

Coherent Inelastic Scattering of Slow Neutrons by a Polyatomic Liquid Element

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An expression for the coherent inelastic-scattering cross section of slow neutrons by a diatomic liquid element has been determined by extending Vineyard's approximation to systems with internal degrees of freedom. The range of validity of the expression obtained has been discussed, taking into account also the energy resolution of the experimental setup. The energy spectrum of neutrons scattered by a sample of liquid bromine has been measured with a triple-axis spectrometer for a fixed value of the modulus of the momentum exchange. Reasonable experimental evidence for the existence of a peak associated with the excitation of the first vibrational level in liquid bromine was obtained in the neighborhood of an energy transfer $\hbar\omega = 0.04$ eV; this is approximately the value established by measurements of conventional spectroscopy in the gaseous phase.

INTRODUCTION

A LARGE amount of information on the dynamical behavior of matter on a microscopic scale is generally obtained, using radiation as a probe, by the analysis of the momentum and energy transfers occurring in a scattering process. It is customary to utilize electromagnetic radiation and electrons for this kind of study; in particular, the possible *momentum transfers* allowed by the system are usually observed in conventional x-ray and electron diffraction techniques, although they do not involve a perceptible energy variation of the incident radiation; the allowed *energy transfers* are usually observed utilizing a high-wavelength electromagnetic radiation (10^3 – 10^8 Å), but they do not involve perceptible momentum transfers. As a consequence, the traditional methods allow investigations limited to a rather narrow range of the *dynamical quantities* connected with any condensed system.

In liquids, for instance, the bonds between different molecules might affect the internal degrees of freedom, relaxing eventually the individuality^{1,2} of the internal modes of vibration. Furthermore, relations between energy and momentum may arise from the influence of the short-range order in a liquid.

At present, the methods of neutron spectrometry offer the possibility of exploring a wide range of energy and momentum transfers; in fact, the "collision time" for thermal neutrons is roughly comparable with the times characteristic of the elementary excitations in a liquid, and the neutron wavelengths are of the same order as the nearest-neighbor interatomic distances.

Most experimental data obtained through slow neutrons scattered by polyatomic liquids concern hydrogenous systems. This is mainly due to the peculiar incoherence of the hydrogen scattering cross section combined with its large magnitude. The observed scattering

is thus almost entirely associated with the motion of individual hydrogen atoms.

It seems, then, advisable to investigate with similar techniques other liquids, and especially those (like heavy halogens) having a sublimation energy not too small compared with the dissociation energy. Such liquids could eventually display, at least in principle, a shift of the quantum levels associated with the internal degrees of freedom. Their less energetic modes, in limiting cases, could be smeared out and eventually disappear because of fairly strong interactions with the surrounding molecules. Furthermore, it is conceivable that, in the near future, improved experimental facilities could eventually allow the determination of possible correlations between momentum and energy transfers, roughly similar to the dispersion relations for the optical branches of polyatomic crystals.

In this work the Vineyard approximation has been extended to the coherent inelastic scattering of slow neutrons by a polyatomic liquid element.³ The formalisms of Van Hove and Zemach and Glauber has been employed to compute the additional error introduced by extending this approximation to systems with internal degrees of freedom. It is found that such an additional error is dependent both on the energy of the quantum level and on the collision time as controlled by the energy resolution of the spectrometer. The differential cross section of liquid bromine for the excitation of one vibrational quantum has been computed. Calculations have been compared with the results of an experiment carried out at extremely low intensities with a triple-axis spectrometer. In this experiment a fixed value of the modulus of the wave vector transfer⁴ has been maintained.

Within the present possibilities of the technique, inherently limited by the available neutron flux, we have

¹ P. G. De Gennes, in *Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 239.

² B. N. Brockhouse, S. Bergsma, B. A. Dasannacharya, and N. K. Pope, in *Proceedings of the Chalk River Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. I, p. 189.

³ It is known that in principle Vineyard's approximation does not faithfully take into account interference effects wherever they are considerable. In the present context the helpful approximations involved in Vineyard's paper seems to be appropriate to a trial treatment of our problem.

⁴ B. N. Brockhouse, in *Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 113.

found reasonable experimental evidence for the existence of a vibrational peak in the neighborhood of 0.04 eV.⁵ Other features of the experimental data are seen to agree with the calculations reported here, but the length of time required to obtain convincing experimental results did not encourage us to perform other measurements for a more extended comparison at other values of the momentum transfer.

MOLECULAR DYNAMICS AND NEUTRON SCATTERING

The partial differential cross section of a molecular system (per steradian and per unit final energy) is written as

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E'} = \frac{1}{\hbar} \frac{k}{k_0} \sum_{l\nu} \sum_{l'\nu'} a_\nu a_{\nu'} \int dt e^{-i\omega t} \times \langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l'\nu'|0)] \rangle, \quad (1)$$

where \mathbf{k}_0 and \mathbf{k} are the wave vectors of the incident and outgoing neutron, respectively, $\mathbf{Q} = \mathbf{k}_0 - \mathbf{k}$ is the wave-vector transfer, a_ν is the bound scattering length of the nucleus of type ν in the l th molecule, $\mathbf{r}(l\nu|t)$ is its Heisenberg position operator, $\hbar\omega = E_0 - E'$ is the energy transfer, and the symbol $\langle \rangle$ indicates the thermal average over the initial states of the system. The summation is extended to all the atoms of the system.

In what follows we will consider a diatomic liquid of

$$\epsilon = 1 - \frac{\langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \rangle \langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l\nu|t)] \rangle}{\langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \rangle} \quad (5)$$

will provide the additional relative error on $\chi_{l\nu, l'\nu'}(\mathbf{Q}, t)$ introduced by extending the Vineyard approximation to a polyatomic element and due to "internal" interference. ϵ can be evaluated following Zemach and Glauber.¹⁰

The positional operator $\mathbf{r}(l\nu|t)$ is expressed in terms of

$$\mathbf{r}(l\nu|t) = \mathbf{R}(l|t) + \mathbf{b}(l\nu|t) + \mathbf{u}(l\nu|t), \quad (6)$$

where $\mathbf{R}(l|t)$ indicates the position of the center of mass of the molecule, $\mathbf{b}(l\nu|t)$ is the vector distance of the

⁵ This is the value reported by several authors who analyzed the absorption and Raman spectra in the gas. (See Refs. 20 and 21). It should be remarked that the high absorption of light in liquid bromine did not allow, as far as we know, a Raman analysis in the liquid phase.

⁶ Nevertheless our consideration can be easily extended to a polyatomic element.

⁷ L. Pauling, Phys. Rev. **36**, 430 (1930).

⁸ G. Vineyard, Phys. Rev. **110**, 999 (1958).

⁹ It is difficult to give a satisfactory justification of the extension of Vineyard's approximation to the motions of pairs of atoms that are close neighbors but belong to different molecules. However, we think that at least the additional errors arising from correlations between the instantaneous direction of these motions will suffer a sort of cancellation in the averaging process.

¹⁰ A. C. Zemach and R. S. Glauber, Phys. Rev. **101**, 118 (1956).

identical nuclei.⁶ We will assume that the internal degrees of freedom can be described by simple independent harmonic motions (vibrations and hindered rotations). Such an assumption is acceptable when the intermolecular forces and the moment of inertia of the molecule are large.⁷ For instance, bromine and iodine are in this category. The translations of the center of mass of the molecules are considered to be free during the time of observation.

The thermal average

$$\langle \chi_{l\nu, l'\nu'}(\mathbf{Q}, t) \rangle = \langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l'\nu'|0)] \rangle \quad (2)$$

is the same as

$$\langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l'\nu'|0)] \rangle, \quad (3)$$

obtained by inserting the identity operator between the two exponential operators.⁸

We may try to approximate (3) with

$$\langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \rangle \times \langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l'\nu'|0)] \rangle. \quad (4)$$

Such a procedure might be assumed to correspond to Vineyard's approximation for $l \neq l'$,⁹ that is for "external" interference. For $l = l'$ we must investigate two cases: (i) $\nu = \nu'$ and (ii) $\nu \neq \nu'$. When $\nu = \nu'$, (3) and (4) are identical. For $\nu \neq \nu'$ a computation of the quantity

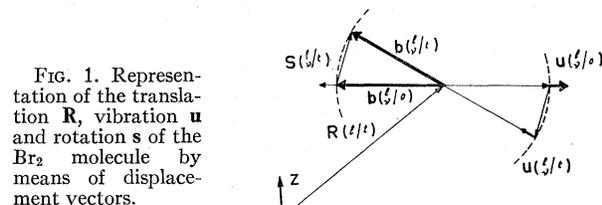
equilibrium position of nucleus ν from the center of mass at time t , and $\mathbf{u}(l\nu|t)$ is the radial displacement of the vibrating nucleus with respect to $\mathbf{b}(l\nu|t)$.

$\mathbf{b}(l\nu|t)$ is written in the form^{11,12}

$$\mathbf{b}(l\nu|t) = \mathbf{b}(l\nu|0) + \mathbf{s}(l\nu|t), \quad (6')$$

where $\mathbf{s}(l\nu|t)$ is the tangential displacement induced by the torsional oscillation (see Fig. 1).

The thermal averages appearing in (5) can now be separated in terms of the translational, vibrational and rotational degrees of freedom.



¹¹ S. C. Krieger and M. S. Nelkin, Phys. Rev. **106**, 290 (1957).

¹² D. Butler, Proc. Phys. Soc. (London) **81**, 276 (1963).

We obtain (for $\nu \neq \nu'$):

$$\epsilon \approx 1 - \frac{\langle \exp[i\mathbf{Q} \cdot \mathbf{u}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{u}(l\nu|0)] \rangle \langle \exp[i\mathbf{Q} \cdot \mathbf{u}(l\nu|0)] \exp[-i\mathbf{Q} \cdot \mathbf{u}(l\nu'|0)] \rangle}{\langle \exp[i\mathbf{Q} \cdot \mathbf{u}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{u}(l\nu'|0)] \rangle} \times \frac{\langle \exp[i\mathbf{Q} \cdot \mathbf{s}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{s}(l\nu|0)] \rangle \langle \exp[i\mathbf{Q} \cdot \mathbf{s}(l\nu|0)] \exp[-i\mathbf{Q} \cdot \mathbf{s}(l\nu'|0)] \rangle}{\langle \exp[i\mathbf{Q} \cdot \mathbf{s}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{s}(l\nu'|0)] \rangle}. \quad (7)$$

Following Zemach and Glauber¹⁰ and averaging over the molecular orientations¹¹ we obtain:

$$\epsilon \approx 1 - \exp(-2Q^2\{\gamma_\nu(0) - \gamma_\nu(t)\} + \{\gamma_r(0) - \gamma_r(t)\}), \quad (8)$$

where

$$\gamma_\nu(t) = \frac{\hbar}{6M\omega_\nu} \frac{Z_\nu^{1/2}}{Z_\nu - 1} (Z_\nu^{1/2} e^{-i\omega_\nu t} + Z_\nu^{-1/2} e^{+i\omega_\nu t}) \quad (9)$$

(and analogously for γ_r), Z being given by $\exp \hbar\omega/K_B T$. In Eq. (9) the γ 's are evidently connected with the mean-square displacements of the nuclei in thermal equilibrium at a temperature T , due to vibrational (ν) and rotational (r) motions of circular frequencies ω_r and ω_ν , respectively; K_B is the Boltzmann constant and M is the mass of a nucleus.

ϵ may be regarded as negligible when¹³

$$2Q^2\{\gamma_\nu(0) - \gamma_\nu(t)\} + \{\gamma_r(0) - \gamma_r(t)\} \ll 1; \quad (10)$$

that is, for a given Q , when either the γ 's or the differences $\gamma(0) - \gamma(t)$ are small.¹⁴

The contribution to ϵ coming from the vibrational motions may be considered to be small, since the recoil energy $\hbar^2 Q^2/2M$ is small compared with the vibrational energy $\hbar\omega_\nu$ [see Eqs. (8) and (9)].

The rotational motions deserve more consideration, since the energies of the hindered rotations may well be smaller than the vibrational energies; this would result in higher values of the γ_r 's. The order of magnitude of γ_r can be deduced on the basis of some computations of Pauling, valid for molecular crystals.⁷ For iodine in its solid phase, for instance, it is found $\gamma_r(0) = 1.3 \times 10^{-2} \text{ \AA}^2$. Therefore, condition (10) can be satisfied only if the difference $\gamma_r(0) - \gamma_r(t)$ is conveniently small at all times which give substantial contributions to the experimental intensity, as determined by the instrumental energy resolution (see Appendix I). At least under suitable experimental conditions, one may then proceed with some confidence to extend the Vineyard approximation [see Eqs. (3) and (4)] to the coherent inelastic neutron scattering by a polyatomic liquid element.

¹³ Note that ϵ is connected with the square of Eq. (2) as follows:

$$\epsilon = 1 - \langle \chi_{\nu\nu}(Q,t) \rangle^2.$$

¹⁴ Note that

$$\gamma(0) > \gamma(0) - \gamma(t).$$

Inserting Eq. (4) in (1), we obtain:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E'} = \frac{1}{\hbar} \frac{k}{k_0} \sum_{l\nu'} \sum_{l\nu''} a_\nu a_{\nu'} \left\{ \int e^{-i\omega t} dt \times \langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \rangle \right\} \times \langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l\nu'|0)] \rangle. \quad (11)$$

For a system of identical nuclei the thermal average in the integral of (11) does not depend on the indexes (l, ν). By writing

$$F(Q) = \sum_{l\nu'} \sum_{l\nu''} \langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \times \exp[-i\mathbf{Q} \cdot \mathbf{r}(l\nu'|0)] \rangle, \quad (12)$$

one gets

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E'} = \frac{1}{\hbar} \frac{k}{k_0} a^2 F(Q) \int e^{-i\omega t} dt \times \langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \rangle. \quad (13)$$

Equation (13) expresses the separation of the interference term $F(Q)$, obtainable by conventional diffraction techniques, from the energy dependent self-correlation part.

Utilizing Eq. (6) one may write the thermal average appearing in (13) as

$$\langle \exp[i\mathbf{Q} \cdot \mathbf{r}(l\nu|t)] \exp[-i\mathbf{Q} \cdot \mathbf{r}(l\nu|0)] \rangle = \langle \chi_{\nu\nu}^t \rangle \langle \chi_{\nu\nu}^* \rangle \langle \chi_{\nu\nu}^* \rangle. \quad (14)$$

This is allowed by the assumed independence of the translational, vibrational and hindered rotational motions.

We shall now develop an expression for the cross section of bromine (see Appendix II). To this end, it is necessary to analyze the time dependence of the $\langle \chi_{\nu\nu} \rangle$'s. Within the frame of the observation time delimited by the energy resolution of the spectrometer ($\sim 2.3 \times 10^{-13}$ sec), it is seen that condition (10) is reasonably satisfied.

During the (small) times involved in our experiment, the translational motions can be faithfully described as free [Eq. (AII.1)].

The hindered rotations, probably associated with a characteristic energy of some meV, are treated in Doppler approximation, that is including only terms up to l^2 in the short-collision-time approximation [Eq.

(AII.2)], after they have been averaged over the molecular orientations.

The vibrational term is derived from Zemach and Glauber [Eq. (3.19) of Ref. 10] by averaging over the molecular orientations¹⁵ [Eq. (AII.3)].

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E'} = \frac{1}{\hbar} \frac{k}{k_0} a^2 F(Q) (\sqrt{\pi}) \frac{\exp[-(\hbar Q^2/6M\omega_v) \coth(\hbar\omega_v/2KT)]}{[(Q^2/4M)KT + \frac{1}{12}(\hbar Q^2/M\omega)\omega_r^2 \coth(\hbar\omega_r/2KT)]^{1/2}} \sum_{n=-\infty}^{\infty} \left(\exp\left\{ -\frac{n\hbar\omega_v}{2KT} \frac{1}{|n|} \right. \right. \\ \left. \left. \times \left[\frac{\hbar Q^2}{12M\omega_v \sinh(\hbar\omega_v/2KT_B)} \right]^{|n|} \right\} \exp\left\{ -\frac{(\omega - n\omega_v)^2}{(Q^2/M)[KT + \frac{1}{3}(\hbar/\omega_r)\omega_r^2 \coth(\hbar\omega_r/2KT)]} \right\} \right). \quad (15)$$

Equation (15) expresses the cross section in terms of the product of two factors: the interference term $F(Q)$, obtainable as a conventional diffraction pattern, and a self-term which—besides the Debye-Waller factor very near to unity associated with the mean square displacement of the vibrating atom—represents the intensity associated with the energy transfer between the neutron and the vibrational quanta, Doppler-broadened by the translational and hindered rotational motions. This latter intensity factor is directly responsible for the low intensity recorded during the experiment. For one-quantum production or annihilation ($n = \pm 1$) the factor $\hbar Q^2/[12M\omega_v \sinh(\hbar\omega_v/2KT_B)]$ represents the effective mean-square displacement of the harmonic oscillator, projected on the scattering vector.

In the case of bromine this intensity factor is of the order of 2×10^{-3} , so that an experimental study of this type is adversely influenced by the severely low value of the signal-to-background ratio.

In actual experiments the energy resolution of the experimental setup must be considered, as suggested also by our previous considerations about ϵ . In our experiment (see Appendix II), the instrumental energy width of the spectrometer combines quadratically with the widths of the Doppler broadening, and actually overwhelms their sum.

THE EXPERIMENT

The differential cross section of liquid bromine at room temperature has been measured in the present experiment by an analysis of the energy spectrum of the scattered neutrons in a range of energy exchange between 30 and 60 meV.

The measurements have been performed utilizing the triple axis crystal spectrometer previously described,^{16,17} installed at the 5 MW Ispra-1 reactor, which allowed us during the energy analysis of the outgoing neutrons to

If the small recoil terms associated with the high value of the mass of bromine are neglected and an average is taken of $F(Q)$ over the possible orientations, the integration indicated in Eq. (14) leads to the following expression for the differential cross section:

keep constant the modulus $\hbar Q$ of the momentum exchanged (see Fig. 2).

This experimental method, utilized here for the first time in the study of a liquid, is an obvious derivation of the well-known “**Q-constant** method” widely used already to measure the dispersion relations in crystals.⁴

Bromine was contained in a small Teflon cylinder 0.4 mm thick. The energy of the monochromatic beam (Al111 as monochromator) was fixed at 150 meV.

The value $Q = 3.6 \text{ \AA}^{-1}$ was chosen as a compromise between the necessities of minimizing the contribution to the width of the resonance peak (which increases as Q) and maximizing the intensity [which is practically a function of the type $QF(Q)$].¹⁸

For low-intensity measurements [2.6 counts per minute], the background must be kept as low as possible and its importance accurately evaluated.

Therefore several series of measurements were performed to check the reproducibility of the signal-to-background ratio. The background has been obtained by turning the Al111 analyzing crystal four degrees off the Bragg reflection. Counting periods lasting about four hours were necessary at any central value of the final energy in the analyzing spectrometer in order to obtain a reasonably low statistical error.

Results are reported in Fig. 3 where any point, whether signal or background, represents an average value obtained through three or more separate runs cor-

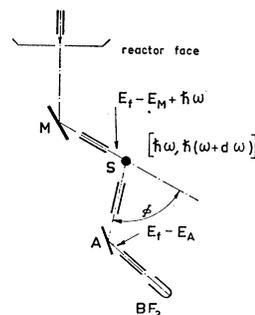


FIG. 2. Experimental setup. M = monochromating crystal, S = sample, A = analyzing crystal, ϕ = scattering angle. The symbol \equiv represents collimators.

¹⁵ M. Nelkin, Phys. Rev. **119**, 741 (1960).

¹⁶ G. Caglioti, E. De Agostino, F. Marsili, A. Paoletti, U. Pellegrini, and F. P. Ricci, Suppl. Nuovo Cimento **23**, 17 (1962).

¹⁷ G. Caglioti and P. Ascarelli, in *Proceedings of the Chalk River Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. I, p. 259.

¹⁸ It should be noticed that the lower but perhaps more suitable value of $Q = 1.6 \text{ \AA}^{-1}$, relative to the first (strong) diffraction peak of $F(Q)$ (Ref. 17), was not practically accessible, owing to the background arising at small scattering angles.

responding to a total counting time per point of approximately twelve hours. In the neighborhood of $\hbar\omega_v = 0.04$ eV the function

$$\text{constant} \times \frac{k}{k_0} \exp\left(-\frac{4 \ln 2 \hbar^2 (\omega_0 - \omega_v)^2}{\Delta^2}\right)$$

suggested by Eq. (AII.4), normalized at the peak value, has been plotted for a visual comparison.

DISCUSSION AND CONCLUSIONS

An expression for the coherent inelastic scattering of slow neutrons by a diatomic liquid element has been derived on the basis of the Vineyard approximation. The specific case of a low-resolution experiment has been discussed within the short-collision-time approximation; this is equivalent to considering low-energy (translational and rotational) motions only as they broaden the energy distribution of neutrons scattered by high-energy modes associated with the internal vibrational degrees of freedom. In these conditions the results turn out to be quite independent of the particular model used for translations and rotations. Therefore, though it is not obvious that the molecular translations should appear free and the harmonic approximation should be appropriate for hindered rotations in a liquid, this does not affect the results since these degrees of freedom are anyhow treated in a short-collision-time approximation.

As far as the experiment is concerned the data of Fig. 3 indicate fair evidence for the existence of a peak at 0.04 eV that possibly emerges from a background of radiation whose trend seems to match, on the low-energy side, the pattern obtained by Coote and Haywood¹⁹ in their experiment covering the region of energy transfer 0–0.02 eV. The value of the energy transfer at the maximum cannot be stated with accuracy, but lies in the expected region of 0.0435 eV.^{20–22} The peak value of the intensity of the neutron group, and the intensity observed in previous studies on the same liquid^{23,17} (10^{-3} : 1) agree in order of magnitude. Finally, the width of the peak seems to be mainly determined by the instrumental resolution (Appendices AI and AII).

We think that increasingly complete data, undoubtedly obtainable with the advent of higher flux neutron beams, would be of real interest for a clearer

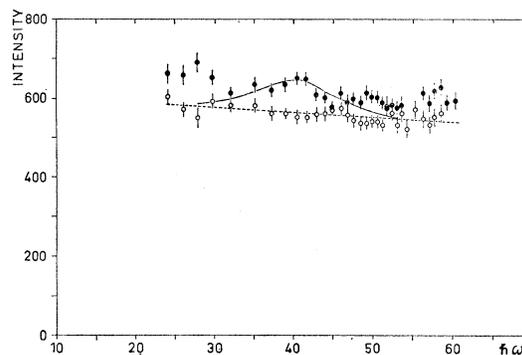


FIG. 3. Bromine energy spectrum. ●—signal; ○—background.

insight into the molecular modes in polyatomic liquid elements.

ACKNOWLEDGMENTS

Dr. J. J. Antal shared in the early stage of the experiment and his helpful interest in this work is very gratefully acknowledged. We wish also to thank Professor N. K. Pope for his comments on the manuscript.

APPENDIX I

In this appendix we discuss in some detail the problem of the instrumental connection between a triple-axis spectrometer and the physical process under study. The instrument is supposed to be set for a Q -constant experiment, with a fixed central value E_M of the energy of the monochromating spectrometer, and a value of the central energy of the analyzing spectrometer which varies around $E_A = E_M - \hbar\omega$.

The counting rate at any given "central" value of the energy at which the analyzing spectrometer may be set is given by:

$$I = A \iint \exp\left[-\frac{(E_f - E_M + \hbar\omega)^2 4 \ln 2}{\Delta_M^2}\right] \times S(Q, \omega) \exp\left[-\frac{(E_f - E_A)^2 4 \ln 2}{\Delta_A^2}\right] d\omega dE_f. \quad (\text{AI.1})$$

In this expression E_f is the final value of the neutron energy, as achieved by the neutron via an energy transfer in the range $\hbar(\omega, \omega + d\omega)$ in the sample, E_M and E_A are the central values of the monochromating and analyzing spectrometers, respectively, and Δ_M and Δ_A are their energy resolutions (full widths at half-maximum), obtainable by generalizing Eq. (14) of Ref. 24 to the case of different collimators^{25,26} (see

²⁴ V. L. Sailor, H. L. Foote, Jr., H. H. Landon, and R. E. Wood, *Rev. Sci. Instr.* **27**, 26 (1956).

²⁵ Nevertheless Δ_A depends on the Bragg angle of the analyzer, and this should in principle be remembered when computing Δ , especially if the region of Bragg angles covered by the analyzing spectrometer is large [see Eq. (AI.4)].

²⁶ G. Caglioti, *Acta Cryst.* (to be published).

¹⁹ G. E. Coote and B. C. Haywood, in *Proceedings of the Chalk River Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, 1962), Vol. I, p. 249.

²⁰ O. Darbyshire, *Proc. Roy. Soc. (London)* **A159**, 93 (1937).

²¹ H. Stammreich, *Phys. Rev.* **78**, 79 (1950).

²² Some evidence for the existence of the vibrational peak around 0.04 eV was also achieved during measurements performed in this laboratory with J. J. Antal, utilizing the inverse beryllium filter technique. [See also, A. D. B. Woods, B. N. Brockhouse, M. Sakamoto, and R. M. Sinclair, in *Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 467].

²³ G. Caglioti and F. P. Ricci, *Nuovo Cimento* **24**, 103 (1962).

Fig. 3). The integral (AI.1) has to be performed over all the values of E_f accepted by the spectrometer for a fixed value of ω , and then over all of the possible energy changes $\hbar\omega$ which the neutron may undergo in the sample within the instrumental resolution. The constant A is a normalization factor which must be evaluated only in absolute intensity measurements, and can be obtained by a calibration of the spectrometer. In the following we will omit constant multiplicative factors arising from integration processes.

We easily obtain:

$$I \propto \int S(Q, \omega) R(\omega_0 - \omega) d\omega, \quad (\text{AI.2})$$

where $R(\omega_0 - \omega)$ turns out to be the energy resolution function of the spectrometer:

$$R(\omega_0 - \omega) \propto \exp[-(4 \ln 2) \hbar^2 (\omega_0 - \omega)^2 / \Delta^2], \quad (\text{AI.3})$$

ω_0 being the energy difference $E_M - E_A$ and

$$\Delta^2 = \Delta_A^2 + \Delta_M^2. \quad (\text{AI.4})$$

The intensity I in (AI.2) has the form of a convolution of the scattering function $S(Q, \omega)$ and the resolution function $R(\omega_0 - \omega)$. From a known theorem on Fourier transforms, (AI.2) can also be written as the Fourier transform of the product of the Fourier transforms $\sum_{l, l'} \chi_{l, l'}(Q, t)$ of $S(Q, \omega)$ and $R(t)$ of $R(\omega)$ as follows:

$$I \propto \int e^{-i\omega_0 t} dt \left\{ \sum_{l, l'} \chi_{l, l'}(Q, t) \times R(t) \right\}. \quad (\text{AI.5})$$

Since

$$R(t) \propto \exp\left[-\frac{t^2 \Delta^2}{16(\ln 2) \hbar^2}\right], \quad (\text{AI.6})$$

the effect of the instrument appears as a weight function controlling the effective interaction time, the latter being defined as (full width at half-maximum)

$$\Delta t = 8(\ln 2) \hbar / \Delta. \quad (\text{AI.7})$$

In our experimental setup Δ was set at 12 meV. Correspondingly Δt turns out to be of the order of 2.3×10^{-13} sec, which is of the right order for treating the translational motions as free, the hindered rotations in the Doppler approximation, and the high-energy vibrational motions in the frame of the usual phonon expansion.

APPENDIX II

In this appendix we derive the expression for the cross section taking into account the results of Appendix I.

The intermediate function $\langle \chi_{\nu\nu}(Q, t) \rangle$ for the transla-

tion of the center of mass (of effective mass $2M$) is

$$\langle \chi_{\nu\nu}^t \rangle \approx \exp[-(Q^2/4M)(i\hbar t + K_B T t^2)]. \quad (\text{AII.1})$$

The analogous quantity for the hindered rotations of the molecule is:

$$\langle \chi_{\nu\nu}^r \rangle \approx \exp\left\{-\left[\frac{i\hbar Q^2}{6M} t + \frac{1}{12} \frac{\hbar Q^2}{M \omega_r}\right] \times \coth\left(\frac{\hbar \omega_r}{2K_B T}\right) \omega_r^2 t^2\right\}. \quad (\text{AII.2})$$

These motions have been treated as a single normal mode of frequency ω_r .

Finally, for the vibrational terms,

$$\langle \chi_{\nu\nu}^v \rangle \approx \exp\left\{-\left[\frac{\hbar Q^2}{6M \omega_v} \coth\frac{\hbar \omega_v}{2K_B T}\right]\right\} \times \sum_{n=-\infty}^{\infty} \exp\left[i n \omega_v t - n \frac{\hbar \omega_v}{2K_B T} \right] \frac{1}{|n|!} \times \left(\frac{\hbar Q^2}{12M \omega_v \sinh(\hbar \omega_v / 2K_B T)} \right)^{|n|}. \quad (\text{AII.3})$$

The product of the $\langle \chi_{\nu\nu} \rangle$'s in the previous formulas must be weighted by the time resolution function $R(t)$ as found in (AI.5) and (AI.6).

The integration is then easily carried out, by neglecting the recoil quantum terms (which are linear in t). These terms are very small because of the high mass of bromine. An expression similar to (15) is then obtained, in which the instrumental energy resolution $\Delta^2/4 \ln 2$ is combined quadratically with

$$\frac{Q^2}{M} K_B T + \frac{1}{3} \frac{\hbar Q^2}{M \omega_r} \left(\coth \frac{\hbar \omega_r}{K_B T} \right) \omega_r^2.$$

In practice, the instrumental term Δ overwhelms the total Doppler width so that the final expression to be used in our experiment can be written, for the creation of one vibrational quantum,

$$I \propto \frac{a^2 k}{\hbar k_0} F(Q) \exp\left\{-\left[\frac{\hbar Q^2}{6M \omega_v} \coth\frac{\hbar \omega_v}{2K_B T}\right]\right\} \times \frac{\hbar Q^2 \exp(\hbar \omega_v / 2K_B T)}{12M \omega_v \sinh(\hbar \omega_v / 2K_B T) \Delta} \times \exp\left[-\frac{\hbar^2 (\omega_0 - \omega_v)^2}{\Delta^2} 4 \ln 2\right]. \quad (\text{AII.4})$$