of $\log[(W_0^2-1)ft]=8.5$ for the 470-kev beta-component indicate either first or second forbidden, or possibly first forbidden, $\Delta I=\pm 2$. Since allowed and second-forbidden transitions involve no parity change, whereas first-forbidden transitions do, and since the parity changes of all three beta-components have to be the same, the parity of the Au^{199} ground level is probably opposite to that of the Hg^{199} levels involved. The spin of the Au^{199} level is therefore probably 3/2, but the possibility of 5/2 cannot be ruled out.

E. Final Conclusions

Hole[10] has found that the decay of Hg^{199m} contains a 159-kev γ-transition. From the half-life of 43 minutes, it would appear that the isomeric transition of 370 kev is a 2^4 magnetic transition to the 159-kev excited level. This would identify the spin of the isomeric level as 13/2 and the parity as opposite to that of the lower levels.

Another point concerns the neutron capture cross section of Au^{198}. If the intensity of the 159-K line is accepted as being present to the extent of 9 percent of the Au^{199} decays, then the cross section is estimated to be 3.8×10^4 barns.

In conclusion, it is significant to point out that if the ground state of Hg^{199} is $p_{1/2}$, as is suggested by Mayer's shell structure model,[11] then the 159-, 209-, and 529-kev excited levels are $f_{5/2}$, $p_{3/2}$, and $i_{13/2}$, respectively, all levels being consistently predicted by the model.

We are indebted to Dr. F. R. Metzger for the use of scintillation counting equipment and for his interest in the problem.

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[10] N. Hole, Arkiv. f. Mat. Astron. Fys. **36A**, No. 9 (1948).

[11] M. G. Mayer, Phys. Rev. **78**, 16 (1950).

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Neutron Diffraction by the Gases N_2, CF_4, and CH_4*

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Neutron diffraction patterns for the gases nitrogen, carbon tetrafluoride, and methane are given for a neutron wavelength of 1.063A. It is found that the coherent scattering cross sections of nitrogen and fluorine are nearly equal to the total cross sections, and that the C—F bond length in carbon tetrafluoride is 1.33A. The error in a semiclassical form of the differential scattering cross section is discussed.

I. INTRODUCTION

NEUTRON diffraction by gases may be used to determine nuclear scattering cross sections and details of molecular structure. In the present paper diffraction patterns are given for nitrogen, carbon tetrafluoride, and methane. From these the bond lengths in carbon tetrafluoride, and the ratio of coherent to total scattering for nitrogen and fluorine are derived.

The present results, together with the patterns for deuterium,[1] oxygen and carbon dioxide,[2] are the only published diffraction patterns for gases. The deuterium measurements were analyzed according to the complete quantum-mechanical formulation.[3–5] Such an approach cannot be used for every gas because in many cases the necessary formulas have not been derived or because of the large amount of computation required even when the formulas are known. This theoretical complexity and the experimental requirement of large neutron fluxes are probably the reasons why the subject has not been developed previously.

The proof that a semiclassical approximation is often applicable[2,4] greatly simplifies the equations and removes one of the obstacles to structure determinations. The error in this approximation is examined below in the light of experimental and theoretical results for nitrogen, and an elementary application is made to the measurement of bond lengths in carbon tetrafluoride.

II. THEORY

In the quantum-mechanical treatment of the scattering of monoenergetic neutrons by molecules of a gas[3,4] a differential cross section is calculated for each possible molecular transition. The formulas given in reference (3) are for deuterium in the center-of-mass system, but Spiers[5,1] has derived the transformation to the laboratory system for a maxwellian distribution of molecular velocities. Similar formulas could be applied to nitrogen because 99.2 percent of the molecules are $N^{14}N^{14}$, the same type of molecule as D_2, but the greater mass and size of the nitrogen molecule would increase the amount of computation for the

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† Now with Isotope Products Ltd., Oakville, Ontario.

[1] D. G. Hurst and N. Z. Alcock, Can. J. Phys. **29**, 36 (1951).

[2] N. Z. Alcock and D. G. Hurst, Phys. Rev. **75**, 1609 (1949).

[3] M. Hamermesh and J. Schwinger, Phys. Rev. **69**, 145 (1946).

[4] J. A. Spiers, Phys. Rev. **75**, 1765 (1949).

[5] J. A. Spiers, National Research Council (Canada) Report CRT-417 (April, 1949). (N.R.C. No. 1940), unpublished.

following reasons. Rotational transitions, which are the only type possible with the neutron energies used in these experiments, involve transfer of angular momentum between the neutron and molecule, the important transitions being those in which the change in rotational quantum number is small. This can be interpreted in terms of classical impact parameters, the principal limitation on the change in angular momentum corresponding to the requirement that the neutron hit the molecule; for example, the maximum change in the rotational quantum number for 90° scattering is given roughly by 2π (nuclear separation/wavelength in the center-of-mass system) which follows from equating the angular momentum change to the angular momentum of the neutron when its impact parameter equals the nuclear separation. From this it can be seen that the larger nuclear separation (1.11A compared to 0.75A) and the smaller neutron wavelength in the center-of-mass system for nitrogen as compared to deuterium increase the possible change in quantum number and consequently the number of transitions from each initial state. Because nitrogen is heavier and larger, the spacing between the rotational energy levels is less and many more initial states are populated at the same temperature. When, as was the case experimentally, the nitrogen is at a higher temperature the number of initial states is still larger. The combination of more initial states and more transitions from each initial state gives about ten times as many transitions to be computed for nitrogen at room temperature as for deuterium at 77.4°K[1] with 0.072-ev neutrons. The need of a simpler method of analysis is thus apparent for nitrogen. For other types of molecule the exact scattering formulas have not yet been given explicitly. However, earlier measurements,[2] were found to agree reasonably with a simple formula discussed in the next paragraph.

In the semiclassical treatment of coherent scattering of x-rays and electrons by molecules[6] the molecule is considered to have a definite orientation and the wavelets scattered by the constituent atoms are added in the direction of observation. The intensity is then calculated and is averaged over all molecular orientations. The semiclassical treatment of neutron scattering is similar,[2,5] but the calculation is performed in the center-of-mass system and a transformation must be made to the laboratory system, taking into account the thermal motions of the molecules. For heavy molecules this transformation is a small correction. The intensity of coherent x-ray scattering through an angle φ is proportional to

$$I(\varphi)=\sum_j \sum_i f_if_j \sin x_{ij}/x_{ij},$$

where i and j refer to atoms in the molecule, f_i is the scattering amplitude of the ith atom, and the sum is taken over all values of i and j, including $i=j$. The quantities x_{ij} are given by

$$x_{ij}=(4\pi r_{ij}/\lambda)\sin(\varphi/2),$$

where r_{ij} is the distance between the atoms i and j, and λ is the wavelength. A similar formula applies for neutron scattering in the center-of-mass system, but because of the effect of nuclear spin, which occurs specifically with neutrons, the scattering amplitude used is the coherent scattering amplitude[7] if $i\neq j$ and is the total scattering amplitude if $i=j$.

More precisely, the semiclassical differential cross section for neutron scattering through an angle θ in the center-of-mass system is

$$\sigma(\theta)=\frac{1}{4\pi}\left(\frac{M}{M+1}\right)^2\sum_j\sum_i(\sigma_j\sigma_i)^{\frac{1}{2}}\frac{\sin x_{ij}}{x_{ij}}, \tag{1}$$

where M is the ratio of the masses of the molecule and neutron, and σ_i is the total bound scattering cross section of the nucleus i if $i=j$, otherwise it is the coherent cross section. In the calculation of x_{ij} the wavelength is that of the incident neutron in the center-of-mass system. This general form is due to Pope;[8] the special case of diatomic molecules having like nuclei with spin 1 has already been given[5] and is discussed in further detail in the Appendix.

The discussion in the preceding paragraphs has ignored the effect of molecular vibration which reduces the scattering at large angles. For x-ray and electron diffraction[9] the extent of the electron cloud and the angular dependence of Rutherford scattering cause the scattering to decrease so steeply with increasing angle as to make the reduction due to vibration very difficult to measure. For neutrons, however, the nuclei act as points and would scatter spherically except for the effect of vibration. The reduction due to vibration is then more in evidence, and the approximation involved in the assumption of a rigid molecule requires investigation. In many molecules only the ground-state vibration occurs at room temperature and the energy of the neutrons (0.072 ev for the present series of measurements) is insufficient to cause transitions to higher vibrational levels. The nuclear scattering then has the structure factor of the probability density of the ground-state vibration. When the neutrons have sufficient energy to cause vibrational transitions, or when more than the ground-state vibration is present, the effect is more complicated.

Deuterium and nitrogen belong to the simpler case and calculations have been made for these molecules. The result for deuterium has been given,[1] and the modification to fit nitrogen is straightforward and was applied to the measurements reported in this paper.

Carbon tetrafluoride is more complicated because one of the four fundamental vibration frequencies corre-

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[6] M. H. Pirenne, *The Diffraction of X-rays and Electrons by Free Molecules* (Cambridge University Press, London, 1946).

[7] E. O. Wollan and C. G. Shull, Phys. Rev. **73**, 830 (1948).

[8] N. K. Pope (unpublished).

[9] R. W. James, *The Optical Principles of the Diffraction of X-rays* (G. Bell & Sons Ltd., London, 1948), Chap. IX.

TABLE I. Corrected experimental intensities with standard deviations.

Scattering gas	Pressure (atmos)	Scattering angle										
		7.7°	15.7°	23.7°	31.7°	39.7°	47.7°	55.7°	63.7°	71.7°	79.7°	87.7°
N_2	30	300.0 ±10.0	299.2 ±7.6	210.8 ±4.4	161.2 ±4.0	141.2 ±3.6	154.8 ±4.0	163.2 ±4.8	173.6 ±4.4	176.0 ±4.0	174.0 ±5.2	161.6 ±4.8
CF_4	31	602.4 ±12.0	303.2 ±7.6	134.4 ±4.0	162.0 ±3.6	173.2 ±2.8	164.0 ±2.8	202.0 ±3.2	230.8 ±3.6	200.0 ±3.2	150.0 ±2.8	134.0 ±2.4
CH_4	14.7	1043 ±16	1068 ±15	984 ±13	940 ±12	872 ±10	764 ±10	674 ±8	584 ±9	490 ±8	434 ±6	390 ±5
CH_4	5.0	398 ±12	397 ±10	409 ±9	384 ±9	334 ±7	308 ±5	274 ±10	227 ±5	206 ±6	173 ±5	152 ±4

sponds to 0.054 ev which is comparable to thermal energies. Consequently there is an appreciable population in the second level at room temperature, and moreover neutrons of 0.072 ev can induce transitions in this mode. As an approximation to the scattering the difference caused by these deviations from the simple case was neglected and it was assumed that the vibration of each nucleus could be represented by the ground state of a three-dimensional harmonic oscillator. The radial density of this state is $\exp[-(r/a)^2]$ where a is $(\hbar/mw)^{\frac{1}{2}}$, m being the mass of the oscillator and $\hbar w$ the separation of the energy levels. The intensity of elastic scattering is proportional to $\exp[-8(\pi a/\lambda)^2 \sin^2(\varphi/2)]$ where φ is the scattering angle. The observed pattern of CF_4 was about 0.93 of the semiclassical curve at 90°. This factor was ascribed to vibration and equated to the intensity ratio just given, with the result that $a=0.045$A, a reasonable value for the mean amplitude of the modes of the CF_4 molecule. In nitrogen the vibration changed the scattering by only about 0.7 percent at 90°; the larger effect in CF_4 is due not to a larger amplitude of vibration, but to the fact that the vibration is three-dimensional instead of linear as in nitrogen.

Another departure from the formula for an isolated rigid molecule occurs because the measurements were made with gases at high pressure. Under these conditions the scattering pattern shows evidence of intermolecular interference. Debye,[10] discussing the corresponding phenomenon in x-ray scattering, named it "the outer effect" and gave a formula for diatomic molecules. This has been used for nitrogen, and has been modified for polyatomic molecules and applied to CF_4.

III. EXPERIMENTAL PROCEDURE

The spectrometer, scattering chamber, and operating procedure have been previously described.[1] The measurements on N_2, CF_4, and CH_4 were made immediately after those on D_2 with similar experimental conditions except that the gases were at room temperature (23°C). The average wavelength of the neutrons was 1.063A with a spread of about ±0.05A. The spectrometer was operated automatically, counts being recorded every 8° through the angular range 7.7° to 87.7°. As with deuterium, the counts from a primary neutron flux monitor were recorded during the time taken for one thousand counts to accumulate in the spectrometer counter, though on some background runs a one hundred count setting was used.

Bottled compressed gases were used for the measurements with no additional purification, except that nitrogen was passed through a dry ice trap to remove traces of water vapor. Samples of the gases were drawn from the gas cell and analyzed in a mass spectrometer. The gas pressures remained constant during the measurements, the slow leak mentioned in connection with the deuterium having been repaired.

The reduction of the measured angular distributions for comparison with theory was carried out as for deuterium:[1] (i) background, which was measured with the cell evacuated, was separated experimentally into fast and slow neutron components, and each treated separately, the fast component being subtracted directly from the total intensity, the slow component being subtracted from the total intensity after correction for loss in transmission through the scattering gas; (ii) the geometry of the scattering system was taken into account by dividing the intensity at each angle by the effective scattering volume; (iii) double scattering was allowed for after the manner described for D_2; the angle whose intensity corresponds to the average intensity due to single scattering was found for N_2 and CF_4 by a numerical integration of the semiclassical

TABLE II. Experimental details.

Gas	Pressure (atmos)	Analysis[a]	Background (percent of meas. intensity)	Double scattering correction
N_2	30	Impurities <0.2 percent	50% at 7.7° 16% at 87.7°	2% to 4%
CF_4	31	0.2 percent CF_3H Trace of water vapor and atmospheric gases	34% at 7.7° 18% at 87.7°	1% to 4%
CH_4	14.7	Impurities <1	23% at 7.7° 7% at 87.7°	3% to 11%
	5.0		44% at 7.7° 16% at 87.7°	2% to 5%

[a] See reference 11.

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[10] P. Debye, Physik. Z. 28, 135 (1927)

angular distribution over 4π-steradians, for CH_4 by integration of an estimated pattern based on the experimental distribution.

IV. EXPERIMENTAL RESULTS

The corrected experimental intensities (expressed as counts per 10^4 monitor counts per cubic inch of scattering gas) are given in Table I. Other experimental information,[11] including some background and double scattering corrections to indicate their magnitude, are given in Table II. The intensities are plotted on Figs. 1 to 3 as functions of the scattering angle.

In Fig. 1, which contains the nitrogen results, the experimental points are shown fitted at 23.7° to a semiclassical diffraction pattern. This is the broken line marked "Theory—1st approximation" and it has been transformed from the center-of-mass coordinates and corrected for thermal motion of the molecules. The curve marked "Theory—2nd approximation" has been corrected for the error in the semiclassical approximation according to the calculations in the Appendix and also for the effect of molecular vibration. At small angles the dotted line shows the "outer effect." The theoretical curves were calculated on the assumption that the coherent scattering cross section equals the total cross section, i.e., $\sigma_{\text{coh}}/\sigma_T = 1$. The molecular parameters used were 1.11A for the internuclear distance and 1.78A for the molecular (collision) radius.

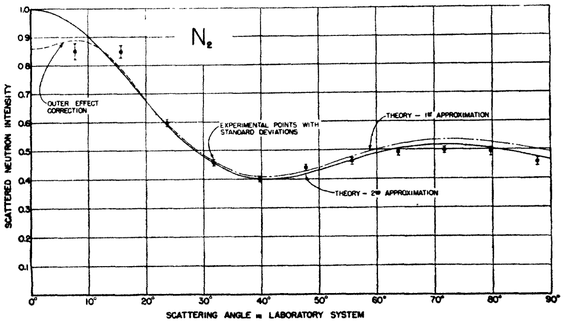

FIG. 1. The scattering of neutrons of wavelength 1.063A from nitrogen at 23°C and 30 atmos pressure. The curves shown are for spin-independent semiclassical scattering uncorrected (1st approximation), and corrected for vibration and deviations from the exact spin-independent formula (2nd approximation). At small angles the calculated effect of intermolecular diffraction is shown dotted. The experimental points are normalized so that the point at 23.7° lies on the curve.

Figure 2 shows the carbon tetrafluoride results fitted in the region of small angles to a semiclassical formula. The coherent cross section of fluorine was assumed to equal the total bound cross section which was taken as 4.1 barns, and the bound cross section of carbon was taken as 5.52 barns. The curve as drawn is for a carbon-fluorine distance of 1.33A. The "outer effect" was calculated for a molecular radius of 2A.

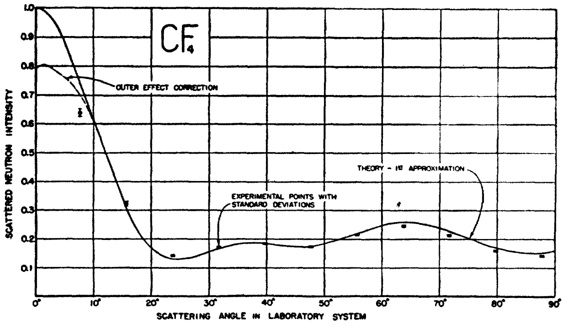

FIG. 2. The scattering of neutrons of wavelength 1.063A from carbon tetrafluoride at 23°C and 31 atmos pressure fitted to a semiclassical equation for spin-independent scattering. The dotted line is the calculated effect of intermolecular diffraction. A value of 1.33A was used for the carbon-fluorine bond length.

The experimental points for methane are plotted in Fig. 3 where the high pressure point for 7.7° has been fitted to unity and the low pressure points have been normalized for best average fit to the high pressure run.

V. DISCUSSION

(a) Nitrogen

The fit of the points to the theoretical curves shows that the 2nd approximation is quite good. Besides the value $\sigma_{\text{coh}}/\sigma_T = 1$ for which the curve is plotted, other values of this ratio were tried, and it is estimated that the ratio of coherent to total bound scattering cross section lies between 0.9 and 1.0. This was at variance with previous measurements but is in agreement with the most recent results.[12]

(b) Carbon Tetrafluoride

The general run of the experimental points is in agreement with the semiclassical equation. There is a decrease of the experimental values relative to the theoretical curve at large angles, and this is attributed

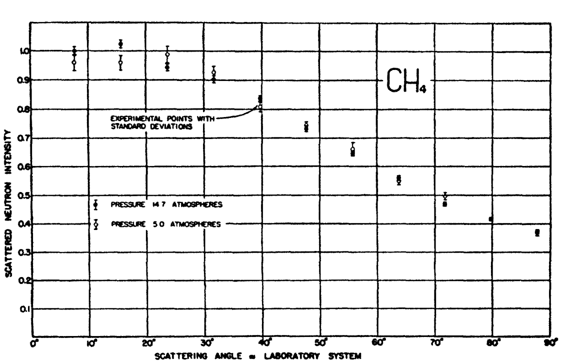

FIG. 3. The scattering of neutrons of wavelength 1.063A from methane at 23°C for 14.7 atmos and 5.0 atmos pressure. The high pressure point at 7.7° has been fitted to unity and the low pressure results normalized for best average fit.

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[11] We are indebted to the Chemical Control Laboratory, Chalk River, for the analyses.

[12] G. H. Goldschmidt and D. G. Hurst, Phys. Rev. 83, 88 (1951). C. G. Shull and E. O. Wollan, Phys. Rev. 81, 527 (1951). A.W. Reynolds and G. W. Johnson, Phys. Rev. 82, 344 (1951).

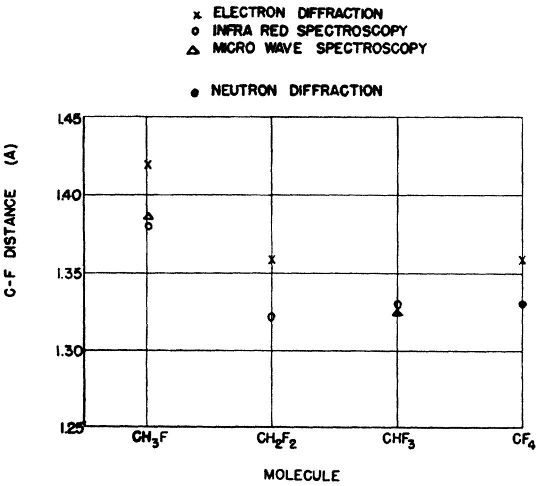

FIG. 4. The carbon-fluorine bond lengths in the fluoro-methanes as observed by various methods (see reference 13).

to vibration and to the approximate nature of the theoretical formula. The simple treatment of vibration, outlined in Sec. II, in which the decrease at 90° was taken as 7 percent (Fig. 2), shows that vibration can account for the major part of this difference.

The carbon-fluorine bond length of 1.33A on which the curve of Fig. 2 is based is smaller than the generally accepted value of this quantity as found by electron diffraction. A comparison of bond lengths in the fluoromethanes is given in Fig. 4.[13] It will be seen that electron diffraction has given consistently greater bond lengths than other methods and that the present result is in agreement with an extrapolation of the spectroscopic results.

The "outer effect" corrections for both CF_4 and N_2 give the general trend of the scattering at small angles, but they do not seem to fit in detail.

(c) Methane

Because slow neutron scattering by hydrogen is almost entirely incoherent, negligible diffraction and "outer effect" are to be expected for methane. The observed decrease of scattering at large angles is due to effects of inelastic scattering and vibration.

The ratio of the scattering at the two pressures was compared with the relative densities of the gas as given by Van der Waals' equation with allowance for transmission losses through the gas cell. The two agreed within 1 percent. This agreement and the similar angular dependence for the two pressures (Fig. 3) justify the methods used for all the gases to correct the experimental counting rates for background and double scattering.

VI. CONCLUSION

It has been shown that measurements of the differential cross sections of gases for monoenergetic neutrons can be analyzed to give coherent cross sections and information about molecular structures. The semiclassical formulas apply to many gases with sufficient accuracy to be used for such analyses.

We thank the Minnesota Mining and Manufacturing Company for supplying the carbon tetrafluoride and an infrared spectrographic analysis of impurities. We are indebted to Dr. N. K. Pope for helpful discussions, and to Mr. R. Semple for computing assistance.

APPENDIX

The semiclassical equation for gas scattering is very simple and a knowledge of its error is of interest because of the complexity of the exact formulas. In this Appendix an approximate expression is derived for the error in the special case of rigid diatomic molecules with like nuclei of spin 1 to which the formulas for deuterium, suitably modified for the mass and size of the molecule, are applicable. The cross section for scattering of a neutron through an angle φ in the laboratory system by such a molecule which undergoes a rotational transition in which the rotational quantum number changes from J to J' is

$$\sigma_{JJ'}(\varphi)=\mu_{JJ'}X(\varphi)(p/p_0)\Sigma_L(2L+1)(2J'+1)C_{LJJ'}j_L^2(kr). \quad \text{(A.1)}$$

This is Eq. (35) of Spiers' report[5] with some changes in notation. The quantity $\mu_{JJ'}$ depends on whether J and J' are even or odd according to Table III; in this table σ_T is the total bound scattering cross section and σ_{coh} is the coherent bound cross section of the nuclei, M is the ratio of the mass of the molecule to the mass of the neutron. p_0 and p are respectively the neutron momentum in the center-of-mass coordinate system before and after the collision. $X(\varphi)$ is the function which transforms from the center-of-mass coordinate system to the laboratory system and has been given exactly for deuterium by Spiers;[5] as this Appendix applies only if $M\gg 1$, a sufficient approximation is $X(\varphi)=1+2p_0/(Mp)\cos\varphi$. L is an integer which takes the values $J+J'$, $J+J'-2$, $\cdots|J-J'|$. $C_{LJJ'}=\frac{1}{2}\int_{-1}^{1}P_L(z)P_J(z)P_{J'}(z)dz$ where $P_n(z)$ is the Legendre function of degree n. $j_L(x)=((\pi/2x))^{\frac{1}{2}}J_{L+\frac{1}{2}}(x)$, where $J_{L+\frac{1}{2}}(x)$ is the bessel function of order $L+\frac{1}{2}$, r is the internuclear distance in the molecule, and $k=(\pi/h)(p_0^2+p^2-2pp_0\cos\theta)^{\frac{1}{2}}$ where h is Planck's constant and θ is the scattering angle in the center-of-mass system.

The differential cross section $\sigma(\varphi)$ is the sum of all the cross sections $\sigma_{JJ'}(\varphi)$ and the computation can involve many terms. Spiers[5] showed that the semiclassical result is obtained if the energy change in the transition $J\rightarrow J'$ is ignored, i.e., if p is put equal to p_0, for then

$$\sigma_{J,\alpha}^*(\varphi)=\Sigma_{J'}{}^{\alpha}\sigma_{JJ'}^*(\varphi)=\mu_{J,\alpha}X^*(\varphi)\tfrac{1}{2}\{1\pm\sin 2k^*r/(2k^*r)\} \quad \text{(A.2)}$$

where an asterisk is used to denote a quantity which has been calculated with $p=p_0$. The sum is taken either for $J-J'$ even, corresponding to the plus sign inside the brackets, or for $J-J'$ odd, corresponding to the negative sign, the symbol α being used to indicate this partition of the values of J'. The differential cross section is the sum over J of these $\sigma_{J,\alpha}^*(\varphi)$. At room temperature two-thirds of the molecules have even values of J and the differential cross section is

$$\begin{aligned}\sigma^*(\varphi)&=X^*(\varphi)\tfrac{1}{2}\{(\tfrac{2}{3}\mu_{oo}+\tfrac{1}{3}\mu_{pp})(1+\sin 2k^*r/(2k^*r))\\&\qquad+(\tfrac{2}{3}\mu_{op}+\tfrac{1}{3}\mu_{po})(1-\sin 2k^*r/(2k^*r))\}\\&=X^*(\varphi)[M/(M+1)]^2\{\sigma_T+\sigma_{\text{coh}}\sin 2k^*r/(2k^*r)\}/(2\pi). \quad \text{(A.3)}\end{aligned}$$

The semiclassical differential cross section is calculated on the basis of elastic scattering and is sometimes assumed to represent a physical process of coherent scattering without change in wavelength.[6] A study of the contributions from (A.1) to the curves of Fig. 3, however, shows that although at angles less than 30° essentially only elastic scattering contributes, between 45° and 80° most of the scattering is associated with a transfer of energy resulting in transitions to $J'=J\pm 2$. These changes in

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[13] H. J. Bernstein and G. Herzberg, J. Chem. Phys. **16**, 30 (1948). Gilliam, Edwards, and Gordy, Phys. Rev. **75**, 1014 (1949).

energy may not be negligible in neutron diffraction, even when (A.3) is a good approximation to the differential cross section.

The difference between $\sigma(\varphi)$ and $\sigma^*(\varphi)$ is

$$\begin{aligned}\Delta\sigma=\sigma(\varphi)-\sigma^*(\varphi)&=\Sigma_J\,\Sigma_{J'}[\sigma_{JJ'}(\varphi)-\sigma_{JJ'}{}^*(\varphi)]\\ &=\Sigma_J\,\Sigma_{J'}(2J'+1)\mu_{JJ'}\Sigma_L(2L+1)C_{LJJ'}\\ &\qquad\times\{X(\varphi)(p/p_0)j_L{}^2(kr)-X^*(\varphi)j_L{}^2(k^*r)\}\end{aligned}$$

where Σ_J means average over the Boltzmann distribution. The semiclassical equation was obtained on the assumption that $p=p_0$. The quantity in the braces { } is a function of the difference p_0-p, and to the first power of $\epsilon=(p_0-p)/p_0$,

$$\begin{aligned}&X(\varphi)(p/p_0)j_L{}^2(kr)-X^*(\varphi)j_L{}^2(k^*r)\\ &\quad=-\epsilon X^*(\varphi)\left\{\frac{1}{2x}\frac{d}{dx}(x^2j_L{}^2(x))-2j_L{}^2(x)M^{-1}\cos\varphi\right.\\ &\qquad\left.+xj(x)j'(x)M^{-1}\cos^2(\varphi/2)\right\}=-\epsilon X^*(\varphi)F_L \qquad \text{(A.4)}\end{aligned}$$

where

$$F_L=\{(1/2x)(d/dx)x^2-2M^{-1}\cos\varphi\}j_L{}^2(x)+xj(x)j'(x)M^{-1}\cos^2(\varphi/2)$$

and

$$x=k^*r=2\pi(r/\lambda)[M/(M+1)]\sin(\theta^*/2).$$

Powers of $1/M$ higher than the first arising from $X(\varphi)$ have been neglected in (A.4). The quantity ϵ is approximately given by

$$\epsilon=-((M+1)/M)(E_1/E)\{J(J+1)-J'(J'+1)\}/4 \qquad \text{(A.5)}$$

where E_1 is the energy of the first rotational level and E is the energy of the incident neutrons, $E_1/E=(2/M)(\lambda/\pi r)^2$.

For neutrons of 0.07 ev scattered by nitrogen $\epsilon=-1.7\times10^{-3}\times\{J(J+1)-J'(J'+1)\}$ and having regard to the distribution of J values at room temperature and the vanishingly small probability for $\varphi<90°$ of transitions involving $|J-J'|>6$, it appears that all values of ϵ which merit consideration are $\ll 1$. The equation for $\Delta\sigma$ to the first power of ϵ is

$$\begin{aligned}\Delta\sigma=X^*(\varphi)\frac{M+1}{M}\frac{E_1}{4E}\sum_J\sum_{J'}(2J'+1)\mu_{JJ'}\sum_L(2L+1)C_{LJJ'}&\\ \times\{J(J+1)-J'(J'+1)\}F_L.&\qquad \text{(A.6)}\end{aligned}$$

The order of summation over L and J' may be changed and

$$\begin{aligned}\Delta\sigma=X^*(\varphi)\frac{M+1}{M}\frac{E_1}{4E}\sum_J\sum_L(2L+1)F_L\sum_{J'}\mu_{JJ'}(2J'+1)C_{LJJ'}&\\ \times\{J(J+1)-J'(J'+1)\}.&\qquad \text{(A.7)}\end{aligned}$$

From the definition of $C_{LJJ'}$ it follows that

$$\Sigma_{J'}(2J'+1)C_{LJJ'}P_{J'}(z)=P_L(z)P_J(z). \qquad \text{(A.8)}$$

Differentiation of both sides with respect to z and use of the formula $(d/dz)P_n(z)=(\pm)^{n+1}n(n+1)/2$ for $z=\pm1$, yields

$$\Sigma_{J'}(2J'+1)C_{LJJ'}J'(J'+1)=L(L+1)+J(J+1).$$

TABLE III. The values of $\mu_{JJ'}$.

J	J'	Transition	Designation	μ
even	even	ortho-ortho	μ_{oo}	$[M/(M+1)]^2(5\sigma_T+3\sigma_{\mathrm{coh}})/8\pi$
odd	odd	para-para	μ_{pp}	$[M/(M+1)]^2(\sigma_T+3\sigma_{\mathrm{coh}})/4\pi$
even	odd	ortho-para	μ_{op}	$3[M/(M+1)]^2(\sigma_T-\sigma_{\mathrm{coh}})/8\pi$
odd	even	para-ortho	μ_{po}	$3[M/(M+1)]^2(\sigma_T-\sigma_{\mathrm{coh}})/4\pi$

From (A.8) with $z=1$, $\Sigma_{J'}(2J'+1)C_{LJJ'}J(J+1)=J(J+1)$. The difference is $\Sigma_{J'}(2J'+1)C_{LJJ'}[J(J+1)-J'(J'+1)]=-L(L+1)$. With the notation μ_{Ja} for $\mu_{JJ'}$ when $J-J'$ is even, μ_{Jb} when $J-J'$ is odd, this gives from (A.7)

$$\Delta\sigma=-X^*(\varphi)((M+1)/M)(E_1/4E)\Sigma_J(\mu_{Ja}z_a+\mu_{Jb}z_b)$$

where

$$z_a=\Sigma_{L\ \mathrm{even}}\,L(L+1)(2L+1)F_L,\quad z_b=\Sigma_{L\ \mathrm{odd}}\,L(L+1)(2L+1)F_L.$$

With $y_\pm=z_a\pm z_b=\Sigma_L(\pm)^LL(L+1)(2L+1)F_L$ the formula for $\Delta\sigma$ becomes

$$\Delta\sigma=-X^*(\varphi)(M/(M+1))(E_1/4E)(y_+\sigma_T+y_-\sigma_C)/2\pi. \qquad \text{(A.9)}$$

$y_\pm$ is readily found from[3]

$$\Sigma_L(2L+1)j_L{}^2(x)P_L(z)=\sin s/s \quad \text{where} \quad s=x[2(1-z)]^{\frac{1}{2}}.$$

Differentiation of both sides with respect to z at $z=\pm1$ leads to

$$\begin{aligned}\Sigma_L(\pm)^LL(L+1)(2L+1)j_L{}^2(x)&=\tfrac{2}{3}x^2 \text{ for the + sign}\\ &=\tfrac{1}{2}(\cos 2x-\sin 2x/2x)\\ &\qquad\qquad \text{for the − sign.}\end{aligned}$$

To obtain $y_\pm$ it is only necessary to operate on both sides so as to transform $j_L{}^2(x)$ to F_L by Eq. (A.4). Then

$$\begin{aligned}y_+&=(4/3)x^2\\ y_-&=\tfrac{1}{4}\{\cos 2x-[(2x)^2+1]\sin 2x/2x\}\end{aligned}$$

neglecting terms in M^{-1}.

The value of $\Delta\sigma=\sigma(\varphi)-\sigma^*(\varphi)$ follows from (A.9) with these values of $y_\pm$, and has been applied to the nitrogen results as shown in Fig. 1.

In the range of x where $\Delta\sigma$ is important y_- is small compared to y_+. A rough value of $\Delta\sigma$ is obtained by retaining only y_+ and also neglecting $1/M$ compared to unity. Then

$$\Delta\sigma=-(8/3M)(\sigma_T/2\pi)\sin^2(\varphi/2) \qquad \text{(A.10)}$$

and for nitrogen the difference between this and the full result as given by (A9) is experimentally unimportant.

The smallness of y_- means that the error in the semiclassical equation is largely independent of coherent effects because, to the extent that (A.10) holds, $\Delta\sigma$ is independent of σ_{coh}. When $\sigma_{\mathrm{coh}}=0$, the semiclassical result except for the reduced mass term is practically billiard ball scattering. This suggests that the chief source of error in the semiclassical equation is in the assumption of a molecular model which is fixed in orientation so that transfer of angular momentum cannot occur.