

## Atomic Motions in Water by Scattering of Cold Neutrons\*

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The inelastic scattering of cold neutrons, of energy about  $4 \times 10^{-3}$  ev, has been used to study the atomic motions in water, mainly in the liquid phase. As a result of the incoherent nature of scattering by protons, the interpretation of the energy changes in terms of atomic motions is particularly simple. The water samples used were extremely thin in order to avoid multiple scattering effects. Instead of the smooth distribution in energy of the scattered neutrons expected for a classical liquid, the experimental results exhibit a number of distinct energy changes. The observed transition energies are (in units of  $10^{-3}$  ev), 61, 21, 8, 5, and 0.5; the first three of these agree with Raman spectroscopy results. The highest energy transition increases in intensity up to the boiling point, but does not shift in energy. For water vapor at 20 atmospheres, a smooth energy distribution is obtained,

which agrees well with the theory of Krieger and Nelkin. The sharp energy levels observed for liquid water indicate that the molecules do not act as free gas atoms of mass 18; in the vapor the effective mass is about 4. An elastic peak is observed that exhibits no spread in energy of the type expected from the theory of classical diffusive motions. Instead, two small but sharp peaks are found to correspond to the gain and loss of  $0.5 \times 10^3$  ev energy; the nature of the transition corresponding to this energy change is unknown. The absence of diffusive broadening shows that the water molecules remain in one location for a relatively long time, about  $10^{-12}$  sec, before undergoing diffusive "jumps." In general, the present experiments show that the atomic motions in water are similar to those in a solid rather than a gas.

## I. INTRODUCTION

NEUTRONS of wavelengths similar to those used in x-ray diffraction, about one Å, exhibit a scattering behavior that is closely similar to x-rays. The primary difference occurs for inelastic scattering, in which energy is exchanged with the lattice vibrations. Whereas lattice vibration energies are insignificant relative to x-ray energies, they are comparable with neutron energies, and as a result measurable energy changes are produced by inelastic scattering of slow neutrons. For neutrons of extremely low energy, about  $10^{-3}$  ev, the exchanges are usually energy gains by the neutrons, and typically much larger than the incident neutron energy. The scattering of these very slow, or "cold" neutrons, has proved to be a valuable tool for the investigation of atomic motions in solids.

When a cold neutron is scattered by a typical solid, the energy of a single "phonon," or quantum of lattice vibration energy, is usually gained by the neutron and the resulting change in energy and momentum of the neutron allows determination of the same quantities for the absorbed phonon.<sup>1</sup> In the determination, conservation of energy and momentum are utilized:

$$\epsilon(\mathbf{q}) = (\hbar^2/2m)(k_f^2 - k_0^2), \quad (1)$$

$$\mathbf{p}(\mathbf{q}) = \hbar[(\mathbf{k}_f - \mathbf{k}_0) - 2\pi\boldsymbol{\tau}] = \hbar[\mathbf{k} - 2\pi\boldsymbol{\tau}]. \quad (2)$$

Here  $\epsilon$  and  $\mathbf{p}$  are the phonon energy and momentum, respectively,  $\mathbf{k}_f$  and  $\mathbf{k}_0$  are the final and initial wave vectors of the neutron,  $\mathbf{k} = \mathbf{k}_f - \mathbf{k}_0$ , and  $\boldsymbol{\tau}$  is a vector of the reciprocal lattice of the solid. The frequency  $\omega$  and

the wave vector  $\mathbf{q}$  of a phonon are related to the energy and momentum by the usual quantum relations  $E = \hbar\omega$  and  $\mathbf{p} = \hbar\mathbf{q}$ .

Some of the first cold neutron measurements<sup>2</sup> of this type supplied information on the atomic motions in aluminum, for example. The measurements give the frequencies of phonons as functions of wave number for acoustic waves travelling in various directions in the crystal, i.e., the dispersion curves. The same method has been used for the more complicated case of crystals containing more than one atom per unit cell, such as germanium<sup>3</sup> and silicon,<sup>4</sup> in which optical as well as acoustic vibrations are observed. These optical modes have higher frequencies than the acoustic waves, and furthermore the frequencies are relatively constant with variation in wave number. In materials in which the nuclear scattering is incoherent (vanadium and hydrogen being the primary examples), the measurements are somewhat simpler because interference effects of waves scattered from different nuclei, expressed by Eq. (2), are absent. In the incoherent case, cold neutron measurements have been reported for vanadium<sup>5</sup> and zirconium hydride.<sup>6</sup>

Although the general type of cold neutron scattering just described occurs in liquids also, usually exhibiting large energy gains, the analysis of the results in terms of atomic motions is much more complex than it is for crystals. Whereas, in some respects, a liquid can be

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<sup>4</sup> H. Palevsky, D. J. Hughes, W. Kley, and E. Tunkelo, Phys. Rev. Letters 2, 258 (1959).

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considered as a polycrystalline solid, its neutron scattering properties cannot be related to definite acoustic and optical dispersion curves. As a result, it is necessary to consider the details of the energy changes resulting from collisions with the moving atoms of the liquid in order to obtain information concerning the motions.

A general theory of the inelastic scattering of neutrons by liquids has been developed by Van Hove,<sup>7</sup> based on his treatment of the disorder scattering of neutrons in iron near the Curie temperature. In this theory, the cross section for scattering with a particular momentum and energy change is expressed in terms of a correlation function  $G(\mathbf{r}, t)$ , which expresses the probability of finding an atom within unit volume at  $\mathbf{r}$  and time  $t$ , with the origin,  $\mathbf{r}=t=0$ , chosen to be the site of any atom in the liquid. As shown by Van Hove, the differential cross section for scattering of neutrons by a system of atoms into unit solid angle  $\Omega$  and unit range of energy change  $\epsilon$  is given by

$$\frac{d^2\sigma}{d\Omega d\epsilon} = \frac{a^2}{2\pi\hbar} \frac{k_f}{k_0} \int \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] G(\mathbf{r}, t) d\mathbf{r} dt, \quad (3)$$

where  $a$  is the scattering length of the nuclei, assumed all identical and of zero spin, hence assuring the absence of isotopic and spin-dependent incoherence. For the general case of nuclei with spin-dependent scattering, the cross section can be written as the sum of coherent and incoherent terms,

$$\frac{d^2\sigma}{d\Omega d\epsilon} = \frac{d^2\sigma_{\text{coh}}}{d\Omega d\epsilon} + \frac{d^2\sigma_{\text{incoh}}}{d\Omega d\epsilon}, \quad (4)$$

where the first term is given by Eq. (3), using the coherent scattering length for  $a$ .

For the incoherent part of the cross section, the phase relation for scattering from two different atoms averages to zero, and Van Hove has shown that  $G(\mathbf{r}, t)$  can be replaced by the simpler "self-correlation function"  $G_s(\mathbf{r}, t)$ , which expresses the probability of finding the atom, initially at the origin, at  $\mathbf{r}$  and at time  $t$ . Thus

$$\frac{d^2\sigma_{\text{incoh}}}{d\Omega d\epsilon} = \frac{a_{\text{incoh}}^2}{2\pi\hbar} \frac{k_f}{k_0} \int \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] G_s(\mathbf{r}, t) d\mathbf{r} dt. \quad (5)$$

Van Hove discussed various general properties of  $G(\mathbf{r}, t)$  but its very generality implies that it cannot be used for detailed predictions of neutron scattering by specific liquids.

Vineyard<sup>8</sup> has considered a "convolution approximation," in which  $G(\mathbf{r}, t)$  in the cross-section expression, Eq. (3), is replaced by a product of the self-correlation function  $G_s(\mathbf{r}, t)$  and the static pair distribution function  $g(\mathbf{r})$ , which expresses the interference effects already known from x-ray studies. The latter function is just

the distribution that is observed for very short interaction times, as in x-ray diffraction, and it expresses the probability that an atom, distinct from the one at the origin, will be found at  $\mathbf{r}$  at time zero. In the Vineyard approximation the coherent scattering cross section is given by

$$\frac{d^2\sigma}{d\Omega d\epsilon} = \frac{a_{\text{coh}}^2}{2\pi\hbar} \frac{k_f}{k_0} \int \int \left[ G_s(\mathbf{r}, t) \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] d\mathbf{r} dt \right. \\ \left. \times \int g(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \right]. \quad (6)$$

For the incoherent part of the scattering cross section the  $g(\mathbf{r})$  term averages to unity, as in the more general case discussed above.

In the convolution approximation, it is possible to treat the energy changes at scattering in a reasonably simple manner, particularly for the limiting cases of short and long interaction times. Vineyard showed that for large changes in neutron momentum, corresponding to short interaction times, the relevant atomic motions would be similar to those of free gas atoms, but that for small momentum changes a diffusive type of motion would apply. In this simple model it was possible to make some quantitative predictions; for example, in the region of diffusive scattering the energy change should be simply related to the diffusion coefficient of the liquid,

$$\epsilon \approx 2\hbar D k^2, \quad (7)$$

where  $D$  is the macroscopic diffusion coefficient and  $\hbar k$  is the momentum transfer in the scattering process. With proper experimental conditions, sufficiently small  $\mathbf{k}$ , it should be possible to verify this predicted energy change.

The method of approach used by Van Hove and by Vineyard is best suited for liquids in which the motions are classical. In this case a smooth distribution of energy changes is expected, rather than sharp energy peaks, which would result if definite quantum levels are present. It is almost impossible to predict in advance whether a given liquid is suitable for the classical treatment, for the applicability depends on the detailed nature of the atomic motions, which are usually unknown. In the present investigation water was studied even though its molecular nature might imply the presence of definite energy levels and hence unsuitability for treatment as a classical liquid by the general theory. The primary motive for the choice of water was the simplicity of interpretation, following from the incoherent nature of the scattering of hydrogen. In addition, the fact that water had already been studied by a number of other methods made it a likely choice for investigation. It is probable that results on the inelastic scattering will be of value to the understanding of water as a moderator in nuclear reactors.

<sup>7</sup> L. Van Hove, Phys. Rev. **95**, 249 (1954).

<sup>8</sup> G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

## SIMPLE PROPERTIES OF LIQUID STRUCTURE

The macroscopic properties of liquids in some respects resemble those of solids and in others the properties of gases, implying that their microscopic structure is intermediate to those of solids and gases. Bulk measurements of many liquid properties have been made but from this information it has not been possible to infer the microscopic spatial relationships, motions, and forces characteristic of atoms in liquids. In spite of many similarities to solids and gases, liquid structure seems to be more complex than either.

Although early theories usually described liquids as gas-like in their structure, more recent work has tended toward a picture in which liquids resemble crystals for very small regions, lacking, however, the long-range order characteristic of crystalline solids.<sup>9</sup> The resemblance to a solid is supported by the small change in density on fusion and the small value of the latent heat of fusion relative to that of vaporization, both implying that the interatomic relationships are similar in the liquid and solid states. Other physical properties, such as specific heat, also support the idea that a liquid, particularly with regard to atomic motions and interatomic forces, resembles a polycrystalline solid.

Diffraction studies, both x ray<sup>10</sup> and neutron,<sup>11</sup> also give strong evidence for a regular arrangement of atoms in liquids, extending for several atom distances around a given atom. The results show, however, that beyond such short distances the atoms are not in a regular array, for the diffraction patterns are not those characteristic of the long-range order of polycrystalline solids. The x-ray and neutron diffraction measurements give the distribution of neighboring atoms relative to a given atom, a distribution that is rather diffuse but shows definite broad peaks extending to the order of several angstroms in distance. This "pair distribution function" is the  $g(r)$  of Eq. (6) and is obtained from the diffraction measurements on the basis of the "static approximation," that the interaction time is negligible. It seems likely that atoms in a liquid are constantly under the influence of forces of 10 to 20 neighbors, hence are not at all able to move freely, as gas atoms, for distances appreciably larger than a small fraction of the atomic spacing.

Thus, diffraction measurements provide valuable data on the geometrical structure of liquid, that is, on the instantaneous picture of the atomic location, but give no information on the motions of the atoms. The close similarity of the specific heats of solids and liquids indicates that the atomic motions must be reasonably similar for the two, at least for the high frequencies that contribute to specific heat. One can make an estimate

of the period of these atomic vibrations in the liquid by analogy with the Debye model for the solid. The velocity of sound in a typical liquid is about 1500 m/sec and for interatomic spacings of 2 Å the period is given by:

$$\frac{2a}{v} = \frac{4 \times 10^{-8}}{1.5 \times 10^5} = 3 \times 10^{-13} \text{ second.}$$

Of course, the presence of a regular lattice arrangement of atoms in a crystal implies that the atomic motions corresponding to phonons of long wavelength must certainly not be the same in a liquid and a solid, in order to account for the fluidity of one and the rigidity of the other. Because the diffusion coefficient is much larger for a liquid than for a solid, it is certain that the atomic motions on a time scale much longer than  $10^{-13}$  sec are not the same, and that the chance for an atom in a liquid to move for an appreciable distance is much greater than for a solid. Thus, for rapid phenomena a liquid is solid-like, and exhibits its characteristic liquid properties primarily for phenomena on a "long" time scale, much greater than  $10^{-13}$  sec. Some information on the motion of atoms in liquids is given by other properties, such as dielectric relaxation and self-diffusion, but measurements of these are sensitive only to times much larger than those typical of the heat motions of the atoms in the liquid.

Water is expected to have even more complicated structure and atomic motions than a monatomic liquid, because of the presence of intramolecular motions. Vibrational motions within the water molecule itself are, of course, well known from studies made with water vapor and these motions are of no particular interest in the study of water as a liquid. The frequencies of the vibrations all appear in infrared absorption and Raman spectroscopy of water vapor. In liquid water additional Raman lines are found,<sup>12</sup> and of these the most energetic is probably a hindered rotation of the water molecule in the potential field of neighboring molecules. Two other lines, difficult to observe because of their low energy, have been similarly interpreted<sup>12</sup> as rotational and translational motions of the water molecule. It is fortunate that for these low energies, where Raman spectroscopy becomes difficult, the cold neutron scattering technique is effective, hence the neutron work serves to extend the energy range much further. A distinct advantage of the study of atomic motions by neutron scattering is that the neutron velocity is comparable to that of the moving atoms, and the corresponding energy changes are easily measured. These energy changes involved in the scattering of cold neutrons make it possible to cover the range from about 0.1 eV, characteristic of the

<sup>9</sup> J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, New York, 1946); J. Leonard Jones and J. A. Pople, *Proc. Roy. Soc. (London)* **A205**, 155 (1951); H. S. Frank, *Proc. Roy. Soc. (London)* **A247**, 481 (1958).

<sup>10</sup> N. S. Gingrich, *Revs. Modern Phys.* **15**, 90 (1943).

<sup>11</sup> D. G. Henshaw, *Phys. Rev.* **105**, 976 (1957).

<sup>12</sup> M. Magat, *Ann. Physik* **6**, 108 (1936); the same energy change, but not the others shown in Fig. 3, has been found in cold neutron experiments by B. N. Brockhouse, *Suppl. Nuovo cimento* **9**, 45 (1958).

hindered rotations, down to  $10^{-3}$  ev, the energy change expected for diffusive type motions.

### EXPERIMENTAL METHOD

The technique used in the present investigation utilizes an incident beam of cold neutrons selected by filtration through a refrigerated block of polycrystalline beryllium. This method was developed several years ago at Brookhaven<sup>2</sup> as a means of obtaining a flux of cold neutrons much higher than that available with conventional neutron monochromators. The first experiments were performed to show the feasibility of cold neutrons scattering as a means of studying atomic motions and the apparatus has since been used for a number of solids—vanadium,<sup>5</sup> germanium,<sup>3</sup> silicon,<sup>4</sup> and zirconium hydride,<sup>6</sup> for example.

The equipment, shown schematically in Fig. 1, has already been described in some detail in connection with the vanadium measurements,<sup>5</sup> hence only an outline and new features will be discussed here. The incident thermal neutrons from the Brookhaven reactor are filtered through a 20-cm cube of polycrystalline beryllium, held at liquid air temperature to increase the transmission of cold neutrons. The filtered beam, of average energy about 0.004 ev and a sharp cutoff at 0.0052 ev, hits a thin sample of the material being studied and some of the neutrons scattered at an angle of  $90^\circ$  pass through a neutron "chopper." The velocity of these neutrons is obtained from the time of flight to a detector 5 meters distant, by means of a 100-channel time analyzer.

In the case of a coherent scatterer, such as aluminum or germanium, it is necessary to use a single crystal and make measurements for various orientations of the scattering sample in order to get full information on the atomic motions. For an incoherent scatterer, however, such as vanadium or hydrogen, there is no need to

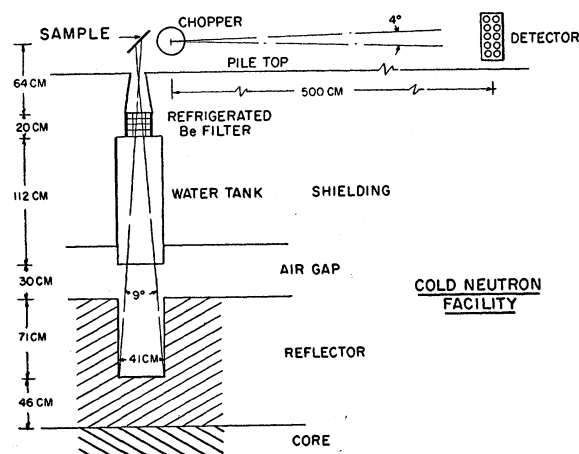


FIG. 1. Experimental arrangement for study of scattering of cold neutrons by water. The incident neutrons are filtered in beryllium and the energies of the scattered neutrons are measured by flight time to the detector. The water tank acts as a shutter and is empty during the measurements.

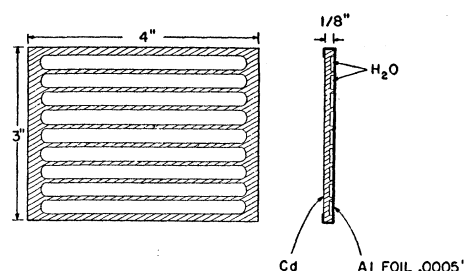


FIG. 2. The aluminum sample holder used for very thin water samples; the slots are milled to the required sample thickness and the Al cover is then pressed flat.

make measurements for different crystal orientations, and furthermore polycrystalline samples may be used. The measurements and analysis are thus much simplified relative to coherent scatterers.

The scattering by water is essentially incoherent because the scattering is predominantly by the hydrogen nuclei. For this case, the experiment consists of recording the flux of scattered neutrons of various energies. Although the measurements for water are simple in principle, it is necessary to make special efforts to utilize extremely thin samples in order to obtain meaningful results. In the present studies it was found that the energy distribution of the scattered neutrons would vary rapidly with sample thickness unless it were less than 0.02 cm. After many attempts, a method was devised to prepare samples of the required thickness, which was reproducible and served very well for the neutron measurements. In this method, a sheet of cadmium approximately  $\frac{1}{8}$  in. thick and 3 in.  $\times$  4 in. in area is first milled flat, then a series of  $\frac{1}{4}$ -in. channels are milled into the cadmium surface to a depth equal to the required sample thickness. The channels are parallel and separated by approximately  $\frac{1}{16}$ -in. cadmium walls, as shown in Fig. 2. A film of water is spread over the channeled face and a sheet of 0.5-mil aluminum foil is placed over the film and rolled flat. The edges of the aluminum are folded over and taped tight with glass scotch tape. The sample holder was arranged so that the temperature could be varied, and a gas cell was also used to study water vapor at a pressure of 20 atmospheres.

An unexpected difficulty in the water measurements arose because extremely small changes in energy were found to occur, relative to other materials in which the scattered neutrons are usually of much greater energy than the incident neutrons. Because of the presence of scattered neutrons so close in energy to the incident beam, it was necessary to make an extremely careful study of the shape of the incident beam itself in order to ascertain the distribution of energy changes for the neutrons scattered with small energy change. The shape of the incident beam was determined by use of a sample of vanadium as scatterer, of such a thickness as to scatter the same fraction of neutrons as the water

samples. Because of the incoherent nature of the scattering of vanadium and the small fraction of inelastic scattering, most of the neutrons are scattered elastically, and the measured energy spectrum reproduces that of the incident beam directly.

Even though measurements were not necessary for various sample orientations, a large number of runs were made to obtain an accurate energy distribution of the scattered neutrons. Various sample thicknesses were studied to determine whether multiple scattering effects were significant, and careful measurements of the energy distribution of the incident beam and the background neutrons were necessary to obtain trustworthy results for the small energy changes. The background was determined by running with an empty sample holder, all other conditions remaining unchanged. The counting rates were of the order of 20 counts per hour in each of 100 timing channels for the thinnest samples, and separate runs were at times as long as three days in order to obtain sufficient statistical accuracy.

#### EXPERIMENTAL RESULTS

As already mentioned, the most suitable method for interpretation of neutron scattering from liquids in terms of atomic motions is determined largely by the nature of the experimental results themselves. If the measured energy distributions of scattered neutrons exhibit only smooth variations in energy, with no evidence of discrete energy levels, then an analysis in terms of Van Hove's correlation function, particularly appropriate to classical motions, is indicated. The  $G(\mathbf{r}, t)$  correlation function gives only the distribution function for atomic positions as a function of time without revealing the specific motions that give rise to the distribution. On the other hand, if discrete energy changes are observed, similar to the optical modes found in solids, it is possible to get information on the specific motions of the atoms directly, without resorting to the correlation function. Thus, before attempting detailed analysis of the results for water, it is best to consider first the entire energy spectrum of scattered neutrons to ascertain if specific energy changes exist.

In Fig. 3 is shown the measured spectrum of neutrons scattered from room-temperature water, over the entire range of neutron flight time for which appreciable intensities were observed. The counting rates shown have been corrected for counter efficiency so that the curve represents the flux of scattered neutrons as a function of flight time. The observed distribution contains a number of peaks, revealing the exchange of energy with definite modes of motion in water. The results show much more detail than is observed for polycrystalline vanadium,<sup>5</sup> and it seems certain that the atomic motions in water are more complicated than in vanadium. The presence of discrete energy changes indicates that the specific atomic motions

responsible for the peaks in Fig. 3 are best studied directly by means of energy changes rather than an analysis in terms of the generalized correlation function. The energy of a particular motion, if large, is obtained simply from the difference between the incident peak of effective energy  $5.0 \times 10^{-3}$  ev, and the observed energy of the peak in the scattered neutron distribution. In the case of the smallest energy change,  $0.5 \times 10^{-3}$  ev, a more detailed analysis is necessitated by the complex shape of the incident distribution.

A most surprising feature of Fig. 3, and one not observed in similar studies with other materials as yet, is the great range of energy changes observed. The large energy change of  $61 \times 10^{-3}$  ev revealed by the prominent peak at  $66 \times 10^{-3}$  ev corresponds to the rather high temperature of  $700^\circ\text{K}$ . At the other end of the distribution there is a change that is much smaller than any observed in other materials thus far, and is, in fact, much less than the energy of the incident cold neutrons. This small energy change is shown by the two small peaks near the prominent elastic peak, for which the energy change is zero. The small energy change amounts to only  $0.5 \times 10^{-3}$  ev and it appears both as a peak just above and just below the elastic peak, representing inelastic scattering in which neutrons gain or lose this amount of energy. The use of cold neutrons is particularly advantageous in this case, for it would be extremely difficult to observe such small changes with higher energy incident neutrons.

Because of the great spread in energy transfer shown by the survey curve in Fig. 3 and the great difference in atomic motions represented, it is desirable to divide

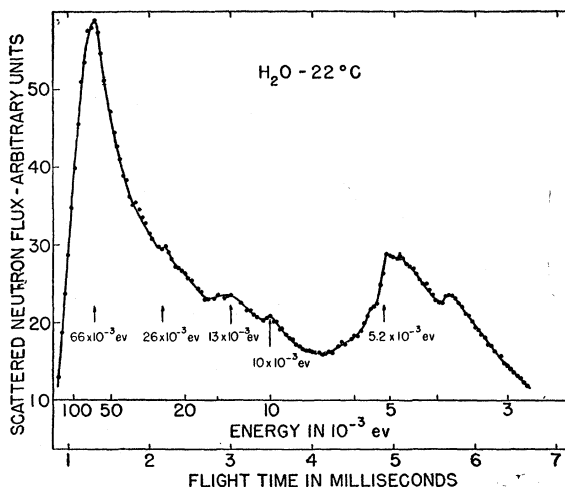


FIG. 3. The time-of-flight spectrum of neutrons scattered by a 0.12-mm water sample, showing the neutron flux in the entire energy range studied. The arrow at  $5.2 \times 10^{-3}$  ev marks the edge of the elastic peak and the others show the inelastic peaks for large energy gains. The energy scale and the values at the peaks refer to the scattered neutrons; the energy gains are less by  $5.0 \times 10^{-3}$  ev, the effective energy of the incident neutrons. The structure near  $4 \times 10^{-3}$  ev results from passage of the thermal neutron beam through aluminum in the reactor structure.

the discussion of the inelastic scattering into the large and the small energy changes.

### A. Large Energy Changes

The very prominent energy gain of  $61 \times 10^{-3}$  ev reveals the presence of a particular motion in water of this energy, presumably a definite quantum transition. The predominance of this energy change implies a distinct component in the temperature agitation of the water molecules. In the present experiments the cold neutrons readily gain one quantum of this energy mode but it will, of course, be an important mechanism as well for loss of energy by faster neutrons as they are being moderated in water.

A specific energy change should increase in intensity as the temperature of the water is raised because of the increase in population of the particular mode of motion. In order to check this expectation, the scattered intensity was measured as a function of the temperature of the water over a range up to the boiling point. The peak corresponding to the  $61 \times 10^{-3}$  ev energy change is shown in Fig. 4 as a function of sample temperature. The intensity of this peak is found to vary exponentially but at a much greater rate than expected from the simple Boltzmann factor,  $e^{-E/kT}$ , with  $E$  taken as  $61 \times 10^{-3}$  ev. The high-energy peak was also found in  $H_2O$  ice and liquid  $D_2O$ , as shown in Fig. 5. Apparently the same transition occurs in both materials, but is shifted to lower energy,  $50 \times 10^{-3}$  ev, in  $D_2O$  and to higher energy,  $74 \times 10^{-3}$  ev, in ice. There is also a definite narrowing of the peak in ice.

The  $61 \times 10^{-3}$  ev level is of sufficiently high energy so that it falls in the low-energy end of the region that can be investigated by Raman spectroscopy. An energy

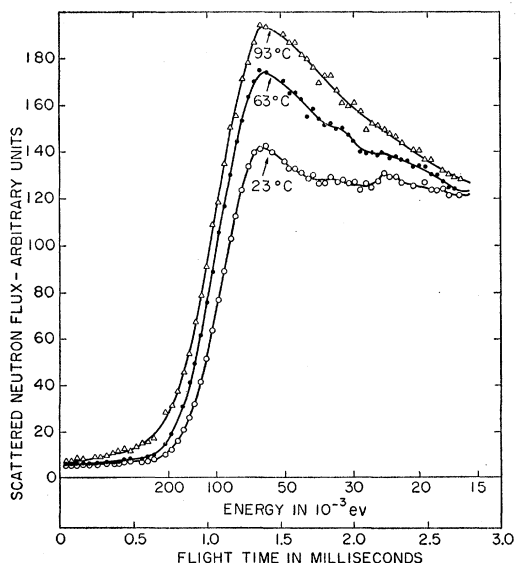


FIG. 4. The high-energy transition,  $61 \times 10^{-3}$  ev, shown for various water temperatures; the peak changes in intensity but not in position. The sample thickness for these runs is 0.8 mm.

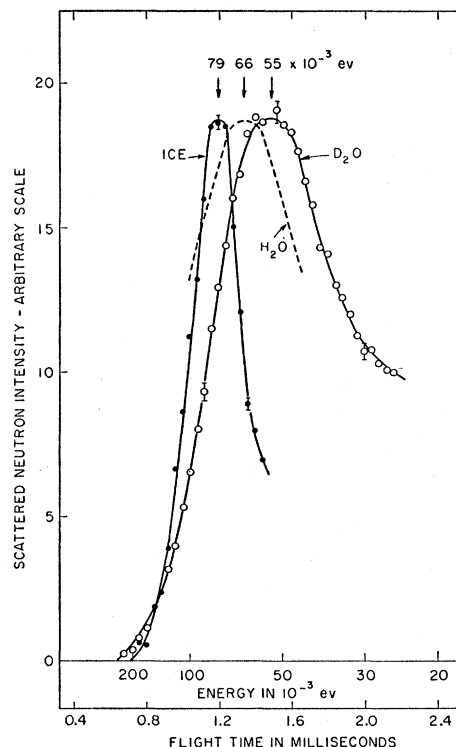


FIG. 5. The high-energy transition measured for  $H_2O$  ice at  $-30^\circ C$  and for  $D_2O$  at  $22^\circ C$ ; the position of the peak for  $H_2O$  at  $22^\circ C$  is shown by the dashed line. The transition energies are less than the quoted energies by  $5.0 \times 10^{-3}$  ev.

change in good agreement with the present result, as shown in Table I, has been detected in Raman spectroscopy measurements with liquid water and interpreted as a hindered rotation of the water molecule in the potential field of its neighbors.<sup>12</sup> This motion is a rotatory oscillation, of much higher energy than the rotation of a free water molecule. Calculations<sup>12</sup> based on a model of a central water molecule in the potential field resulting from four nearest neighbors gives very nearly the observed energy for this motion.

The finding of the prominent motion in water identified as a hindered rotation, both by Raman spectroscopy and scattering of cold neutrons, gives confidence in the latter, much newer technique. Furthermore, it is fortunate that the energy involved is near the lower limit of the Raman technique and the upper energy limit of the neutron technique, for the latter then serves to extend the results of Raman spectroscopy to much lower energy. Actually, the scattering of cold neutrons can be considered as a Raman effect, which is useful for small energy changes because of the low energy of the incident neutrons. In line with these considerations it is not surprising that the energy changes shown in Fig. 3 are easily observed with cold neutrons but are seen only with difficulty in Raman spectroscopy of liquid water.

In the present work with water at room temperature

TABLE I. Comparison of the large energy changes with results of Raman spectroscopy<sup>a</sup>; the listed errors for the latter are estimated from the published curves. All energies are in units of  $10^{-3}$  ev.

Energy of observed neutron peak	Transition energy	Transition energy, Raman
$66 \pm 2$	$61 \pm 2$	$62 \pm 7$
$26 \pm 1$	$21 \pm 1$	$25 \pm 5$
$13 \pm 1$	$8 \pm 1$	$7.5 \pm 2$
$10 \pm 0.3$	$5 \pm 0.4$	...

<sup>a</sup> See reference 12.

it is seen that there are three distinct peaks in the energy region 10 to  $50 \times 10^{-3}$  ev, corresponding to energy gains of 21, 8 and  $5 (\times 10^{-3})$  ev. The first two of these were observed by Raman spectroscopy,<sup>12</sup> Table I, but only as barely resolved peaks. The  $8 \times 10^{-3}$  ev transition, like that of  $61 \times 10^{-3}$  ev, was interpreted by Magat<sup>12</sup> as a hindered rotation of a central molecule in the field of its four neighbors, and the  $21 \times 10^{-3}$  ev transition as a vibration of the central molecule, similar to an optical vibration in a solid. There can be little doubt that the energy peaks are caused by motions of roughly this type but their precise nature can hardly be decided in view of the lack of knowledge of the precise potential field in water.

The motions just discussed have an important bearing on the manner in which neutrons lose energy by collisions in water during the process of moderation in a nuclear reactor. It is well known that for neutrons of several ev energy the interaction with water is the same as that with free protons, in other words the "effective mass" of the object struck is that of the proton. For purposes of calculation of the moderating power of water for neutrons of various energies, it is usually sufficiently accurate to consider the neutron as interacting with an object of increasing effective mass as the neutron energy decreases. In many of these calculations it has been assumed that the neutron interacts with mass points of mass 18 below a certain energy, an assumption based on the belief that the entire molecule recoils as a unit, without rotation, when hit by the neutron.

Although the present results refer to energy transfer from water to neutrons, rather than the reverse process characteristic of moderation, the results are nevertheless applicable to the latter case as well. Thus we conclude from the results of Fig. 3 that there is no evidence of behavior in which the effective mass at collision is 18, but that instead there are rather specific motions of particles, affected greatly by the potential of their neighbors. If the collisions of neutrons with water were the same as those with points of mass 18, the observed energy distribution, which is easily calculated, would be a very broad distribution with a peak at about  $10 \times 10^{-3}$  ev, much different from the

observed distribution showing definite structure. Brockhouse<sup>12</sup> interpreted his results on neutron scattering as evidence of mass 18 behavior, but because of the higher incident neutron energy used (0.03 ev), the details of the present energy changes could not be detected.

Of course, water molecules free from the influence of their neighbors would not scatter neutrons as if their mass were 18, as can easily be ascertained by studying the energy changes at scattering from water vapor. In order to investigate the scattering from water vapor itself in the present set of experiments, a vapor sample was prepared in which the vapor was held at a temperature of  $510^\circ\text{K}$  and a pressure of 20 atmospheres. For this case the distribution of scattered neutrons, shown in Fig. 6, reveals no structure at all, but instead a very broad distribution in energy. For scattering by free water molecules, the behavior is not at all that of points of mass 18° but the scattering must include the rotational motions of the individual water molecules as well.<sup>13</sup>

In Fig. 6 the observed energy distribution of scattered neutron flux is compared with that computed from formulas for the differential scattering cross section by Krieger and Nelkin,<sup>14</sup> which include the various possible motions of water molecules. The theoretical assumptions upon which these formulas were derived are that the molecular rotational and vibrational effects are separable, and that the combined effects of rotation and translation can be approximated by the Sachs-Teller mass-tensor.<sup>13</sup> A further assumption, which holds well for the present measurement, is that the incident neutron energies are large compared with rotational level separation but smaller than the first vibrational state of  $\text{H}_2\text{O}$  vapor. In view of the necessity for appreciable experimental corrections to the data,

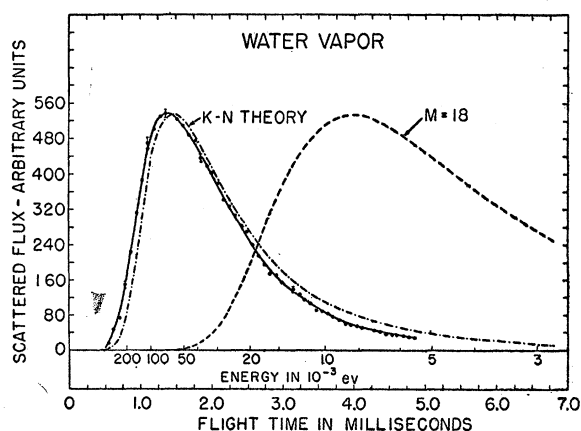


FIG. 6. The time-of-flight spectrum of neutrons scattered from water vapor at 20-atmospheres pressure. The dashed curve is the calculated distribution based on the formulas developed by Krieger and Nelkin, reference 14.

<sup>13</sup> R. G. Sachs and E. Teller, Phys. Rev. **60**, 18 (1941).

<sup>14</sup> T. J. Krieger and N. S. Nelkin, Phys. Rev. **106**, 290 (1957).



such as counter efficiency and chopper transmission, and the approximations made in the theory, the agreement is considered to be very satisfying. The distribution does not correspond to that of a point of a particular mass but if one were to approximate the observed distribution by one expected for a particular effective mass it would turn out that the mass would be about 5 rather than 18. Because of the difficult experimental corrections and the corresponding difficulty in making an accurate calculation for the vapor phase it appears that more careful experiments or theoretical calculations are hardly justified.

### B. Small Energy Changes

A fortunate circumstance connected with the use of cold neutrons is that for small changes in energy it should be possible to study the type of scattering caused by the diffusive motions of the water molecules. This type of inelastic scattering has been discussed by Van Hove<sup>7</sup> and by Vineyard<sup>8</sup> but the experimental conditions used in most investigations of liquids so far have not been in the appropriate range for observation of diffusive motions.

In a neutron scattering experiment, the conditions for observation of diffusive motions are most easily stated in terms of the momentum change at scattering.<sup>8</sup> The momentum change,  $\hbar k$ , defines a certain distance,  $1/k$ , and the appropriate interaction time  $t$  is that required for the neutron to move the distance  $1/k$ :

$$t = \frac{1}{kv} \quad (8)$$

where  $v$  is the velocity of the incident neutron. If  $t$  for a particular experiment is smaller than the time required for an atom to make a diffusive "jump," then the energy changes will result mainly from collisions with freely moving, rather than diffusing, atoms. The "jump" time, if taken to be equal to the period of temperature oscillation of the molecules,<sup>15</sup> is expected to be about  $10^{-13}$  sec, although the time between collisions should be definitely smaller. Vineyard<sup>8</sup> gives  $MD/kT$  as an estimate of the time at which diffusive motions begin, and this estimate would be  $10^{-14}$  sec for water, much less than the atomic vibration period, as it should be for the time of collision with a neighboring molecule. The experiments done with higher neutron energies<sup>16</sup> typically involve only large momentum changes, hence small interaction times, conditions not appropriate for observation of the diffusive scattering.

Considering only energy changes small compared with the incident energy, we find that the momentum

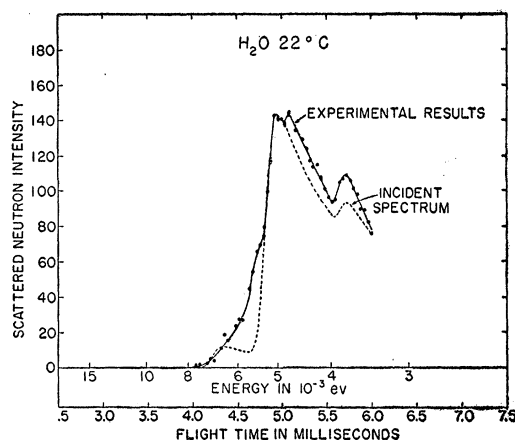


FIG. 7. The elastic peak of scattered neutrons compared with the incident spectrum (dashed line), illustrating the lack of energy broadening and the structure corresponding to gain and loss of  $0.5 \times 10^{-3}$  ev energy. The experimental curve goes to zero at  $8 \times 10^{-3}$  ev because of subtraction of the extrapolated high-energy transitions.

change in the present experiment is about  $2 \text{ \AA}^{-1}$ ; corresponding to this distance is a time, given by Eq. (8), of  $10^{-13}$  sec, a time at which diffusive motions should definitely be evident, on the usual view<sup>8</sup> of the diffusion process. The actual experimental results in the low-energy region, however, shown in Fig. 7, reveal that the energy spectrum of scattered neutrons at the position of the sharp cutoff in the incident spectrum,  $5.2 \times 10^{-3}$  ev, is exactly the same as the incident spectrum.<sup>17</sup> Hence, somewhat surprisingly, there is no diffusive motion evident, which would be manifested as a broadened spectrum of scattered neutrons. Instead, there are some small and extremely sharp energy changes, which will be discussed shortly. These small but sharp energy changes observed in the present work were completely unexpected, for the scattering of cold neutrons by other materials always resulted in energy changes that, if sharp, were large compared with the incident neutron energy.

The magnitude of the smooth energy broadening that is expected to arise from diffusive motions in the liquid is given<sup>8</sup> by the simple formula, Eq. (7), based on the assumption that the interaction time is large enough for diffusion to be manifested, a condition that is expected to hold for the present measurements. The energy spread predicted by Eq. (7) would easily be observable in the present experiment, as was checked by computation of the expected broadened energy distribution. In the computation, the incident energy spectrum was modified by the known resolution of the equipment and the energy spread, assumed Gaussian in shape. Comparison of this computed curve, shown in Fig. 8, with the experimental spectrum shows an

<sup>15</sup> N. F. Mott and R. W. Gurney, *Reports on Progress in Physics* (The Physical Society, London, 1938), Vol. 5, p. 46.

<sup>16</sup> B. N. Brockhouse, *Suppl. Nuovo cimento*, **9**, 45 (1958); I. Pelah, W. Whittemore, and A. W. McReynolds, *Phys. Rev.* **113**, 767 (1959).

<sup>17</sup> The results of Fig. 7 differ markedly from those of B. N. Brockhouse, *Phys. Rev. Letters* **2**, 287 (1959), who did not find the sharp peaks but rather a broadening about  $\frac{2}{3}$  of that expected from Eq. (7).



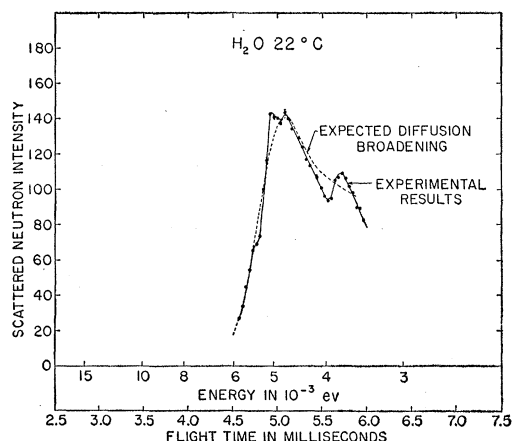


FIG. 8. The elastic peak compared with the distribution expected from broadening resulting from classical diffusive motions of the water molecules.

amount of diffusive scattering much less than expected from the simple theoretical formula, in fact, there is no evidence at all for a smooth energy broadening.

It is worthy of mention that the prominent elastic peak itself is not at all typical of the scattering of cold neutrons, for in most solids elastic (coherent) scattering is impossible for cold neutrons because the neutron wavelength is greater than twice lattice spacing. For the prominent elastic scattering found in the present work, the effective mass of the scatterer must be much larger than that of a single water molecule, implying strong binding of the scattering proton in the liquid medium. An apt analogy is supplied by the incoherent elastic scattering of cold neutrons by vanadium, used here to study the incident spectrum.

A more sensitive test of diffusive motions was made by measurements with the water sample at an elevated temperature of 45°C because  $D$ , and hence the expected energy spread, is larger. The results are shown in Fig. 9 and again there is no spread observed, but rather an elastic peak plus the small, sharp energy changes. It is estimated from the statistical error of the experimental points that the diffusive type of energy spread is less than 10% of the value predicted by Eq. (8).

As the observed scattering in the immediate region of the incident neutron energy is elastic instead of the broadening expected from diffusive motions, it appears likely that there is something wrong in the simple theory underlying Eq. (8). This equation was based on the assumption that molecules in a liquid move as free gas atoms for a short time only, about  $10^{-14}$  sec, then collide with each other, these movements constituting the diffusion process. The results of Figs. 8 and 9 show that this picture is definitely not correct, and that the atoms probably remain near one position for a number of oscillations before migrating to a new region in a diffusive "jump." This point of view has been expressed already by Frenkel<sup>9</sup> on the argument that the atoms in a liquid must vibrate for several periods in

order to have a specific heat so nearly like that of a solid body.

The present measurements reveal in a direct manner that during a time of at least  $10^{-13}$  sec the water molecules do not diffuse appreciably. Using a more detailed model than that employed here,<sup>8</sup> Singwi and Sjölander<sup>18</sup> conclude from the present results that the residence time is greater than  $4 \times 10^{-12}$  sec. When they finally undergo diffusive jumps, the molecules must move a larger distance than usually assumed, if the diffusion coefficient is to retain its known value. For example, if the water molecules should vibrate about 10 periods before they move to a new position, the average "jump" distance must then be greater by  $(10)^{1/2}$  than the value assumed in the classical theory.<sup>15</sup>

It would be difficult to change the experimental conditions to reveal diffusive motions of the type that would occur after a long residence time of some 10 or more atomic oscillations in a particular position. The requirements of Eq. (8) mean that very small momentum changes would have to be used, and the energy changes would then be undetectably small, at least for the presently available experimental techniques.

The small peaks observed on either side of the elastic peak represent inelastic scattering in which the neutrons emit or absorb the same amount of energy,  $(0.5 \pm 0.15) \times 10^{-3}$  ev. This energy change is obtained from a detailed analysis of the shape of the observed, relative to the incident, distribution rather than the simple peak-to-peak distance, and is somewhat smaller than the  $0.7 \times 10^{-3}$  ev reported earlier.<sup>19</sup> Evidently there is an

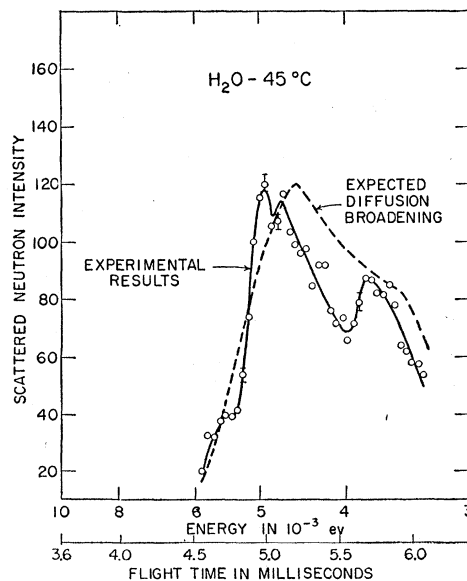


FIG. 9. The elastic peak compared with the expected diffusive broadening for a temperature of 45°C; the broadening is less than 10% of the theoretical value.

<sup>18</sup> K. S. Singwi and A. Sjölander, *Bull. Am. Phys. Soc.* **5**, 168 (1959).

<sup>19</sup> D. J. Hughes, H. Palevsky, W. Kley, and E. Tunkelo, *Phys. Rev. Letters* **3**, 91 (1959).

interaction with a definite quantized motion in the liquid and, like the larger discrete energy changes, it is best treated directly rather than by means of the general  $G(\mathbf{r}, t)$  correlation function. A most surprising aspect of the energy change is its small size relative to the energy levels already known in liquid water from the results of Raman spectroscopy. It is also far smaller than observed for solids in cold neutron work.

The energy is of the same magnitude as the computed<sup>20</sup> and measured<sup>21</sup> prominent transitions in the rotational spectrum of the free water molecule. It is tempting to ascribe the small energy found in the present work to motions similar to the rotational transition in water vapor, but it is a rather unexpected result that in liquid water there are molecules that are free to rotate. These molecules cannot be completely free, of course, for in that case the large energy changes characteristic of gas scattering, Fig. 5, would result. We have already seen that the water molecules seem to be affected greatly by their surroundings, because the hindered rotation has an energy about 100 times greater than the observed small energy change. The possibility that at least some water molecules may be able to rotate freely in liquid water may be related to the finding<sup>22</sup> that positronium atoms are found to exist for surprisingly long times in liquid water, a phenomenon that implies the existence of atoms relatively free of their surroundings within the liquid. On the other hand, it is possible that there is some change in configuration of the atoms that represents a small change in potential energy, which would account for the extremely low-energy transition observed. Thus far, there has been no evidence from other types of measurements with liquid water that would indicate an origin for such a transition.<sup>23</sup>

In order to gain more information on the low-energy transitions, the energy region near the elastic peak was measured for H<sub>2</sub>O at higher temperature, and for D<sub>2</sub>O at room temperature. The measurements at 45°C with H<sub>2</sub>O, Fig. 9, reveal energy transitions of about the same value as observed for room temperature, hence it appears as if the magnitude of the energy transition is not a sensitive function of temperature. Similarly, the measurements with D<sub>2</sub>O also exhibit energy changes of about the same magnitude, although it would not be possible to detect a difference in the transition energy smaller than about 20%.

Even though the present measurements do not give

sufficient information to reveal the nature of the atomic motions in water giving rise to the small energy change, they do illustrate the potency of cold neutron scattering as a means of detecting extremely low-energy transitions in liquids.

### CONCLUSION

The results of the present experiments on the atomic motions in water can be summarized by stating that these motions resemble much more closely those of the solid, rather than the vapor, phase. Even without a careful analysis of the motions responsible for the energy changes, the general appearance of the energy distributions for water, vapor, and ice reveal a close similarity of the solid and liquid phases but great differences between these and water vapor.

The fundamental reason why neutron interactions reveal the resemblance between water and ice so clearly, rather than the fluidity of water, is that the interaction time involved is short, much shorter than the usual types of measurement, such as diffusion and dielectric relaxation. For rapid interactions, of the order of  $10^{-13}$  sec, the molecules are vibrating about fixed positions and the behavior of the liquid is similar to that of a solid. For phenomena occurring in much larger times, water would exhibit its typical fluidity and diffusive motions. Most of the usual types of measurements, of course, refer to this longer time range.

These considerations concerning the resemblance of water to a solid for phenomena occurring in short times has already been discussed in detail by Frenkel.<sup>9</sup> His arguments were of course not based on neutron scattering for the present technique was not available when his theory was formulated. The present measurements, however, furnished a striking and direct demonstration of Frenkel's idea that rigidity and fluidity could both obtain in a liquid. Thermal vibrations and other rapid changes must be similar to those of solids, whereas for times longer than the typical residence time of an atom, the liquid property of fluidity is observed.

It was also found in the present work that, because of the specific quantum motions, these motions could be determined most easily from the energy changes directly, rather than by use of the Van Hove  $G(\mathbf{r}, t)$  correlation function. The present measurements, of course, do not give any information on the location of the water molecules relative to each other but only on their motions. This lack of spatial information, however, is not serious for the atomic locations, the pair correlation function, can be obtained by conventional x-ray diffraction. The Van Hove correlation approach would be more suitable for some classical liquid, perhaps a liquid metal, in which quantum motions of a detailed nature are not observed. Of the specific motions found in the present work perhaps the most interesting is that corresponding to the extremely small energy change. Although of the same magnitude as known levels of the free water molecule, its real nature in liquid water is not at all certain as yet.

<sup>20</sup> G. W. King, R. M. Hainer, and P. C. Cross, *Phys. Rev.* **71**, 433 (1947).

<sup>21</sup> W. C. King and W. Gordy, *Phys. Rev.* **93**, 407 (1954).

<sup>22</sup> J. McGervey and S. DeBenedetti, *Phys. Rev.* **114**, 495 (1959).

<sup>23</sup> Recent Raman spectroscopy results of B. P. Stoicheff indicate a low-energy transition that agrees with the present work, although changes this small have previously not been detected by means of Raman spectroscopy. We wish to thank Dr. Stoicheff for supplying these results before publication. L. B. Borst, *Phys. Rev. Letters* **4**, 131 (1960), has suggested a transition analogous to ortho-para-hydrogen conversion as an explanation of the  $0.7 \times 10^{-3}$  ev transition, and pointed out its possible role in cooling neutrons to very low temperature.