PHYSICAL REVIEW VOLUME 148, NUMBER 1 5 AUGUST 1966

Intramolecular Coherent Scattering of Neutrons by CD_4 Gas*

R. E. WEST,† R. M. BRUGGER,‡ AND G. W. GRIFFING‡
Atomic Energy Division, Phillips Petroleum Company, Idaho Falls, Idaho

(Received 4 March 1966)

Measurements on the scattering of neutrons by gaseous CD_4 at a temperature of 306°K have been taken on the Materials Testing Reactor (MTR) phased chopper velocity selector for a range of energy transfers between zero and 156 meV and momentum transfers between 1.0 Å^{-1} and 14 Å^{-1}. Comparison of the data with theoretical calculations shows excellent quantitative agreement. The influence of intramolecular coherent scattering is most evident at small energy transfers. However, the intramolecular coherent scattering is also quite prominent when the energy transfer becomes comparable in magnitude to the energy of a vibrational state. At a temperature of 306°K, approximately 3% of the molecules are in excited vibrational states. In spite of the small percentage of vibrationally excited molecules in the gas, it is found that the contribution to the scattering by the vibrationally excited molecules becomes significant at an energy transfer of about 72 meV and dominates the scattering at larger energy transfers.

I. INTRODUCTION

INELASTIC scattering of neutrons from gaseous samples has, until this experiment, been restricted to samples containing hydrogen.[1–10] The reason was that, at reasonable sample pressure, only the bound-atom scattering cross section of hydrogen was large enough (≈80 b/atom) to give adequate counting rates. Recently, it became feasible to do inelastic scattering measurements on gaseous samples not containing hydrogen due to the achievement of increased neutron intensities with the Materials Testing Reactor (MTR) velocity selector[11] by moving it to a higher flux beam hole.

Experimental results on neutrons scattered by gaseous CD_4 are of particular interest since, as pointed out by one of the authors,[12] the scattering will exhibit momentum-transfer-dependent structure due to interference by intramolecular scattering. The influence of the vibrationally excited moelcules on the scattering is also of interest. These contributions were found to become significant at an energy transfer of 72 meV and increase in importance as the energy transfer increased. In addition, the experimental results present a further test of the theory[13] on the scattering of neutrons by spherical-top molecules.

This paper reports on a detailed comparison between the experimental results and the theoretical calculations. In general, there is excellent agreement.

II. EXPERIMENTAL INFORMATION

The experiment was conducted using the MTR velocity selector.[14] Data were taken at incident energies of 49.6, 61.6, and 69.6 meV with 15 scattering detectors ranged between 15° and 145°. The sample and the scattering paths between 15° and 90° were in a helium atmosphere[11] to limit air scattering.

The sample was contained in a 12-cm high, 5-cm-diam, 7075 aluminum can having 0.010-cm walls. A similar evacuated can was used as the "open." The CD_4 had the following isotopic composition: atom %, D=99.7; compound molecule %, CD_4=97.4, CHD_3 =1.1, N_2=1.4, O_2=0.04, deuterated ethane 0.1. The sample can was filled to 196 psig, which gave a thin sample with respect to multiple scattering and intermolecular interactions. The transmission of the sample was approximately 0.96.

III. METHOD OF CALCULATION

It will be seen in the discussion of the results that, for energy transfers greater than about 72 meV, there are contributions to the scattering by molecules which are in the lowest vibrational excited states. Previous studies[12,13] were concerned with the case for which contributions from the excited vibrational states could be ignored. Consequently, it will be necessary to extend the method of computations so that such contributions to the scattering are included.

---

* Work performed under the auspices of the U. S. Atomic Energy Commission.

† Now at the University of Arizona, Tucson, Arizona.

‡ Now with Idaho Nuclear Corporation, Idaho Falls, Idaho.

[1] P. D. Randolph, R. M. Brugger, K. A. Strong, and R. E. Schmunk, Phys. Rev. **124**, 460 (1961).

[2] K. A. Strong, G. D. Marshall, R. M. Brugger, and P. D. Randolph, Phys. Rev. **125**, 922 (1962).

[3] R. M. Brugger, V. S. Rainey, and H. L. McMurry, Phys. Rev. **136**, A106 (1964).

[4] Y. Harker and R. M. Brugger, J. Chem. Phys. **42**, 275 (1965).

[5] K. A. Strong, Y. Harker, and R. M. Brugger, J. Chem. Phys. **42**, 1568 (1965).

[6] F. J. Webb, in *Proceedings of the Conference on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. I, p. 457.

[7] D. Bally, V. Tarina, and S. Todireanu, in *Proceedings of the Conference on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. I, p. 451.

[8] W. Glaser, G. Ehret, and A. Merkel, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. II, p. 167.

[9] J. M. Carpenter (private communication).

[10] E. A. Straker, J. Chem. Phys. **13**, 4134 (1965).

[11] R. M. Brugger, Nucl. Instr. Methods **32**, 303 (1964). Also P. D. Randolph (private communication).

[12] G. W. Griffing, Phys. Rev. **136**, A988 (1964).

[13] G. W. Griffing, Phys. Rev. **124**, 1489 (1961); in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. I, p. 435. In this reference there is a misprint in the expressions for $\sigma_{pp'}$ and σ_{Cp}. As given they are too large by a factor of 2.

[14] R. M. Brugger and J. E. Evans, Nucl. Instr. Methods **12**, 75 (1961).

Consider the expression for the partial differential cross section given by Zemach and Glauber[15] for the scattering event in which the momentum of the neutron changes from k_0 to k with an energy transfer ϵ in a collision with a molecule which simultaneously undergoes a transition from an initial state ψ_i to a final state ψ_f. This expression is

$$\sigma_{fi}(E_0,\epsilon,\theta)=(2\pi)^{-1}(k/k_0)\sum_{\nu,\mu} a_{\nu\mu}\int_{-\infty}^{\infty} e^{-i\epsilon t}\langle fi|\nu\mu\rangle dt\,, \quad (1)$$

with

$$a_{\nu\mu}=A_\nu A_\mu+C_\nu C_\mu\delta_{\nu\mu}$$

and

$$\langle fi|\nu\mu\rangle=e^{i(E_i-E_f)t}\langle\psi_i|\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_\nu)|\psi_f\rangle \times\langle\psi_f|\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}_\mu)|\psi_i\rangle.$$

The bound coherent and incoherent scattering lengths of the νth nucleus are given by A_ν and C_ν, and $\mathbf{r}_\nu$ is the position vector of that nucleus. The scattering angle is denoted by θ and the momentum transferred to the neutron in the collision by $\boldsymbol{\kappa}$. The initial and final total energy of the molecule are denoted by E_i and E_f. The system of units is such that $\hbar$ has unit magnitude. In thermal equilibrium, the struck molecule will have a probability p_i of being in some initial state so the cross section to be compared with experiment is obtained by taking a thermal average over the initial states and summing over all energetically possible final states, that is,

$$\sigma(E_0,\epsilon,\theta)=\sum_{i,f} p_i\sigma_{fi}(E_0,\epsilon,\theta)\,. \quad (2)$$

In particular for the CD_4 molecule, (2) can be written as

$$\sigma(E_0,\epsilon,\theta)=4\sigma_{dd}(E_0,\epsilon,\theta)+12\sigma_{dd'}(E_0,\epsilon,\theta) +8\sigma_{\mathrm{C}d}(E_0,\epsilon,\theta)+\sigma_{\mathrm{CC}}(E_0,\epsilon,\theta)\,, \quad (3)$$

where

$$\sigma_{dd}(E_0,\epsilon,\theta)=(2\pi)^{-1}a_{dd}(k/k_0)\sum_{i,f} p_i\int_{-\infty}^{\infty}\langle fi|dd\rangle dt$$

and the remaining terms are similarily defined. In (3), d denotes a deuteron, d' a different deuteron in the same molecule, and C the carbon nucleus.

Further separation of the term in brackets in the integral of (3) into factors corresponding to translational, rotational, and vibrational modes of the molecule is accomplished in the same manner as in Ref. 13. Here, only the factor pertaining to the thermal average of the expectation value of the vibrational mode will be considered since the other factors have been previously discussed in Ref. 13. Before proceeding with considerations of this factor, some remarks on the quantity to be compared with experimental results are pertinent. Multiplying (3) by $[(k_0/k)\exp(\epsilon/2T)]$ defines the function

$$S(\kappa,\epsilon)=S_{dd}(\kappa,\epsilon)+S_{dd'}(\kappa,\epsilon)+S_{\mathrm{C}d}(\kappa,\epsilon)+S_{\mathrm{CC}}(\kappa,\epsilon)\,, \quad (4)$$

where

$$S_{dd}(\kappa,\epsilon)=4(k_0/k)\exp(\epsilon/2T)\sigma_{dd}(E_0,\epsilon,\theta)$$

and the remaining terms on the right-hand side of (4) are similarly defined. $S(\kappa,\epsilon)$ will be referred to as the scattering law. Presentation of the experimental data in the form of the scattering law permits considerable condensation of the results as well as an internal consistency check of the results. It is well known that the scattering law has the property [16] that

$$S(\kappa,\epsilon)=S(\kappa,-\epsilon)\,. \quad (5)$$

Thus, it is a matter of choice whether the computations are done for energy gain, such as was chosen in our calculations, or for energy loss. Experimentally, for large energy transfers, only the results for energy gain were observed since the neutron energy was insufficient to excite the vibrational states. As will be seen later, our calculations show that contributions to the scattering law by vibrationally excited molecules will start to become significant when the energy transfer is equal to approximately $\frac{1}{2}$ the energy of the vibrational state and increase in importance as the energy transfer becomes larger.

Let us consider the thermal average of the expectation value of the vibrational mode. For a particular vibrational mode λ, Zemach and Glauber obtained the result that

$$\langle \chi_{\nu\mu}{}^{(\lambda)}\rangle_T=\exp\{-[(X_\nu{}^{(\lambda)})^2+(X_\mu{}^{(\lambda)})^2](4\omega_\lambda)^{-1} \times\coth(\omega_\lambda/2T)\}\sum_{n=-\infty}^{\infty} e^{N(n,\lambda)}I_n(y_{\nu\mu}{}^{(\lambda)})\,, \quad (6)$$

where

$$y_{\nu\mu}{}^{(\lambda)}=X_\nu{}^{(\lambda)}X_\mu{}^{(\lambda)}/2\omega_\lambda\sinh(\omega_\lambda/2T)\,,$$

$$X_\nu{}^{(\lambda)}=\boldsymbol{\kappa}\cdot\mathbf{C}_\nu{}^{(\lambda)}\,,$$

and

$$N(n,\lambda)=[i(n\omega_\lambda t)-(n\omega_\lambda/2T)].$$

$\mathbf{C}_\nu{}^{(\lambda)}$ is the amplitude vector of the νth nucleus in the λth vibrational mode and ω_λ the frequency of the mode. The temperature T is in units of Boltzmann's constant. $I_n(y)$ is the modified Bessel function of argument y and order n. The total contribution of the vibrational modes consists of a product of terms like (6) over all modes. Thus, the total contribution is

$$W_{\nu\mu}=\prod_\lambda\langle\chi_{\nu\mu}{}^{(\lambda)}\rangle_T\,. \quad (7)$$

Since the struck molecule will have random orientations relative to the neutron beam, it is necessary to average (7) over all molecular orientations Ω. For subsequent discussions, it is convenient to specify our numbering

---

[15] A. C. Zemach and R. J. Glauber, Phys. Rev. **101**, 118 (1956).

[16] P. Schofield, Phys. Rev. Letters 4, 239 (1960).

TABLE I. Mode numbering system.

Mode	Energy (eV)	Degeneracy
1	0.258	Singly
2, 3	0.135	Doubly
4, 5, 6	0.280	Triply
7, 8, 9	0.123	Triply

system for the vibrational modes[17] of CD_4 and the corresponding energies in Table I.

As an approximation to (6), only the first term is retained in the power-series expansion of the modified Bessel function since the maximum of its argument does not exceed about 0.05. In addition, $\coth(x)$ is replaced by unity since it differs from unity by only about 1%. Let us now consider (7). Only those terms will be retained which, when used in (4), will give significant contributions to the computed scattering for the range of energy transfers under consideration. This gives

$$W_{\nu\mu}=\exp\{-\textstyle\sum_\lambda[(X_\nu{}^{(\lambda)})^2+(X\lambda^{(\lambda)})^2](4\omega_\lambda)^{-1}\}$$
$$\times\left\{1+\frac{e^{N(1,2)}(X_\nu{}^{(2)}X_\mu{}^{(2)}+X_\nu{}^{(3)}X_\mu{}^{(3)})}{4\omega_2\sinh(\omega_2/2T)}+\frac{e^{N(1,7)}(X_\nu{}^{(7)}X_\mu{}^{(7)}+X_\nu{}^{(8)}X_\mu{}^{(8)}+X_\nu{}^{(9)}X_\mu{}^{(9)})}{4\omega_7\sinh(\omega_7/2T)}\right\}. \tag{8}$$

In taking the product, consistent with our approximations, we have neglected all terms involving a product of excited states. The first term in (8) correspond to the ground-state vibration, the second term the doubly degenerate excited state (0.135 eV), and the third term the triply degenerate excited state (0.123 eV). It is emphasized that (8) is not an approximation to (7) but rather it consists of those terms in (7) that will give significant contributions to the computed scattering when used in (4).

Finally, it is necessary to average (8) over molecular orientations. For the ground-state term, sufficient accuracy is obtained by averaging in the exponent of the exponential.[18] For the terms involving the jth excited state, the average is approximated by assuming that

$$\langle\exp\{-\textstyle\sum_\lambda[(X_\nu{}^{(\lambda)})^2+(X_\mu{}^{(\lambda)})^2](4\omega_\lambda)^{-1}\}X_\nu{}^{(j)}X_\mu{}^{(j)}\rangle_\Omega$$
$$=\langle\exp\{-\textstyle\sum_\lambda{}'[(X_\nu{}^{(\lambda)})^2+(X_\mu{}^{(\lambda)})^2](4\omega_\lambda)^{-1}\}\rangle_\Omega$$
$$\times\langle\exp\{-[(X_\nu{}^{(j)})^2+(X_\mu{}^{(j)})^2](4\omega_j)^{-1}\}$$
$$\times X_\nu{}^{(j)}X_\mu{}^{(j)}\rangle_\Omega, \tag{9}$$

where the prime on the summation means that the jth mode is missing. The average of the first term on the right-hand side of (9) is approximated by averaging in the exponent of the exponential. An approximation to the average of the second term is accomplished by expanding the exponential and retaining terms to the fourth order of κ. The result is

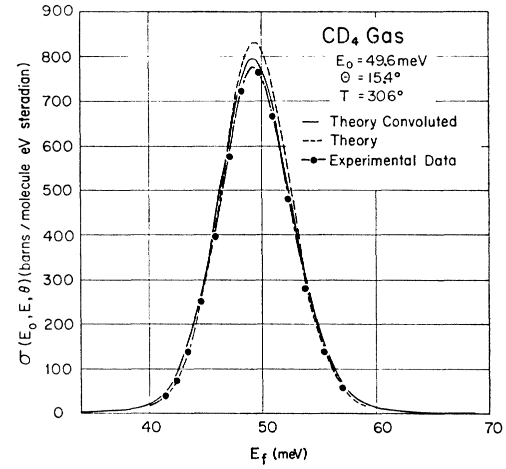

FIG. 1. An example of convoluting the theory with the energy resolution function of the velocity selector. The partial differential cross section is shown as a function of the final energy of the neutron and compares the convoluted theory with the data.

$$\langle\exp\{-[(X_\nu)^2+(X_\mu)^2](4\omega)^{-1}\}X_\nu X_\mu\rangle_\Omega$$
$$=(\mathbf{C}_\nu\cdot\mathbf{C}_\mu)(\kappa^2/\omega)[(\tfrac{1}{3})-(C_\nu{}^2+C_\mu{}^2)(\kappa^2/40\omega)]. \tag{10}$$

These approximations result in expressions which are convenient for numerical computations and comparisons with the experimental results suggest that they are adequate. In addition, a few numerical results were obtained using approximations to a higher order in κ which indicated that no undue error will result from the use of the above approximations.

The explicit analytical forms for the various forms for the various cross sections are given in the Appendix. Here, we mention that the partial differential cross section can be written as

$$\sigma(E_0,\epsilon,\theta)=\sigma^{(0)}+\sigma^{(3)}+\sigma^{(2)}, \tag{11}$$

where $\sigma^{(0)}$, $\sigma^{(3)}$, and $\sigma^{(2)}$ are the contributions to the scattering by molecules in the ground state, in the triply degenerate excited state (0.123 eV), and in the doubly degenerate excited state (0.135 eV), respectively.

IV. DATA AND COMPARISONS WITH THEORY

An example of the inelastic scattering data taken at a scattering angle of 15.4° with an incident neutron energy of 49.6 meV and a sample temperature of 306°K is shown in Fig. 1. Also shown is the theoretical curve and this curve convoluted with the energy resolution function of the velocity selector. The data and resolution-broadened theoretical curve are considered to be in good agreement with the data falling below the

---

[17] T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1946), p. 226.

[18] T. J. Krieger and M. S. Nelkin, Phys. Rev. **106**, 290 (1957).

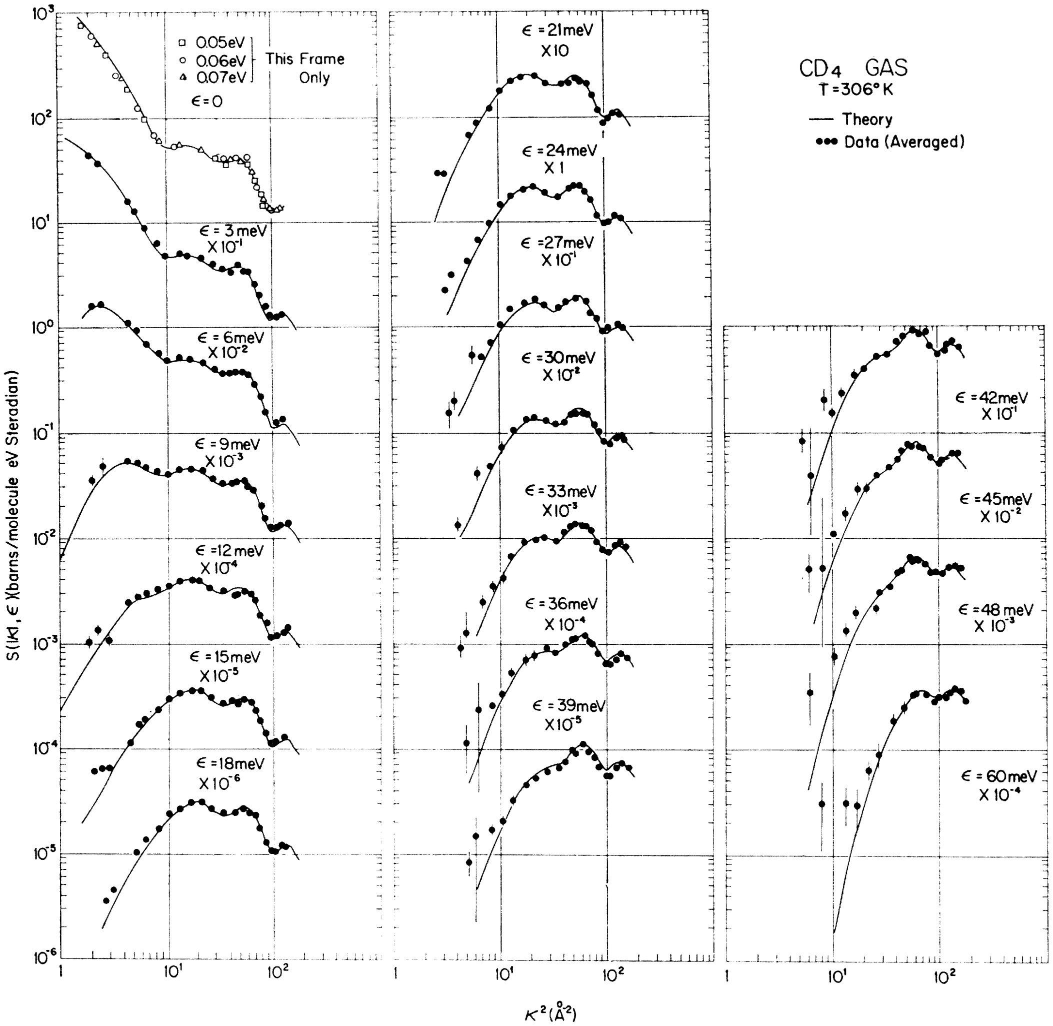

FIG. 2. Comparison of the theoretical and experimental scattering law as a function of κ^2 for various selected energy transfers. The vertical bar on an experimental point indicates the statistical error. The magnitude of the scattering law has been multiplied by the indicated power of 10 before plotting. Thus, $\times 10^{-6}$ indicates the scale of the ordinate is to be multiplied by 10^6.

convoluted curve by about 3%. This is approximately the limit of the absolute error of calibration of any one detector. There is no normalization of the experimental data or the theoretical curves in Fig. 1. This is also true for all subsequent comparisons between the data and the theory.

Presentation of the data is divided into two parts: The data for which the energy transfer ϵ is small enough so that the contributions to the scattering from vibrationally excited molecules are small compared to the contributions from molecules in the vibrational ground state are presented later in Fig. 2. The data for which the energy transfer ϵ is large enough so that the excited vibrational contribution is significant or may even be the dominant contribution are presented later in Fig. 4. The data are presented in scattering law as a function of κ^2. Except for zero energy transfer, the data obtained for the three incident neutron energies and fifteen scattering angles have been averaged[19] over small intervals of κ^2. There is some caution that must be observed in reading the magnitude of the scattering law since the scale on the ordinate has been reduced by the indicated power of 10. Thus, $\times 10^{-6}$ indicates that the scale of the ordinate is to be multiplied by 10^6. Presenting individual curves for each energy transfer was adopted for the sake of clarity.

Figure 2 shows the experimental results compared to the theoretical calculations which are given by the solid-line curves. It will be noted that, in general, there is excellent agreement between the experimental and theoretical results as to the magnitude and the features

---

[19] R. E. Schmunk, Phys. Rev. **136**, A1303 (1964).

of the scattering law. The deviations will now be commented upon.

For zero energy transfer and $\kappa^2 < 10$ Å^{-2} the experimental results are slightly lower than the theoretical results. This deviation is undoubtedly due to resolution effects for which the data have not been corrected. The effect of energy resolution was examined for a particular case in Fig. 1. For $\kappa^2 > 10$ Å^{-2} the experimental data are relatively less sensitive to resolution effects and no deviations are noted.

For $\epsilon \geq 9$ meV and $\kappa^2 < 10$ Å^{-2} there is a tendency for the experimental results to lie above the theoretical results. This is probably due to a combination of resolution effects, the small percentage of hydrogen in the sample, and the multiple scattering in the sample. Qualitatively each of these effects would tend to produce the observed deviation. No attempts were made to correct the data for such possible effects since no satisfactory method for making the corrections was available to us. It is emphasized that this deviation between the experiment and theory is no reason to suspect any inadequacy of the theory.

It is instructive to examine the partial contributions of the direct and interference terms to the scattering law. The theoretical results for zero energy transfer are shown in Fig. 3. That the interference terms are contributing more than the direct terms to the scattering law for the smallest values of κ^2 may be understood by an examination of (4). For example, in Fig. 3 it is seen that $S_{dd'}$ is larger than S_{dd}. In part, the reason is because there is a factor 12 multiplying the cross section $\sigma_{dd'}$ in the definition of $S_{dd'}$, while a factor 4 multiplies the cross section σ_{dd} in the definition of S_{dd} and for small values of κ^2 the cross sections $\sigma_{dd'}$ and σ_{dd} are approximately equal.

The structure of the curves for the interference terms arise because of interference between the neutron waves scattered from individual nuclei of the molecule. The prominence of the structure depends on the relative magnitude of the coherent scattering length as compared to the incoherent scattering length and its details upon the shape and the size of the molecule. This presents the possibility of obtaining information on molecular structure by neutron methods in somewhat analogous manner as that employed by electron diffraction techniques.[20,21] For a qualitative understanding of the structure in Fig. 3, it is sufficient to consider the molecule as fixed in space relative to the neutron beam. The scattering law for the interference terms is then proportional to

$$e^{-i\boldsymbol{\kappa}\cdot(\mathbf{r}_i-\mathbf{r}_j)},$$

where $\mathbf{r}_i$ and $\mathbf{r}_j$ are the position vectors of the ith and jth nuclei. Averaging over all possible molecular orientations gives

$$S_{ij} \propto j_0(\kappa r_{ij}), \qquad (12)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $\kappa = 2k_0 \sin(\theta/2)$. The zeros of S_{cd} in Fig. 3 are given correctly by (12) since, as may be seen by an examination of the analytical expression in (4), precisely this term appears in the more correct considerations. If the zeros of $S_{dd'}$ in Fig. 3 were due to a term of the form given by (12) they would determine the distance between the deuterons. For the first zero, one obtains a distance of 1.59 Å. For the remaining zeros, one obtains a distance quite close to the accepted distance of 1.78 Å. These distances would all be the same if (12) gave the correct behavior of the contribution of the $S_{dd'}$ to the scattering. However, (12) is useful since it does give a qualitative understanding of the scattering by quite simple considerations.

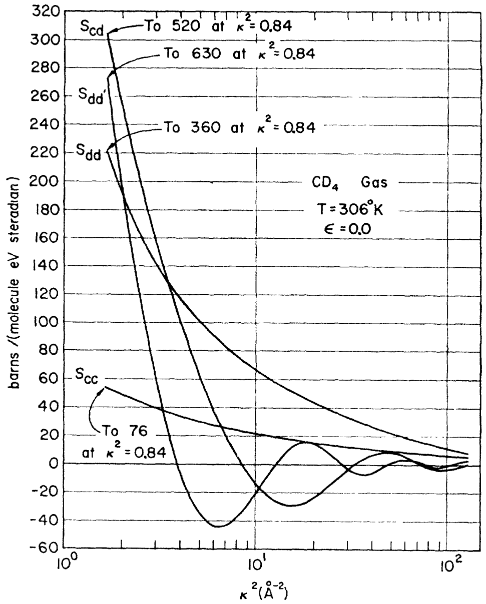

FIG. 3. Compuated partial contributions to the scattering law as a function of κ^2 for zero energy transfer. The arrows indicate the magnitude obtained for the various cruves at the last point computed which was $\kappa^2 = 0.84$ Å^{-2}.

The remaining experimental data are presented in Fig. 4. For these data the energy transfer ϵ is large enough so that contributions to the scattering by the vibrationally excited molecules are a significant factor. These data are compared to the theoretical results as given by the solid-line curves. Before discussing the comparisons, it is of interest to note the population density of the excited molecules. Assuming the vibrational states are populated according to the Boltzmann thermal distribution function, we find that approximately 96.8% of the molecules are in the ground vibrational state, 2.6% in the first triply degenerate

---

[20] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Claredon Press, Oxford, England, 1952), Chap. IV.

[21] R. J. Glauber discusses some of the advantages of using neutrons as compared to electrons and x rays in *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1962), Vol. IV, p. 571.

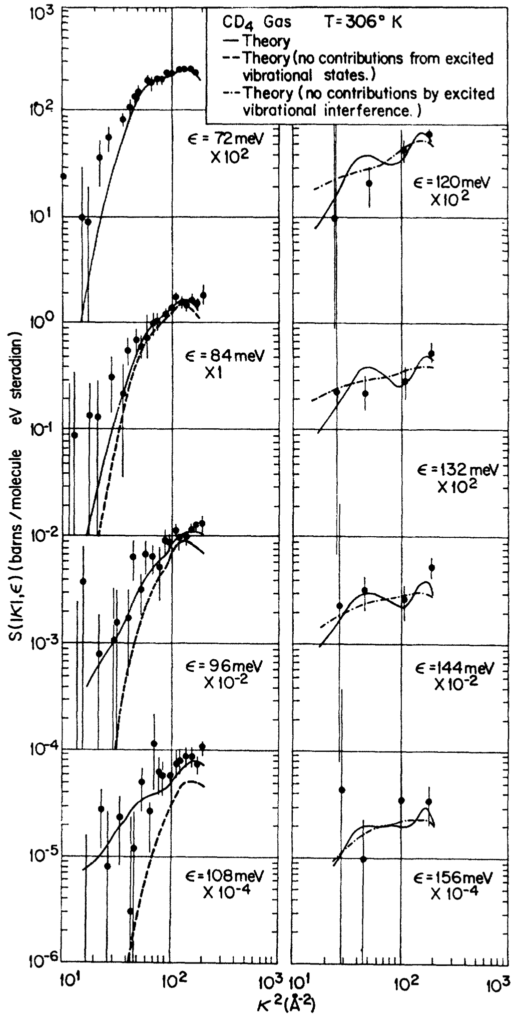

FIG. 4. Comparison of the theoretical and experimental scattering law as a function of κ^2 for various selected energy transfers. The increasing importance of the excited molecules to the scattering as the energy-transfer increases can be noted in the curves on the left-hand side by comparing the solid-line curve which includes this contribution and the dashed-line curve which does not include this contribution. In the curves on the right-hand side the dot-dash curves do not include the contribution by excited vibrational interference terms while the solid-line curve includes this contribution. The vertical line on the experimental points indicates the statistical error. The magnitude of the scattering law has been multiplied by the indicated power of 10 before plotting, as in Fig. 2.

excited state (0.123 eV), and 0.6% in the first doubly degenerate excited state (0.135 eV).

Confining our attention to the curves on the left-hand side of Fig. 4, the broken-line curves are the theoretical results obtained if the contributions from the vibrationally excited molecules are ignored while these contributions are included in the solid-line curves. For $\epsilon = 72$ meV only the solid-line curve is shown since it was not possible to show a difference between the two curves. It is observed that for a given energy transfer the relative contribution to the scattering by the vibrationally excited molecules increases as the momentum transfer decreases. In addition, this contribution becomes more important as ϵ increases. Indeed, for $\epsilon = 108$ meV the contribution to the scattering by the vibrationally excited molecule is the dominant contribution and no agreement with the experimental results would be possible without its inclusion. Even though the population density of the vibrationally excited molecules is small compared to those in the ground state, it is just those vibrationally excited molecules which can give neutron energy transfers large enough to be observed. Detailed comparisons between the experimental data and theoretical results are not possible because of the rather large uncertainties associated with the experimental data. However, the comparison does establish the importance of the contributions to the scattering by the vibrationally excited molecules. In addition, it is noted that these contributions become important at energy transfers much smaller than the energy at which the energy transfer would be in reasonance with the energy of the excited state.

Finally, let us consider the curves on the right-hand side of Fig. 4. The dot-dash curves are the theoretical results obtained when the vibrationally excited interference terms are ignored while the solid-line curve includes these contributions. There are few experimental points so perhaps no comparison with the theoretical results should be made. Nevertheless, a comparison suggests that one feature predicted by the theory which is due to contributions by interference scattering may have been observed. This feature is the apparent observed increase of the scattering law occurring at values of κ^2 greater than 100 Å^{-2}.

An additional feature which is evident in this investigation is worthy of mention. In Fig. 2 it is noted that the structure in the scattering law "damps out" as the energy transfer increases. An examination of the theoretical calculations indicates that this is due to the relatively faster decrease with increasing energy transfers of the interference contributions with respect to the direct contributions. However, in Fig. 4 it is noted that as the energy transfer approaches in magnitude to that of the energy of the vibrational level, these interference contributions are once again responsible for the structure in the scattering law. With further increase of the energy transfer as depitcted in the last frame, the interference contributions are "damping out" once more.

V. SUMMARY

The work presented in this paper was initiated to investigate in detail the scattering of neutrons by a gaseous sample for which coherent scattering would be a dominate feature. It supplements the previous work[1] on gaseous CH$_4$. In contrast to those results which showed little evidence of coherent scattering, the scattering law for gaseous CD$_4$ shows quite pronounced momentum-dependent coherent structure. The coherent structure is most prominent for elastic scattering and becomes less prominent as the energy transfer increases unitl it has about disappeared at an energy transfer of 72 meV.

The scattering law data for $\epsilon > 84$ meV is definitely enhanced by contributions from the de-excitation of vibrationally excited molecules in the first excited state of the triply degenerate mode (0.123 eV) and the first excited state of the doubly degenerate mode (0.135 eV) even though only about 3% of the molecules are excited. In addition, the theory indicates that for energy transfers which are in resonance with these states the coherent structure is again quite pronounced. In general, there is excellent agreement of the experimental results and the theory.

APPENDIX

The approximations which were used permit the partial cross sections to be written as

$$\sigma_{\nu\mu}=\sigma_{\nu\mu}{}^{(0)}+\sigma_{\nu\mu}{}^{(3)}+\sigma_{\nu\mu}{}^{(2)}\,. \tag{A1}$$

The partial cross sections for the triply and doubly vibrationally excited state can be coveniently expressed by making use of the expression for the partial cross sections $\sigma_{\nu\mu}$ for the ground state which have been given previously[13] for CH$_4$. However, it is necessary to modify these expressions for the partial cross sections $\sigma_{\nu\mu}$ by subtracting ω_7 in the case of the triply excited state and ω_2 in the case of the doubly excited state from the definition of α given in Ref. 13. With the understanding that this modification has been made, our approximations for the partial cross sections of the excited states are

$$\begin{aligned}\sigma_{\nu\mu}{}^{(3)}=\sigma_{\nu\mu}\Big\{&\exp[-(\omega_7/2T)+\kappa^2\Gamma_{\nu\mu}{}^{(7)}][4\sinh(\omega_7/2T)]^{-1}\Big[(1/3)\Big(\frac{\kappa^2}{\omega_7}\Big)(\mathbf{C}_\nu{}^{(7)}\cdot\mathbf{C}_\mu{}^{(7)}+\mathbf{C}_\nu{}^{(8)}\cdot\mathbf{C}_\mu{}^{(8)}+\mathbf{C}_\nu{}^{(9)}\cdot\mathbf{C}_\mu{}^{(9)})\\ &-(1/20)\Big(\frac{\kappa^2}{\omega_7}\Big)^2(\mathbf{C}_\nu{}^{(7)}\cdot\mathbf{C}_\mu{}^{(7)})[(\mathbf{C}_\nu{}^{(7)}\cdot\mathbf{C}_\mu{}^{(7)})+(\mathbf{C}_\nu{}^{(8)}\cdot\mathbf{C}_\mu{}^{(8)})+(\mathbf{C}_\nu{}^{(9)}\cdot\mathbf{C}_\mu{}^{(9)})]\Big]\Big\}\,,\\ \sigma_{\nu\mu}{}^{(2)}=\sigma_{\nu\mu}\Big\{&\exp[-(\omega_2/2T)+\kappa^2\Gamma_{\nu\mu}{}^{(2)}][4\sinh(\omega_2/2T)]^{-1}\Big[(1/3)\Big(\frac{\kappa^2}{\omega_2}\Big)(\mathbf{C}_\nu{}^{(2)}\cdot\mathbf{C}_\mu{}^{(2)}+\mathbf{C}_\nu{}^{(3)}\cdot\mathbf{C}_\mu{}^{(3)})\\ &-(1/20)\Big(\frac{\kappa^2}{\omega_2}\Big)^2(\mathbf{C}_\nu{}^{(2)}\cdot\mathbf{C}_\mu{}^{(2)})[(\mathbf{C}_\nu{}^{(2)}\cdot\mathbf{C}_\mu{}^{(2)})+(\mathbf{C}_\nu{}^{(3)}\cdot\mathbf{C}_\mu{}^{(3)})]\Big]\Big\}\,,\end{aligned}\tag{A2}$$

where

$$\Gamma_{\nu\mu}{}^{(\lambda)}=(1/12\omega_\lambda)[(C_\nu{}^{(\lambda)})^2+(C_\mu{}^{(\lambda)})^2]\,.$$

The value of the parameters[17,22,23] used in the computations were $C_{\mathrm{C}}=0$, $A_{\mathrm{C}}=0.64\times10^{-12}$ cm, $C_d=-0.41\times10^{-12}$ cm, $A_d=0.65\times10^{-12}$ cm, $b=1.093\times10^{-8}$ cm, $I=10.66\times10^{-40}$ gm cm^2, $\gamma_{dd}=4.02\times10^{-19}$ cm^2, $\gamma_{\mathrm{CC}}=3.57\times10^{-20}$ cm^2, and $M=53.51\times10^{-24}$ g.

For the various products involving the vibrational amplitude vector, it is convenient to use a number subscript on the vector to identify a particular deuteron of the molecule. The deuterons are numbered as in the paper by Pope.[23] The values used in the computations were:

$\mathbf{C}_1{}^{(2)}\cdot\mathbf{C}_2{}^{(2)}+\mathbf{C}_1{}^{(3)}\cdot\mathbf{C}_2{}^{(3)}=0.31\times10^{24}$ g^{-1} and the same value for the pair (3,4).

$\mathbf{C}_1{}^{(2)}\cdot\mathbf{C}_4{}^{(2)}+\mathbf{C}_1{}^{(3)}\cdot\mathbf{C}_4{}^{(3)}=-0.244\times10^{24}$ g^{-1} and the same value for the pairs (1,3), (2,3), and (2.4).

$\mathbf{C}_{\mathrm{C}}{}^{(2)}\cdot\mathbf{C}_1{}^{(2)}+\mathbf{C}_{\mathrm{C}}{}^{(3)}\cdot\mathbf{C}_1{}^{(3)}=0$ and the same value for the pairs (C,2), (C,3), and (C,4)

$\mathbf{C}_1{}^{(7)}\cdot\mathbf{C}_2{}^{(7)}+\mathbf{C}_1{}^{(8)}\cdot\mathbf{C}_2{}^{(8)}+\mathbf{C}_1{}^{(9)}\cdot\mathbf{C}_2{}^{(9)}=0.0897\times10^{24}$ g^{-1} and the same value for all other pairs.

$\mathbf{C}_{\mathrm{C}}{}^{(7)}\cdot\mathbf{C}_1{}^{(7)}+\mathbf{C}_{\mathrm{C}}{}^{(8)}\cdot\mathbf{C}_1{}^{(8)}+\mathbf{C}_{\mathrm{C}}{}^{(9)}\cdot\mathbf{C}_1{}^{(9)}=0.256\times10^{24}$ g^{-1} and the same value for all other pairs of carbon nucleus and deuteron.

$(C_1{}^{(2)})^2+(C_2{}^{(2)})^2=0.150\times10^{24}$ g^{-1} and the same value for all ther pairs.

$(C_1{}^{(7)})^2+(C_2{}^{(7)})^2=0.116\times10^{24}$ g^{-1} and the same value for all other pairs.

$(C_{\mathrm{C}}{}^{(7)})^2+(C_1{}^{(7)})^2=0.069\times10^{24}$ g^{-1} and the same value for all other pairs of carbon nucleus and deuteron.

---

[22] G. E. Bacon, *Neutron Diffraction* (Oxford University Press, London, 1955), p. 125.

[23] N. K. Pope, Can. J. Phys. **30**, 597 (1952).