOW NEUTRON SCATTERING KERNELS FOR H_2O AT 423°K and 550°K

H. L. McMurry

SUMMARY

The McMurry-Russell (MR) model for water assumes that 10 percent of the molecules are free and the rest are divided equally between aggregates in which the effective masses for H scattering are 75 and 150. Each aggregate exhibits characteristic frequencies in the range $0 < E \leq 0.125$ eV which are chosen to make the calculated scattering agree with Brugger's room temperature data.

This report describes a simple modification in which the fraction of free molecules in the MR model is adjusted to give a least squares fit to Haywood's 423°K data and to Page's 550°K data. The fractions of free molecules are 0.25 and 0.28, respectively.

Agreement with the 423° data is reasonably good. Agreement with the 550° data is only fair. In both cases the modified MR model is in better agreement than the Nelkin (N) model.

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SLOW NEUTRON SCATTERING KERNELS FOR H_2O AT 423°K AND 550°K

H. L. McMurry

I. INTRODUCTION

In a previous report¹ a model, called the McMurry-Russell (or MR) model, was described which permits calculating the slow neutron scattering by room temperature water in agreement with data taken at the MTR. This report describes modifications to this model designed to give optimum agreement with Haywood's data² for water at 423°K , and for Page's data³ at 550°K . For comparison results calculated using the Nelkin model at these temperatures are included.

II. THE MR MODEL FOR WATER

The MR model¹ treats water as a mixture of 10 percent of free H_2O molecules, together with 45 percent each of two types of molecular aggregates in which the effective scattering masses for H atoms are 150 and 75 atomic units. The free H_2O molecules exhibit the two internal stretching vibrations near 0.46 eV, and the deformation mode of 0.2 eV energy.⁴ The aggregates are treated as large molecules exhibiting three types of normal modes. One type has characteristic vibrational energies E_T in the range $0 < E_T \leq 0.025$ eV which are assumed to involve mainly translational motions of the H_2O molecules. A second type with characteristic energies in the range $0.025 < E_T \leq 0.125$ eV are modes in which torsional oscillations of the H_2O molecules dominate. Finally, each H_2O molecule in an aggregate is assumed to exhibit the same internal modes as occur in the free molecules. Characteristic energies of both internal stretching modes

were taken to be 0.46 eV which is near the experimental values, and the experimental value of 0.2 eV was used for the deformation mode. The vibrational amplitudes, which appear in the neutron scattering equations, were calculated from a normal coordinate analysis.

The characteristic energies and vibration amplitudes for the low energy modes ($E_T \leq 0.125$ eV) in the aggregates were selected to bring the calculated scattering into agreement with the data.

Table I presents the parameters which characterize the MR model for H_2O . Separate entries are given for the free molecules and each aggregate. Molecule 1 is the free H_2O and the $f_1 = 0.1$ denotes the fraction of H_2O molecules in the system which are free. The M_{H1} and M_{O1} are the effective scattering masses for H and O atoms, respectively, in molecule 1. Aggregates 2 and 3 contain bonded H_2O molecules in which the effective scattering masses M_{H2} and M_{H3} for H atom scattering are 150 and 75, respectively. The masses M_{O2} and M_{O3} are taken to be 150 and 75 also. The numbers $f_2 = f_3 = 0.45$ indicate that each aggregate contains 45 percent of the H_2O molecules in the system.

The rows headed by E_T list the characteristic energies for the normal modes for that aggregate. Included in each list is a mode of zero frequency which corresponds to the lumped sum of the translational and rotational degrees of freedom of the entire aggregate.

The rows headed by $\bar{\delta}_{HT}$ and $\bar{\delta}_{OT}$ contain effective reciprocal masses for the atoms in each normal mode. Physically these quantities are related to the average squared vibration amplitudes $\langle \Delta r_{VT}^2 \rangle$ by the relation⁵

$$\langle \Delta r_{VT}^2 \rangle = \frac{\bar{\delta}_{VT} \hbar^2}{2E_T} = 0.208 \times 10^{-2} \frac{\bar{\delta}_{VT}}{E_T} (\text{\AA}^2) \quad (1)$$

TABLE I

MR MODEL PARAMETERS ^aA. Molecule 1; $f_1 = 0.1$; $M_{H1} = 1.89$; $M_{O1} = 17.0$

$E_{\tau 1}(\text{eV})$	0.0	0.2	0.46
$\bar{\delta}_{H\tau 1}$	1.590	0.5	0.91
$\bar{\delta}_{O\tau 1}$	0.1760	0.0045	0.0070

B. Molecule 2; $f_2 = 0.45$; $M_{H2} = 150$; $M_{O2} = 150$

$E_{2\tau}(\text{eV})$	0.0	0.005	0.01	0.015	0.02	0.025	0.05	0.075	0.1	0.125	0.2	0.46
$\bar{\delta}_{H\tau 2}$	0.02	0.013	0.018	0.020	0.018	0.047	0.35	0.45	0.3	0.354	0.5	0.91
$\bar{\delta}_{O\tau 2}$	0.02	0.0005	0.005	0.01	0.01	0.015	0.02	0.025	0.03	0.0405	0.0045	0.007

C. Molecule 3; $f_3 = 0.45$; $M_{H3} = 75$; $M_{O3} = 75$

$E_{\tau 3}(\text{eV})$	0.0	0.0075	0.0125	0.0175	0.0225	0.0375	0.0625	0.0875	0.1125	0.2	0.46
$\bar{\delta}_{H\tau 3}$	0.04	0.027	0.019	0.022	0.024	0.019	0.69	0.54	0.038	0.5	0.91
$\bar{\delta}_{O\tau 3}$	0.04	0.0005	0.005	0.01	0.015	0.02	0.025	0.030	0.0305	0.0045	0.007

^aAll aggregates contain a vibrational mode of zero energy. The $\bar{\delta}_{vol}$ for this mode determines M_{vl} through the relation $M_{vl} = 3/\bar{\delta}_{vol}$.

In Eq. (1) subscript v refers to either the H or O atom and τ refers to the mode. For semi-rigid molecules with known force constants, the $\bar{\delta}_{v\tau}$ can be obtained from a normal coordinate analysis.⁵ They must obey the sum rule⁶

$$\sum_{\tau} \bar{\delta}_{v\tau} = \frac{3}{m_v} \quad (2)$$

In Eq. (2) m_v is the mass of atom v in atomic units and the sum is over all modes, including the mode with zero frequency.

III. MODIFYING THE MR MODEL

The kernels for calculating the scattering at the elevated temperatures were obtained simply by altering f_1 , keeping $f_2 = f_3$ and, of course, retaining the requirement $f_1 + f_2 + f_3 = 1.0$. The f_1 giving optimum agreement with Haywood's data was determined from a least squares analysis. His data can be expressed in terms of the scattering law function $S(\kappa^2, \beta)$ defined by

$$S(\kappa^2, \beta) = \sqrt{\frac{E_0}{E}} e^{\beta/2} \sigma(E_0, E, \mu) \quad (3)$$

In Eq. (3), E_0 and E denote the energies of the incident and scattered neutron, respectively, $\beta = (E - E_0)/kT$, κ^2 is the square of the neutron momentum change divided by $\hbar^2$ and μ is the cosine of the scattering angle. The $\sigma(E_0, E, \mu)$ is the partial differential scattering cross section in barns/eV x sr x H₂O.

The least square analysis was as follows. Let $S_H(i)$ denote Haywood's observed value for a particular κ^2 and β . Let $S_1(i)$, $S_2(i)$ and $S_3(i)$ denote $S(\kappa^2, \beta)$ values calculated for this κ^2 and β for the free molecules, and molecules in aggregates 2 and 3, respectively.

Then the calculated $S(i)$ is given by

$$\begin{aligned}
 S(i) &= f_1 S_1(i) + \frac{1-f_1}{2} \left[S_2(i) + S_3(i) \right] \\
 &= f_1 \left[S_1(i) - \frac{S_2(i) + S_3(i)}{2} \right] + \frac{S_2(i) + S_3(i)}{2}
 \end{aligned} \tag{4}$$

It is convenient to consider the ratio $[S(i) - S_H(i)] / (S_H(i))$ and to choose f_1 so the following sum is minimized

$$\sum_i \left[\frac{S(i) - S_H(i)}{S_H(i)} \right]^2 = \sum_i \left[f_1 \phi_1(i) + \phi_2(i) \right]^2 \tag{5}$$

$$\phi_1(i) = \frac{S_1(i) - [S_2(i) + S_3(i)]/2}{S_H(i)}$$

$$\phi_2(i) = \frac{[S_2(i) + S_3(i)]/2 - S_H(i)}{S_H(i)}$$

This leads to

$$f_1 = \frac{\sum_i \phi_1(i) \phi_2(i)}{\sum_i \phi_1^2(i)} \tag{6}$$

In applying Eq. (6), up to six κ_i^2 were used in the range $1.0 < \kappa_i^2 \leq 256 \text{ \AA}^{-2}$ for each of eleven β_i values for 423°K water, and 15 β_i values for 550°K water, the β_i being in the range $0.1 \leq \beta_i \leq 3.0$.

In making the least squares analysis for the 550° data, the input parameters were such that the low energy mode at 0.005 eV was treated classically. This was unintentional but comparisons with calculations where the mode was treated quantum mechanically show that the inclusion of this mode would not alter the agreement significantly.

IV. RESULTS AND DISCUSSION

Optimum agreement was obtained using $f_1 = 0.25$ and $f_2 = f_3 = 0.375$ for 423°K water, and $f_1 = 0.28$ and $f_2 = f_3 = 0.36$ for 550°K water.

Calculated and measured results for 423°K water are shown in Fig. 1, and the 550°K water in Fig. 2. Nelkin model^{1,7} calculations are included for comparison. In the MR model the parts of the $S(\kappa^2, \beta)$ vs κ^2 curves for κ^2 below the maxima are most sensitive to the free molecule content. It is in this region that the least squares fitting was most beneficial in improving agreement between the calculations and the measurements. For κ^2 values beyond the maxima in the $S(\kappa^2, \beta)$ vs κ^2 curves, the calculated results are low for all values of β at 423°K, and for β above about 0.5 for 550°K.

Considering the simplicity of the method of modifying the MR model, the agreement is quite good, particularly for the 423° data. It might be possible to gain improvement by altering the characteristic vibrational energies in the clusters to reflect the greater looseness expected in the structure at elevated temperatures, and by incorporating features to represent the long time diffusive motion better. However, elaborate efforts to obtain a model giving calculations in agreement with present data will not be wise until more is known about the amount of multiple scattering in the data.⁸ Furthermore, extension

of the data to lower values of κ^2 appears to be crucial in any attempt to produce a model which is a good representation of the molecular dynamics and serves as a basis for calculating the scattering with high reliability. Such a model would need to take better account of anharmonicities. It would need to describe the long term motions realistically, and averages of the scattering by molecules in different orientations might require more adequate treatment.

It is worth pointing out that a scaled MR model has been optimized to agree with D_2O data at 295°K and 423°K.⁹ The values of f_1 were 0.17 and 0.54, respectively. There seems to be no consistency in the variations of f_1 with temperature for D_2O as compared to H_2O .

Fig. 1. Comparison of observed and calculated scattering laws for H_2O at 423°K . Data from B. C. Haywood, Ref. 2

Fig. 2 Comparison of observed and calculated scattering laws for H₂O at 550°K. Data from D. I. Page, Ref. 3

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