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AN EVALUATION OF THE KRIEGER-NELKIN
METHOD FROM CALCULATIONS OF SLOW
NEUTRON SCATTERING BY CH_4

H. L. McMurry, G. W. Griffing
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This report provides a detailed reference of calculation methods and results used in this laboratory and is of value mainly to groups working here. A paper, "Inelastic Scattering of Slow Neutrons from Methane" by P. D. Randolph, R. M. Brugger, K. A. Strong, and R. E. Schmunk, comparing experimental results with computations based on methods in this report has been accepted for publication in The Physical Review.

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SUMMARY

The differential scattering cross section $\sigma(E_0, \epsilon, \hat{p}_0, \hat{p})$ of a material for neutrons tells the probability that a scattering event involving a neutron of energy E_0 will cause an energy change ϵ and a change in direction from $\hat{p}_0$ to $\hat{p}$. Calculations of neutron energy distributions mean free paths, etc., in a material require a knowledge of $\sigma(E_0, \epsilon, \hat{p}_0, \hat{p})$.

When E_0 is near kT and less than the energy for breaking chemical bonds in the material the theory for calculating σ is complicated. Few data are available in this region and for this reason a recent approximate method devised by Krieger and Nelkin to simplify the calculation of σ for gases is attractive as a start toward developing feasible computational methods.

This report evaluates the accuracy of the K.N. approximation by using it to calculate σ values for methane and comparing these with results from a more rigorous, but much more time consuming, calculation which avoids most of the K.N. simplifications.

Calculations were made up to 0.306 ev energy which is sufficient to excite the two lowest methane vibrations. The agreement is best when E_0 is too low to excite vibrations, but it is still good at 0.306 ev. Over this energy range the K.N. method should yield good values for methane of such quantities as the total cross section $\sigma(E_0)$, average energy loss per collision, etc.

The K.N. method is a promising means for simplifying calculations. However, it becomes cumbersome when E_0 is high enough so many vibrational transitions are possible. Furthermore, the methane calculations are relatively easy because its symmetrical structure makes it easy to calculate the normal modes of vibration; and permits considering impacts on only one of the four equivalent hydrogens. Hence, further simplifications are needed to make it possible to calculate σ for any gas over the entire range of energies where chemical binding and thermal motions are important.

Adaptations of the K.N. method to treating liquids and solids will meet these problems as well as others arising from the importance of inter-molecular forces.

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AN EVALUATION OF THE KRIEGER-NELKIN METHOD FROM CALCULATIONS OF SLOW NEUTRON SCATTERING BY CH₄

I INTRODUCTION

Advances in reactor physics have come to the point where more accurate information about the differential scattering cross sections, $\sigma(E_0, \epsilon, \hat{p}_0 \cdot \hat{p})$ and $\sigma(E_0, \hat{p}_0 \cdot \hat{p})$, and the total scattering cross section $\sigma(E_0)$ are needed for moderators. Here E_0 denotes the neutron energy prior to collision with a moderator atom, ϵ the change in neutron energy resulting from the collision and $\hat{p}_0 \cdot \hat{p}$ the cosine of the angle between the incident and final neutron momenta (in the laboratory system).

Since data are currently being obtained for energies E_0 only up to 0.1 ev, and some time will elapse before any but moderators comprising pure materials are studied, theoretical procedures for estimating the needed cross sections are under development. One of the promising computational methods is that of Krieger and Nelkin⁽¹⁾ which achieves simplifications by approximating the matrix elements which appear in the expression for $\sigma(E_0, \epsilon, \hat{p}_0 \cdot \hat{p})$ as a product of matrix elements for the different degrees of freedom in the scattering system. For gases this means translational, rotational, and vibrational degrees of freedom. Furthermore, in the case of gases each factor is averaged separately over molecular orientation, and approximate methods are used to obtain expressions for these averages in the cases of the rotational and vibrational factors. Computations by Griffing and McMurry⁽²⁾ have used this method to calculate $\sigma(E_0, \lambda, \hat{p}_0 \cdot \hat{p})$, $\sigma(E_0, \hat{p}_0 \cdot \hat{p})$ and $\sigma(E_0)$ for gaseous CH₄. The results on $\sigma(E_0, \lambda, \hat{p}_0 \cdot \hat{p})$ agree quite well with recent measurements by Randolph and Brugger using the MTR slow neutron velocity selector.

The effect of the K. N. approximations is difficult to assess directly. As one means of studying this, more exact calculations have been made on CH_4 for comparison with the K. N. method. The "exact" method⁽³⁾ is correct except for treating the rotations classically, neglecting rotation-vibration interaction, and assuming the vibrational motions are governed by a harmonic force law.* The K. N. method makes those approximations as well as the ones already mentioned. This report describes the computational procedure and presents a detailed comparison of results for CH_4 from the exact and the K. N. methods.

* Henceforth the word "exact" will be used without quotation marks. It always means a Born approximation calculation which is rigorous except for treating rotations classically, neglecting rotation-vibration coupling, and assuming harmonic force laws for the vibrations.

II THEORETICAL

A. Equations for the Partial Differential Cross Sections

1. The General Expression

The quantity derived most directly from the experimental data is $\sigma(E_0, \lambda, \hat{p}_0 \cdot \hat{p})$ where λ is the wavelength of the scattered neutron. The theoretical expression for this function is conveniently written as a sum of partial cross sections associated with different amounts of vibrational excitation.

$$\sigma(E_0, \lambda, \hat{p}_0 \cdot \hat{p}) = \sum_{n_1, n_2, \dots, n_N} \sigma_{1, 2, \dots, N}^{n_1, n_2, \dots, n_N} \quad (1)$$

In Eq.(1) the subscripts $1, 2, \dots, N$ denote which of the N normal modes is excited (or de-excited) and the superscript just above reveals the change in quantum number for this mode. If n_i is positive it means that the collision of the neutron with the molecule results in a transfer to the molecule of $n_i \hbar \omega_i$ units of vibrational energy. Here ω_i is the frequency of the i^{th} normal mode in angular units. If n_i is negative the collision involves a molecule in an excited vibrational state and results in a transfer of vibrational energy to the neutron. If any $n_i = 0$ it will be omitted as a superscript and i will be omitted as a subscript. As an example, $\sigma_{1, 3}^{2, 1}$ denotes a partial differential cross section associated with exciting normal mode No. 1 by $2\hbar\omega_1$ and normal mode No. 3 by $\hbar\omega_3$, all other normal modes being neither excited nor de-excited. The partial differential cross section associated with no vibrational excitation will be denoted by σ^0 . This exception to the convention of omitting all $n_i = 0$ is necessary to distinguish σ^0 from the total σ .

2. The Exact Equation

The exact expression (assuming a classical treatment of rotation, harmonic vibrations, zero rotation-vibration interaction, and using the Born approximation, but no others) for $\sigma_{1, 2, \dots, N}^{n_1, \dots, n_N}$ for the case

where temperatures are too low to excite vibrations thermally is given by Eq.116 of (3). It is*

$$\sigma_{1,2,\dots,N}^{n_1, \dots, n_N} = 0.007146 \left[E_0/kT \right]^{\frac{1}{2}} \left[m_n/M \right]^{-\frac{1}{2}} \left[1/\lambda_0 \right] \left[Z^4/\Phi^{\frac{1}{2}} \right] \sum_{v,v'} \left\{ \psi_{vv',1,2,\dots,N}^{n_1, n_2, \dots, n_N} \right\} \quad (2)$$

$$\psi_{vv',1,2,\dots,N}^{n_1, n_2, \dots, n_N} = \left[A_v^2 + C_v^2 \right] \int \langle x_{vv,v}^o \rangle_T F_{v,1,2,\dots,N}^{n_1, \dots, n_N} \prod_{\ell} \left(f_{vv,\ell} \right)^{n_{\ell}} / n_{\ell}! \times d(\cos\theta) dx d\varphi \quad (3a)$$

$$\psi_{vv',1,2,\dots,N}^{n_1, n_2, \dots, n_N} = A_v A_{v'} \int \langle x_{vv,v}^o \rangle_T \frac{e^{\left[i 2\pi\Phi^{\frac{1}{2}}/\lambda_0 \right] \left\{ \tilde{A}_Z \left[\rho_v^o - \rho_{v'}^o \right] \right\}}}{x_{v',1,2,\dots,N}^{n_1, \dots, n_N}} \prod_{\ell} \left[\left(f_{vv',\ell} \right)^{n_{\ell}} / n_{\ell}! \right] d(\cos\theta) dx d\varphi \quad (3b)$$

* The constant in front of Eq.116 has been rewritten to be in terms of dimensionless quantities E_0/kT , m_n/M , and λ_0/λ . Also, a factor $1/2\pi$ has been inserted so that σ is in units of per steradian.

The following relations and parameters appear in Eqs.(2) and (3)

$$0.0071464 = \sqrt{\pi/8\pi^3}$$

$$m_n = \text{neutron mass}$$

$$M = \text{mass of the molecule}$$

$$\lambda_o = h/\sqrt{2m_n E_o} = 0.2860/\sqrt{E_o(\text{ev})} = \text{wavelength in } \text{\AA}^o \text{ of the incident neutron of energy } E_o$$

$$Z = \lambda_o/\lambda$$

$$\Phi(Z) = Z^2 + 1 - 2Z \hat{p}_o \cdot \hat{p}$$

$$\hat{p}_o \cdot \hat{p} = \text{Cosine of the angle between the incident and scattered neutron directions in the laboratory system.}$$

$$E_\ell = \hbar\omega_\ell = \text{vibrational energy associated with the } \ell^{\text{th}} \text{ normal mode}$$

$$[\tilde{A}_Z] = \begin{bmatrix} -\sin\theta \cos\chi & \sin\theta \sin\chi & \cos\theta \end{bmatrix}$$

This is a three element row matrix* in which the elements are functions of the Eulerian angles θ, ϕ, χ . In defining these angles $\underline{p} - \underline{p}_o$ in the laboratory system is chosen for the Z axis. The elements in $[\tilde{A}_Z]$ are the direction cosines between Z and x, y, z axes fixed in the molecule.

* In (3) this row matrix is denoted by $[A_Z]$ instead of the transpose $[\tilde{A}_Z]$. The notation here is more consistent with using $\begin{bmatrix} \end{bmatrix}$ to denote a column matrix and $\begin{bmatrix} \sim \end{bmatrix}$ a row matrix

$$\begin{bmatrix} \rho_v^0 - \rho_{v'}^0 \\ \rho_v^0 - \rho_{v'}^0 \\ \rho_v^0 - \rho_{v'}^0 \end{bmatrix} = \begin{bmatrix} x_v^0 - x_{v'}^0 \\ y_v^0 - y_{v'}^0 \\ z_v^0 - z_{v'}^0 \end{bmatrix} \quad \text{where } x_v^0, x_{v'}^0 \text{ etc. denote equilibrium} \\ \text{coordinates for atoms } v, v' \text{ relative to} \\ \text{the } x, y, z, \text{ axes.}$$

The factor $\langle x_{vv'}^0 \rangle_T$ as given by Eq.(94) of (3) is

$$\langle x_{vv'}^0 \rangle = \exp \left\{ \left(-m_n \Phi / 2 \right) \sum_{\ell} \left\{ \left(\tilde{A}_Z [T_{v\ell}] \right)^2 + \left(\tilde{A}_Z [T_{v'\ell}] \right)^2 \right\} \left(E_o / E_{\ell} \right) \coth \left(E_{\ell} / 2kT \right) \right\} \quad (4)$$

where $T_{v\ell}$ is a three element column matrix which gives the displacement of the atom relative to axes rotating with the molecule in terms of the normal coordinate Q_{ℓ} . This means

$$\begin{bmatrix} \Delta x_v \\ \Delta y_v \\ \Delta z_v \end{bmatrix} = \begin{bmatrix} T_{vx,\ell} \\ T_{vy,\ell} \\ T_{vz,\ell} \end{bmatrix} Q_{\ell} \quad \left(\text{cf. Eq.(33) of (3)} \right)$$

Here Δx_v etc. are displacements of atom v relative to the axes rotating with the molecule.

The quantity $F_{v,1,2\dots N}^{n_1,\dots,n_N}$ is obtained from Eq.(106) of (3)* by factoring out $\left(m_n / M \right)^{-1/2}$ from $G_{v,n_1,n_2\dots n_N}$. In terms of $Z = \lambda_o / \lambda$

it is

*The notation used here which employs superscripts as well as subscripts on F is more explicit than that used in (3).

$$F_{n_1 \dots n_N} = \frac{e^{-E_0} \left\{ Z^2 - 1 + \left(\frac{m_n}{M} \right) \phi \alpha_v + \left(\frac{\sum_{\ell} n_{\ell} E_{\ell}}{E_0} \right)^2 \right\}}{4kT\phi \left(\frac{m_n}{M} \right) \alpha_v} \quad (5)$$

$$\alpha_v = \frac{1}{\alpha_v^2}$$

$$\alpha_v = 1 + M[A_Z] \tilde{R}_v I^{-1} R_v [A_Z] \quad (6)$$

$$R_v = \begin{bmatrix} 0 & -z_v^0 & y_v^0 \\ z_v^0 & 0 & -x_v^0 \\ -y_v^0 & x_v^0 & 0 \end{bmatrix} \quad (7)$$

where x_v^0 , y_v^0 , z_v^0 are equilibrium positions for atom v relative to axes fixed in the molecule.

The I^{-1} is the reciprocal of the moment of inertia tensor. When principal axes are used, as in CH_4

$$I^{-1} = \begin{bmatrix} \frac{1}{I_{xx}} & 0 & 0 \\ 0 & \frac{1}{I_{yy}} & 0 \\ 0 & 0 & \frac{1}{I_{zz}} \end{bmatrix} \quad (8)$$

where I_{xx} etc. are the moments of inertia about the axes rotating with the molecule, and in the present treatment which neglects effects due to centrifugal distortion, are computed with the atoms in their equilibrium positions.

The $f_{vv;l}$ as given by Eq.(114b) of (3) is

$$f_{vv;l} = \left(E_o/E_l \right) \Phi_m \left(\tilde{A}_Z [T_{vl}] \right) \left(\tilde{A}_Z [T_{v'l}] \right) \quad (9)$$

3. The Krieger-Nelkin Approximation

The simplest Krieger-Nelkin approximation is to express the average over orientation in Eq.(2) as a product of the averages of the separate factors. Exponential factors are averaged in the exponentials. This means replacing α_v by

$$\bar{\alpha}_v = M/M_v = \left[1/8\pi^2 \right] \int \alpha_v d(\cos\theta) d\phi dX \quad (10)$$

and writing the average of $\prod_{v,1 \dots N}^{n_1, \dots, n_N}$ as

$$\prod_{v,1,2 \dots N}^{n_1, \dots, n_N} = e^{\frac{-E_o \left\{ Z^2 - 1 + \left(m_n/M \right) \Phi \bar{\alpha}_v + \left(\sum_l n_l/E_o \right) \right\}^2}{4kT\Phi}} \frac{1}{\left(m_n/M \right) \bar{\alpha}_v} \frac{1}{\bar{\alpha}_v^{\frac{1}{2}}} \quad (11)$$

Assuming $\text{Coth}(E_l/2kT) \approx 1$ the expression for average of $\langle x_{vv;l}^o \rangle_T$ over molecular orientation is expressed in the form

$$\langle x_{vv;l}^o \rangle_{T,\Omega} = \prod_l \langle x_{vv,l}^o \rangle_{T,\Omega}^{\frac{1}{2}} \langle x_{v',v',l}^o \rangle_{T,\Omega}^{\frac{1}{2}} \quad (12)$$

where

$$\langle x_{vv,l}^o \rangle_{T,\Omega}^{\frac{1}{2}} = e^{-\left[\Phi/8\pi^2 \right] \left[E_o/E_l \right] \left[n/2 \right] \left[\tilde{T}_{vl} \right] \left[T_{vl} \right] \int \cos^2 \theta_{vl} d(\cos \theta_{vl}) d\phi dX}$$

Hence

$$-\left[\frac{m_n}{6}\right] \sum_{\ell} \left[\tilde{T}_{v\ell} \right] \left[T_{v\ell} \right] + \left[\tilde{T}_{v'\ell} \right] \left[T_{v'\ell} \right] \left(E_o / E_{\ell} \right) \cdot$$

$$\langle \chi_{vv';v}^o \rangle_{T,\Omega} = e \quad (13)$$

In forming the average in Eq.(13) the vector $T_{v\ell}$ is considered to make an angle $\theta_{v\ell}$ with $\frac{\mathbf{K}}{h} = \mathbf{p} - \mathbf{p}_o$. The components of $[T_{v\ell}]$ are identical with those of $\underline{c}_{v\ell}$ of K. N. divided by h . In vector notation $\underline{c}_{v\ell}/h = T_{v\ell}$. The M_v in Eq.(10) is the mass tensor factor of Eq.(13) of K. N.

After these insertions Eq.(2) is integrated over $\cos\theta$, ϕ , and χ . This introduces a factor $8\pi^2$ into the term corresponding to ψ_{vv} . The $\psi_{vv'}$ term has a factor

$$e^{\left[i 2\pi\Phi^{\frac{1}{2}}/\lambda_o \right] \left[\tilde{A}_Z \right] \left[\rho_v^o - \rho_{v'}^o \right]}$$

The K. N. method averages this as follows

$$\left(1/8\pi^2 \right) \int e^{\left[i 2\pi\Phi^{\frac{1}{2}}/\lambda_o \right] \left[\tilde{A}_Z \right] \left[\rho_v^o - \rho_{v'}^o \right]} x d(\cos\theta) d\phi d\chi \simeq \left(1/8\pi^2 \right) \int e^{\left[i 2\pi\Phi^{\frac{1}{2}} b_{vv'} \cos\theta \right] / \lambda_o} x d(\cos\theta) d\phi d\chi$$

$$= \frac{\sin \left(2\pi\Phi^{\frac{1}{2}} b_{vv'} / \lambda_o \right)}{\left(2\pi\Phi^{\frac{1}{2}} b_{vv'} / \lambda_o \right)} \quad (14)$$

It is convenient to multiply $8\pi^2 \times 0.007146$ and to write

$$\sigma_{1,2,\dots,N}^{n_1,n_2,\dots,n_N} = 0.5642 \left[E_o / kT \right]^{\frac{1}{2}} \left[\frac{n}{M} \right]^{-\frac{1}{2}} \left[1/\lambda_o \right] \left[Z^4 / \Phi \right]^{\frac{1}{2}} \left\{ \sum_{v,v'} \bar{\psi}_{vv';1,2,\dots,N}^{n_1,\dots,n_N} \right\} \quad (15)$$

$$\bar{\psi}_{vv',1,2,\dots,N}^{n_1,\dots,n_N} = \left[A_v^2 + C_v^2 \right] \langle \chi_{vv';v}^o \rangle_{T\Omega} \bar{F}_{v,1,2,\dots,N}^{n_1,\dots,n_N} \prod_{\ell} \left(\overline{f_{vv,\ell}} \right)^{n_{\ell}} / n_{\ell}! \quad (16a)$$

$$\bar{\psi}_{vv;1,2..N}^{n_1, \dots, n_N} = A_v A_{v'} \langle \chi_{vv;v}^0 \rangle_{T\Omega} \frac{\sin \left(2\pi \Phi_{vv}^{1/2} / \lambda_0 \right)}{\left(2\pi \Phi_{vv}^{1/2} / \lambda_0 \right)}$$

$$\bar{F}_{v;1,2..N}^{n_1, \dots, n_N} \prod_l \left(\overline{f_{vv;l}} \right)^{n_l} / n_l! \quad (16b)$$

$$\left(\overline{f_{vv,l}} \right)^{n_l} = \left\{ \left(E_0 \Phi_{nn} / E_l \right) \left[\tilde{T}_{vl} \right] \left[T_{vl} \right] \right\}^{n_l} \frac{\int_{-1}^1 (\cos \theta_{vl})^{2n_l} d(\cos \theta_{vl})}{\int_{-1}^1 d(\cos \theta_{vl})}$$

or

$$\left(\overline{f_{vv,l}} \right)^{n_l} = Q_{vl}^{n_l} / [n_l + 1] \quad (17)$$

$$Q_{vl} = \left[E_0 / E_l \right] \Phi_{nn} \left[\tilde{T}_{vl} \right] \left[T_{vl} \right] \quad (18)$$

A less satisfactory approximation which has the advantage of simplifying some computations is to use

$$\left(\overline{f_{vv,l}} \right)^{n_l} \simeq \left(\overline{f_{vv,l}} \right)^{n_l} = \left(Q_{vl} / 3 \right)^{n_l} \quad (19)$$

when $v \neq v'$ the expressions for $\left(\overline{f_{vv;l}} \right)^{n_l}$ and $\left(\overline{f_{vv;l}} \right)^{n_l}$ analogous to Eqs. (17) and (19) are not so easily obtained. However, for CH_4 the energies required to excite vibrations are large and the terms in $\left(\overline{f_{vv;l}} \right)^{n_l}$ with $n_l \neq 0$ can be safely neglected.

A plausible way of improving on Eq.(16a) is to use

$$\langle \chi_{vv,v}^0 \rangle_T = e^{-Q_{vl} \cos^2 \theta_{vl}} = \sum_{j=0}^{\infty} (-1)^j Q_{vl} \cos^{2j} \theta_{vl} / j!$$

This leads to using

$$\begin{aligned} \bar{\psi}_{vv,1,2\dots N}^{n_1,\dots n_N} &= [A_v^2 + C_v^2] \bar{F}_{v,1,2\dots N}^{n_1,\dots N} \int_{-1}^1 \left[\prod_{\ell} \left[\frac{n_{\ell}}{Q_{v\ell}/n_{\ell}}! \right] [\cos \theta_{v\ell}]^{2n_{\ell}} \right. \\ &\quad \times \frac{1}{2} \sum_j \left[(-1)^j Q_{v\ell}^j / j! \right] [\cos \theta_{v\ell}]^{2j} \left. \right] d(\cos \theta_{v\ell}) \\ &= [A_v^2 + C_v^2] \bar{F}_{v,1,2\dots N}^{n_1,\dots N} \prod_{\ell} \left[\frac{n_{\ell}}{Q_{v\ell}/n_{\ell}}! \right] \sum_j (-1)^j Q_{v\ell}^j / [j! (2(n_{\ell}+j)+1)] \quad (20) \end{aligned}$$

In this approximation the expression for the direct scattering is

$$\sigma_{1,2,\dots N}^{n_1,\dots n_N} d = 0.5642 \left(E_0 / kT \right)^{\frac{1}{2}} \left[1 / \lambda_0 \right] \left[Z^4 / \Phi^{\frac{1}{2}} \right] \left\{ \sum_v (A_v^2 + C_v^2) \bar{\psi}_{v,1,2,\dots N}^{n_1,\dots n_N} \right\} \quad (21)$$

$$\bar{\psi}_{v,1,2,\dots N}^{n_1,\dots n_N} = \left(m_n / M \right)^{-\frac{1}{2}} \bar{F}_{v,1,2,\dots N}^{n_1,\dots n_N} \prod_{\ell} \left[\frac{n_{\ell}}{Q_{v\ell}/n_{\ell}}! \right] \sum_{j=0}^{\infty} (-1)^j Q_{v\ell}^j / [j! (2(n_{\ell}+j)+1)] \quad (22)$$

4. Treatment of Degeneracy

When two or more vibrational modes are degenerate the scattering data cannot separate excitations of one from the others. Hence it is desirable to write the equation for the differential scattering cross section in such a form that all excitations of degenerate modes involving a given number of quanta are grouped together. Thus suppose modes r, s, t , are degenerate. Consider $\sum_r \sum_s \sum_t \sigma_{1,2,r,s,t,\dots N}^{n_1,n_2,n_r,n_s,n_t,\dots n_N}$ subject to the restriction $n_r + n_s + n_t = n$ where n is a constant. The exact Eqs.(3a), (3b) then involve

$$F_{v,1,2,\dots,r,s,t}^{n_1,n_2,\dots,n_r,n_s,n_t} \left[\prod_{l \neq r,s,t} (f_{vv;l})^{n_l/n_l!} \right] \\ \times \left\{ \sum_{r,s,t} \prod_{r,s,t} \left[(f_{vv;r})^{n_r/n_r!} \right] \left[(f_{vv;s})^{n_s/n_s!} \right] \left[(f_{vv;t})^{n_t/n_t!} \right] \right\} \quad (23)$$

The condition on n_r, n_s, n_t is such that the sum in (23) is given by

$$\sum_{r,s,t} \prod_{r,s,t} \frac{(f_{vv;r})^{n_r} (f_{vv;s})^{n_s} (f_{vv;t})^{n_t}}{n_r! n_s! n_t!} = \\ \sum_{j=0}^n \sum_{k=0}^j \left[(f_{vv;r})^{n-j} / (n-j)! \right] \left[(f_{vv;s})^{j-k} / (j-k)! \right] \left[(f_{vv;t})^k / k! \right] \\ = \left[f_{vv;r} + f_{vv;s} + f_{vv;t} \right]^{n/n!} \quad (24)$$

this can be derived from (23) by putting

$$n_r = n - j$$

$$n_s = n - n_r = k$$

$$= j - k$$

$$n_t = k$$

and then comparing with what is obtained when (24) is expanded twice by the binomial theorem.

Degenerate vibrations cannot be treated in this way on the K. N. method unless Eq.(19) is used and then only for the terms with $v = v'$. Then Eq. (24) becomes

$$\begin{aligned}
& \sum_{r,s,t} \prod_{r,s,t} \frac{\left(\bar{f}_{vv,r}\right)^{n_r} \left(\bar{f}_{vv,s}\right)^{n_s} \left(\bar{f}_{vv,t}\right)^{n_t}}{n_r! n_s! n_t!} \\
&= \frac{\left(Q_{vr}+Q_{vs}+Q_{vt}\right)^n}{3^n n!} = \frac{\left(\bar{f}_{vvr}+\bar{f}_{vvs}+\bar{f}_{vvt}\right)^n}{n!} \quad (25)
\end{aligned}$$

Eqs.(21) and (22) do not permit this simplification.

III APPLICATION TO CH₄

A. The Equations for CH₄

1. Simplifications Due to Symmetry.

The CH₄ molecule is tetrahedral. All four hydrogens are equivalent as are the 4 C-H pairs and the 6 H-H pairs. Hence the sums over v and v' in Eqs.(2),(15) and (21) can be condensed by considering only one H atom when $v = v'$, and one H-H' pair and one C-H pair when $v \neq v'$, then

$$\begin{aligned} \sum_{vv'} \psi_{vv';1,2,\dots,N}^{n_1,\dots,n_N} &= {}^4\psi_{HH;1,2,\dots,N}^{n_1,\dots,n_N} + \psi_{CC;1,2,\dots,N}^{n_1,\dots,n_N} \\ &+ 12\psi_{HH';1,2,\dots,N}^{n_1,\dots,n_N} + {}^4\psi_{CH;1,2,\dots,N}^{n_1,\dots,n_N} \\ &+ {}^4\psi_{HC;1,\dots,N}^{n_1,\dots,n_N} \end{aligned} \quad (26)$$

2. Parameters for CH₄ In the Exact Method.

To proceed it is necessary to express the factors appearing in Eqs.(2) and (3). The simplest expressions are obtained when the H atom is placed on the z axis and has coordinates $0, 0, r$ and the H' atom has coordinates $2\sqrt{2}r_0/3, 0, -r_0/3$. Then $\alpha_H(\mu^2)$ as given by Eq.(6) is

$$\alpha_H(\mu^2) = 1 + [3/8][M/m_p]\sin^2\theta$$

$$= 7 - 6\mu^2$$

$$\mu = \cos\theta$$

$$[\tilde{A}_Z][\rho_H^0 - \rho_H^0] = (r_0/3) [2\sqrt{2} \sin\theta \cos\chi + 4 \cos\theta]$$

$$[\tilde{A}_Z][\rho_C^0 - \rho_H^0] = r_0 \cos\theta$$

$$F_{H,1,2,\dots,N}^{n_1,\dots,n_N} = \frac{e^{\frac{-4E_0}{kT\Phi} \frac{[\delta_H + (\sum_{\ell} n_{\ell} E_{\ell})/E_0]^2}{\alpha_H}}}{\alpha_H^{\frac{1}{2}}}$$

$$\delta_H = Z^2 - 1 + (\Phi/16) (7 - 6\mu^2) = Z^2 - 1 + (\Phi/16) \alpha_H \quad (27)$$

$$F_{C,1,2,\dots,N}^{n_1,\dots,n_N} = e^{\frac{-4E_0}{kT\Phi} \left[\delta_C + \left(\sum_{\ell} n_{\ell} E_{\ell} \right) / E_0 \right]^2}$$

$$\delta_C = Z^2 - 1 + \Phi/16$$

The $\langle \chi_{vv;v}^0 \rangle_T$, $f_{vv;l}$ etc. require a knowledge of the normal coordinates. In the Appendix the normal coordinates derived by Pope⁽⁴⁾ for CH_4 are used to obtain these quantities. The results, assuming

$\coth(E_{\ell}/2kT) \simeq 1$, are

$$\langle \chi_{HH;v}^0 \rangle_T = e^{-2.232E_0\Phi} \times e^{-2.374E_0\Phi\mu^2} \quad (28)$$

$$\langle \chi_{HH;v}^0 \rangle_T \simeq \langle \chi_{HH,v}^0 \rangle_{T\Omega}^*$$

*The $\langle \chi_{HH;v}^0 \rangle_T$ is a complicated function of $\cos^2\theta$ and $\cos^2\chi$. The terms involving $\langle \chi_{HH;v}^0 \rangle_T$ will contribute only at energies so low that $\langle \chi_{HH;v}^0 \rangle_T \simeq 1$ and the approximation used here should be reasonable.

$$\langle \chi_{CC,v}^0 \rangle_T = e^{-0.1028E_0 \phi} \quad (28)(\text{cont'd.})$$

$$\langle \chi_{CH,v}^0 \rangle_T = e^{-1.167E_0 \phi} \times e^{-1.187E_0 \phi \mu^2}$$

$$\langle \chi_{HC,v}^0 \rangle_T = \langle \chi_{HC,v} \rangle_T$$

In Pope's notation mode 1 is nondegenerate (0.361 eV), modes 2 and 3 are doubly degenerate (0.188 eV), modes 4, 5, 6 are triply degenerate (0.374 eV) and modes 7, 8, 9 are triply degenerate (0.162 eV). The following results are obtained in the Appendix

$$f_{HH,1} = 0.6925E_0 \phi \mu^2$$

$$f_{HH,2} + f_{HH,3} = 1.330E_0 \phi (1-\mu^2)$$

$$f_{HH,4} + f_{HH,5} + f_{HH,6} = 0.7868E_0 \phi - 0.5351E_0 \phi \mu^2 \quad (29)$$

$$f_{HH,7} + f_{HH,8} + f_{HH,9} = 0.1151E_0 \phi + 3.547E_0 \phi \mu^2$$

$$f_{CC,1} = f_{CC,2} = f_{CC,3} = 0$$

$$f_{CC,4} + f_{CC,5} + f_{CC,6} = 0.0200E_0 \phi$$

$$f_{CC,7} + f_{CC,8} + f_{CC,9} = 0.08282E_0 \phi$$

Expressions for the $f_{HH,l}$, $f_{CH,l}$, $f_{HC,l}$ could be derived just as those for the direct scattering terms. However, for neutron energies sufficiently high to justify using terms with $n_l > 0$ the $v \neq v'$ terms make only a small contribution. In the treatment they will be omitted since they involve double integrations of complicated functions involving both $\cos\theta$ and $\cos\chi$.

3. Parameters for CH_4 on the K. N. Method

If $\bar{\mu}^2 = \frac{1}{3}$ is used wherever μ^2 appears in the parameters in Par.2 the averages needed in the K.N. method are obtained. The results are

$$\bar{\alpha}_H = 5; \bar{\alpha}_C = 1$$

$$b_{vv'} = (2\sqrt{2/3})r_o$$

$$F_{H,1,2..N}^{n_1, \dots, n_N} = e^{\frac{-4E_o}{kT\phi} \frac{[\bar{\delta}_H + (\sum_{\ell} n_{\ell} E_{\ell})/E_o]^2}{\bar{\alpha}_H}} ; \bar{\delta}_H = Z^2 - 1 + (5/16)\phi$$

$$F_{C,1,2..N}^{n_1, \dots, n_N} = e^{\frac{-4E_o}{kT\phi} [\delta_C + (\sum_{\ell} n_{\ell} E_{\ell})/E_o]^2} ; \bar{\delta}_C = \delta_C$$

$$\langle \chi_{HHv}^o \rangle_{T,\Omega} = e^{-3.023E_o\phi}$$

$$\langle \chi_{HH'v}^o \rangle_{T,\Omega} = \langle \chi_{HH}^o \rangle_{T,\Omega} \quad (30)$$

$$\langle \chi_{CC,v}^o \rangle_{T,\Omega} = e^{-0.1028E_o\phi}$$

$$\langle \chi_{CH,v}^o \rangle_{T,\Omega} = e^{-1.563E_o\phi}$$

$$\langle \chi_{HC,v}^o \rangle_{T,\Omega} = \langle \chi_{CH,v}^o \rangle_{T,\Omega}$$

$$Q_{H1}/3 = \bar{f}_{HH,1} = 0.2306E_0 \phi$$

$$Q_{H2}/3 = Q_{H3}/3 = \bar{f}_{HH,2} = \bar{f}_{HH,3} = 0.4453E_0 \phi$$

$$Q_{H4}/3 = Q_{H5}/3 = Q_{H6}/3 = \bar{f}_{HH,4} = \bar{f}_{HH,5} = \bar{f}_{HH,6} = 0.2028E_0 \phi$$

$$Q_{H7}/3 = Q_{H8}/3 = Q_{H9}/3 = \bar{f}_{HH,7} = \bar{f}_{HH,8} = \bar{f}_{HH,9} = 0.4323E_0 \phi$$

$$Q_{C1}/3 = Q_{C2}/3 = Q_{C3}/3 = \bar{f}_{CC,1} = \bar{f}_{CC,2} = \bar{f}_{CC,3} = 0$$

$$Q_{C4}/3 = Q_{C5}/3 = Q_{C6}/3 = \bar{f}_{CC,4} = \bar{f}_{CC,5} = \bar{f}_{CC,6} = 0.00667E_0 \phi$$

$$Q_{C7}/3 = Q_{C8}/3 = Q_{C9}/3 = \bar{f}_{CC,7} = \bar{f}_{CC,8} = \bar{f}_{CC,9} = 0.02761E_0 \phi$$

4. Omission of Terms in $\sum \sigma_{1,2,\dots,N}^{n_1,\dots,n_N}$

In practice terms in $\sum \sigma_{1,2,\dots,N}^{n_1,\dots,n_N}$ corresponding to excitations $n_{\ell} + \hbar\omega_{\ell}$ larger than E_0 are negligible. As an example of how this limits the required calculations Table I lists the partial differential cross sections $\sigma_{1,2,\dots,N}^{n_1,\dots,n_N}$ which must be considered for neutrons in several energy ranges up to 0.36 ev.

TABLE I

Terms Required in $\sum_{\sigma_{1,2,\dots,N}}^{n_1,\dots,n_N}$ as a Function of E_o^*

Neutron Energy Range	Terms in $\sum_{\sigma_{1,2,\dots,N}}^{n_1,\dots,n_N}$ Required**
$E_o < 0.162$ ($E_o < E_{7,8,9}$)	σ^o
$0.162 < E_o < 0.188$ ($E_{7,8,9} \leq E_o < E_{2,3}$)	$\sigma^o + (\sigma_7^1 + \sigma_8^1 + \sigma_9^1)$
$0.188 \leq E_o < 0.324$ ($E_{2,3} \leq 2E_{7,8,9}$)	$\sigma^o + (\sigma_7^1 + \sigma_8^1 + \sigma_9^1) + (\sigma_2^1 + \sigma_3^1)$
$0.324 \leq E_o < 0.350$ ($2E_{7,8,9} \leq E_o < E_{7,8,9} + E_{2,3}$)	$\sigma^o + (\sigma_7^1 + \sigma_8^1 + \sigma_9^1) + (\sigma_2^1 + \sigma_3^1)$ $+ (\sigma_7^2 + \sigma_8^2 + \sigma_9^2 + \sigma_{7,8}^{1,1} + \sigma_{7,9}^{1,1} + \sigma_{8,9}^{1,1})$
$0.350 < E_o < 0.361$ ($E_{7,8,9} + E_{2,3} \leq E_o < 2E_{2,3}$)	$\sigma^o + (\sigma_7^1 + \sigma_8^1 + \sigma_9^1) + (\sigma_2^1 + \sigma_3^1)$ $+ (\sigma_7^2 + \sigma_8^2 + \sigma_9^2 + \sigma_{7,8}^{1,1} + \sigma_{7,9}^{1,1} + \sigma_{8,9}^{1,1})$ $+ (\sigma_2^2 + \sigma_3^2 + \sigma_{2,3}^{1,1})$

* Terms corresponding to the same excitation are in brackets.

** When $n_i = 0$ it is omitted as a superscript, and the associated i is omitted as a subscript, except for σ^o when all $n_i = 0$.

5. The Exact Equations for CH₄

The present calculations are for neutron energies $E_0 < 0.32$ ev. and require only σ^0 , $\sigma_7^1 + \sigma_8^1 + \sigma_9^1$ and $\sigma_2^1 + \sigma_3^1$. The specific cross section equations are given as an illustration. The following constants⁽¹⁾ are used

$$\begin{aligned} A_H &= -0.42 \times 10^{-12} & A_C &= 0.64 \times 10^{-12} \\ C_H &= 2.52 \times 10^{-12} & C_C &= 0.0 \\ 4(A_H^2 + C_H^2) &= 26.12 \text{ barns.} & A_C^2 &= 0.41 \text{ barns} \\ 12 A_H^2 &= 2.117 \text{ barns,} & 4 A_H A_C &= -1.075 \text{ barns} \end{aligned}$$

Applying Eqs. (27), (28), and (29) to obtain Eq. (2) gives

$$\sigma^0(E_0, \lambda, \underline{\hat{p}} \cdot \underline{\hat{p}}) =$$

$$\begin{aligned} & 2.256 \left[E_0/kT \right]^{\frac{1}{2}} \left[1/\lambda_0 \right] \left[Z^4/\Phi^{\frac{1}{2}} \right] \left\{ 13.06 e^{-2.23E_0\Phi} \int_{-1}^1 e^{-2.37E_0\Phi\mu^2} x e^{\frac{-(4E_0/kT\Phi)(\delta_H^2/\alpha_H)}{\alpha_H^{\frac{1}{2}}}} d\mu \right. \\ & \quad + 0.41 e^{-0.103E_0\Phi} x e^{\frac{-(4E_0/kT\Phi)(\delta_C^2)}{\alpha_H^{\frac{1}{2}}}} \\ & \quad + 1.058 e^{-2.23E_0\Phi} \int_{-1}^1 e^{-2.37E_0\Phi\mu^2} x e^{\frac{-(4E_0/kT\Phi)(\delta_H^2/\alpha_H)}{\alpha_H^{\frac{1}{2}}}} \\ & \quad \times \cos\left(9.16\Phi^{\frac{1}{2}}\mu/\lambda_0\right) J_0\left(6.48\Phi^{\frac{1}{2}}(1-\mu^2)^{\frac{1}{2}}/\lambda_0\right) d\mu \\ & \quad \left. - 0.538 e^{-1.17E_0\Phi} \int_{-1}^1 \frac{-1.19E_0\Phi\mu^2}{e} x \left[e^{\frac{-(4E_0/kT\Phi)(\delta_H^2/\alpha_H)}{\alpha_H^{\frac{1}{2}}}} + \frac{-4E_0\delta_C^2/kT\Phi}{e} \right] \cos\left(6.87\Phi^{\frac{1}{2}}\mu/\lambda_0\right) d\mu \right\} \end{aligned} \quad (32)$$

Eq.(32) makes use of the relation

$$\int_0^{2\pi} e^{ia \cos X} dX = 2\pi J_0(a)$$

The following relations hold

$$\lambda_0(A^\circ) = (0.2860)/E_0^{\frac{1}{2}} \cdot (E_0 \text{ in ev.})$$

$$2.256 = 2x \left(\frac{m}{M} \right)^{\frac{1}{2}} \times 4\pi^2 \times 0.007146 = \frac{4}{\pi}$$

$$9.162A^\circ = 2\pi \times \frac{4}{3} r_0 ; 6.478A^\circ = 2\pi \times \frac{2\sqrt{2}}{3} r_0 ; r_0 = 1.0936A^\circ$$

$$6.871A^\circ = 2\pi r_0$$

When indirect terms are omitted ($v \neq v'$)

$$\begin{aligned} \sigma_7^1 + \sigma_8^1 + \sigma_9^1 &= 2.256 \left[E_0/kT \right]^{\frac{1}{2}} \left(1/\lambda_0 \right) \left(Z^4/\phi^{\frac{1}{2}} \right) E_0 \phi \left\{ \right\} \\ \left\{ \right\} &= \left\{ 13.06 e^{-2.23E_0\phi} \int_1^1 \frac{e^{-2.37E_0\phi\mu^2} \left(4E_0/kT\phi \right) \left\{ \delta_H + 0.162/E_0 \right\}^2}{\alpha_H^{\frac{1}{2}} e^{-\left(4E_0/kT\phi \right) \left\{ \delta_C + 0.162/E_0 \right\}^2}} \times (0.115 + 3.547\mu^2) d\mu \right. \\ &\quad \left. + 0.0336 e^{-0.103E_0\phi} \right\} \end{aligned} \quad (33)$$

$$\sigma_2^1 + \sigma_3^1 = 2.256 \left[E_o/kT \right]^{\frac{1}{2}} \left(1/\lambda_o \right) \left(Z^4/\phi^{\frac{1}{2}} \right) E_o \phi \left\{ \right. \\ \left. \left\{ \right\} = \left\{ 17.41 e^{-2.23E_o \phi} \int_{-1}^1 \frac{e^{-2.37E_o \phi \mu^2} (4E_o/kT\phi)^{\frac{1}{2}} \left(\delta_H + 0.188/E_o \right)^2}{\alpha_H^{\frac{1}{2}} x (1-\mu^2)} d\mu \right\} \right\} \quad (34)$$

The following definitions hold in Eqs.(33) and (34)

$$0.0336 \text{ barns} = 0.41 \times 0.08282. \text{ (the } 0.08282 \text{ is from } f_{CC,7} + f_{CC,8} + f_{CC,9})$$

$$17.41 \text{ barns} = 13.06 \times 1.330. \text{ (the } 1.330 \text{ is from } f_{HH,2} + f_{HH,3})$$

6. The K.N. Equations for CH₄

The simplest K.N. approximation for σ^o corresponding to using the parameters in Eqs.(30) and (31) is found directly by using $\bar{\mu}^2 = \frac{1}{3}$ wherever μ^2 appears in Eqs.(32), (33) and (34). This leads to

$$\sigma^o = 2.256 \left[E_o/kT \right]^{\frac{1}{2}} \left(1/\lambda_o \right) \left(Z^4/\phi^{\frac{1}{2}} \right) \left\{ \right. \\ \left\{ \right\} = \left\{ 11.68 e^{-3.02E_o \phi} - \left[4/5 \right] \left[E_o/kT\phi \right] \left(\bar{\delta}_H \right)^2 \right. \\ \left. + 0.41 e^{-0.103E_o \phi} - \frac{4E_o \bar{\delta}_C^2}{kT\phi} \right. \\ \left. + 0.948 e^{-3.02E_o \phi} - \left[4/5 \right] \left[E_o \bar{\delta}_H^2/kT\phi \right] \frac{\sin \left[39.2(E_o \phi)^{\frac{1}{2}} \right]}{\left[39.2(E_o \phi)^{\frac{1}{2}} \right]} \right. \\ \left. - 1.075 e^{-1.56E_o \phi} \left[0.447 e^{-\left[4/5 \right] \left[E_o/kT\phi \right] \left(\bar{\delta}_H \right)^2} - \left(4E_o/kT\phi \right) \left(\bar{\delta}_H \right)^2 \right] \frac{\sin \left[24.2(E_o \phi)^{\frac{1}{2}} \right]}{\left[24.2(E_o \phi)^{\frac{1}{2}} \right]} \right\} \quad (35)$$

The following factors appear in Eq.(35)

$$11.68 \text{ barns} = 26.12/\sqrt{5} = 26.12/\bar{\alpha}_H^{\frac{1}{2}}$$

$$0.9472 \text{ barns} = 2.117/\sqrt{5}$$

$$0.4472 = 1/\sqrt{5}$$

$$24.2E_O^{\frac{1}{2}} = (2\pi r_O)/\lambda_O = (6.87E_O^{\frac{1}{2}})/0.2860$$

$$39.2E_O^{\frac{1}{2}} = (2\pi b_{HH'})/\lambda_O$$

$$b_{HH'} = (2 \pi/\sqrt{3})r_O$$

This same approximation gives for $\sigma_7^1 + \sigma_8^1 + \sigma_9^1$ and $\sigma_2^1 + \sigma_3^1$ the following results when terms in v & v' are omitted.

$$\begin{aligned} \sigma_7^1 + \sigma_8^1 + \sigma_9^1 &= 2.256 \left[E_O/kT \right]^{\frac{1}{2}} \left(1/\lambda_O \right) \left(Z^4/\Phi^{\frac{1}{2}} \right) E_O \Phi \\ &\times \left\{ 15.15 e^{-3.02E_O \Phi} e^{-\frac{4}{5} [E_O/kT\Phi] [\bar{\delta}_H + 0.162/E_O]^2} \right. \\ &\quad \left. + 0.0339 e^{-0.103E_O \Phi} e^{-\frac{4}{5} [E_O/kT\Phi] [\bar{\delta}_C + 0.162/E_O]^2} \right\} \quad (36) \end{aligned}$$

$$\begin{aligned} \sigma_2^1 + \sigma_3^1 &= 2.256 \left[E_O/kT \right]^{\frac{1}{2}} \left(1/\lambda_O \right) \left(Z^4/\Phi^{\frac{1}{2}} \right) E_O \Phi \\ &\times \left\{ 10.36 e^{-3.02E_O \Phi} e^{-\frac{4}{5} [E_O/kT\Phi] [\bar{\delta}_H + 0.188/E_O]^2} \right\} \quad (37) \end{aligned}$$

$$15.15 = 11.68 \times 1.297. \quad (\text{The } 1.297 \text{ comes from } \overline{(f_{HH,7} + f_{HH,8} + f_{HH,9})} = Q_{H,7})$$

$$10.36 = 11.68 \times 0.8866. \quad (\text{The } 0.8866 \text{ comes from } \overline{(f_{HH,2} + f_{HH,3})} = 2Q_{H2}/3)$$

The averaging procedure given by Eqs.(20) and (24) leads to

$$\begin{aligned} \sigma^0 &= 2.256 \left[E_0/kT \right]^{\frac{1}{2}} \left[1/\lambda_0 \right] \left[Z^4/\Phi^{\frac{1}{2}} \right] \\ &\times \left\{ 11.68 e^{-\frac{4}{5} [E_0/kT\Phi] [\bar{\delta}_H]^2} \times S_0(0.692E_0\Phi) S_0^2(1.33E_0\Phi) S_0^3(0.609E_0\Phi) \right. \\ &\quad \times S_0^3(1.297E_0\Phi) \\ &\quad + 0.41 e^{-\frac{4}{5} [E_0/kT\Phi] [\bar{\delta}_D]^2} \times S_0^3(0.020E_0\Phi) S_0^3(0.0828E_0\Phi) \quad (38) \\ &\quad + \frac{0.947 e^{-3.02E_0\Phi}}{x} \frac{e^{-\frac{4}{5} [E_0/kT\Phi] [\bar{\delta}_H]^2}}{x} \frac{\sin \left[\frac{39.2(E_0\Phi)^{\frac{1}{2}}}{[39.2(E_0\Phi)^{\frac{1}{2}}]} \right]}{[39.2(E_0\Phi)^{\frac{1}{2}}]} \\ &\quad \left. - 1.075 e^{-1.563E_0\Phi} \left[0.447 e^{-\frac{4}{5} [E_0/kT\Phi] [\bar{\delta}_H]^2} + e^{-\frac{4}{5} [E_0/kT\Phi] [\bar{\delta}_D]^2} \right] \frac{\sin \left[\frac{24.2(E_0\Phi)^{\frac{1}{2}}}{[24.2(E_0\Phi)^{\frac{1}{2}}]} \right]}{[24.2(E_0\Phi)^{\frac{1}{2}}]} \right\} \end{aligned}$$

In Eq.(38)

$$S_n(aE_0\Phi) = \left[1/n! \right] \sum_{j=0}^{\infty} (-1)^j \frac{(aE_0\Phi)^{j+n}}{j!(2j+2n+1)}$$

Eq.(37) has $n = 0$ in every case. Eqs. (39) and (40) which follow will use $n = 0$ and $n = 1$.

$$\begin{aligned}
\sigma_7^1 + \sigma_8^1 + \sigma_9^1 &= 2.256 \left[E_o/kT \right]^{\frac{1}{2}} \left[1/\lambda_o \right] \left[Z^4/\phi^{\frac{1}{2}} \right] \left\{ \right. \\
\left. \right\} &= \left\{ 34.89 e^{\frac{-[4E_o/5kT\phi][\bar{\delta}_H + 0.162/E_o]^2}{}} \times S_o(0.692E_o\phi) S_o^2(1.33E_o\phi) S_o^3(0.609E_o\phi) \right. \\
&\quad \times S_o^2(1.297E_o\phi) S_1(1.297E_o\phi) \\
&\quad \left. + 1.23 e^{\frac{-[4E_o/kT\phi][\bar{\delta}_C + 1.62/E_o]^2}{}} \times S_o^3(0.020E_o\phi) S_o^2(0.0828E_o\phi) S_1(0.0828E_o\phi) \right\} \\
&\quad (39)
\end{aligned}$$

$$\begin{aligned}
\sigma_2^1 + \sigma_3^1 &= 2.256 \left[E_o/kT \right]^{\frac{1}{2}} \left[1/\lambda_o \right] \left[Z^4/\phi^{\frac{1}{2}} \right] \left\{ \right. \\
\left. \right\} &= \left\{ 23.36 e^{\frac{-[4E_o/5kT\phi][\bar{\delta}_H + 0.188/E_o]^2}{}} \times S_o(0.692E_o\phi) S_o(1.33E_o\phi) S_1(1.33E_o\phi) \right. \\
&\quad \left. \times S_o^3(0.609E_o\phi) \times S_o^3(1.297E_o\phi) \right\} (40)
\end{aligned}$$

The following factors appear in Eqs.(39, 40)

$$34.89 = 3 \times 11.63$$

$$1.23 = 3 \times 0.41$$

$$23.36 = 2 \times 11.68$$

B. Results

The calculations were carried out on an IBM 650 computer. The dependence of σ on Z for a given E_0 and $\hat{p}_0 \cdot \hat{p}$ can be calculated about 50 times faster on the K.N. methods than on the more rigorous procedure which requires integration over μ . (In molecules of lower symmetry than CH_4 the Eulerian angle χ would appear as well as θ in the exponential of Eq.(4). This would further complicate the numerical work). The K.N. computations are fast enough so it is practical to calculate at small intervals in Z and $\hat{p}_0 \cdot \hat{p}$. It is then easy to carry out numerical integration over λ to get $\sigma(E_0, \hat{p}_0 \cdot \hat{p})$ and, subsequently, over $\hat{p}_0 \cdot \hat{p}$ to get $\sigma(E_0)$. Values of $\sigma(E_0)$ calculated in this way for CH_4 agree well with experimental data⁽²⁾.

Figs. 1 and 2 compare σ^0 calculated from Eqs.(32), (35) and (38) for incident neutrons of 0.015 and 0.10 ev energy and scattering angles of 16.3, 84.7 and 163.7°. Fig.3 gives a similar comparison for 0.306 ev neutrons and shows the separate contributions σ^0 , $\sigma_7^1 + \sigma_8^1 + \sigma_9^1$ and $\sigma_2^1 + \sigma_3^1$ which are associated with no vibrational excitation, excitation of any one of the triply degenerate modes of 0.162 ev energy, and excitation of either of the doubly degenerate modes of 0.188 ev energy, respectively.*

The contribution of the direct scattering by carbon to σ^0 is the same in the exact** and both K.N. methods and this contribution is shown in Figs. 1,2 and 3. Carbon scattering contributes very little to the vibrational scattering cross sections $\sigma_7^1 + \sigma_8^1 + \sigma_9^1$ and $\sigma_2^1 + \sigma_3^1$ in Fig. 3.

The following conclusions can be drawn from an examination of Figs. 1,2 and 3.

1. All three methods predict the maxima of the $\sigma(E_0, \lambda, \hat{p}_0 \cdot \hat{p})$ vs. Z curves to come at about the same Z values at all energies and angles. These maxima agree most closely at the lower energies E_0 . For the forward angle the agreement is quite good on all methods, and for all energies, since there is then little energy transfer and the maximum is always near $Z = 1$.

2. At 0.1 ev and below there are small differences of up to 10% between the K.N. and exact methods when Z is near the maximum. At 0.015 ev for all three angles the K.N. methods are low when Z is less than that for the maximum, and high when Z is higher. At 0.1 ev the K.N. method is close for Z away from the maximum, but falls below at the maximum. These effects are such that integration to give $\sigma(E_0, \hat{p}_0 \cdot \hat{p})$ could give a result close to that for the exact method.

* The meanings and notations for the total cross section σ and the partial cross sections σ^0 , σ_7^1 etc. are defined in connection with Eq.(1) on p. 3.

** See footnote on p. 2.

3. The discrepancies in magnitudes are much larger at 0.306 ev and increase as the scattering angle increases. At the high angles the exact σ^0 result is lower than either of the K.N. methods at all angles. The simplest K.N. procedure is closer to the exact result than the more elaborate one.

At the forward angle the vibrational terms are negligible but their contribution is significant at the higher angles, particularly at 163.7° . Here the exact method gives higher peak values for $\sigma_7^1 + \sigma_8^1 + \sigma_9^1$ and $\sigma_2^1 + \sigma_3^1$ than do the K.N. methods. Thus the net discrepancies between the K.N. and exact methods is reduced when the σ^0 and $\sigma_7^1 + \sigma_8^1 + \sigma_9^1$ and $\sigma_2^1 + \sigma_3^1$ terms are added. Under any circumstances the cross sections for scattering to backward angles are small relative to those for forward scattering.

4. The simplest K.N. method is about as close, or is distinctly closer, to the exact result than the more elaborate procedure based on Eq.(21). Hence nothing is to be gained by using the more elaborate K.N. method.

5. The direct scattering from carbon, which is calculated in the same way on all three methods, contributes significantly only to σ^0 . It becomes relatively more important as E_0 increases, and has the highest relative importance at the backward scattering angle. While it is practically negligible at 0.015 ev it is significant at 0.1 ev for the higher scattering angles. At 0.306 ev it is important at all but the smallest scattering angle. Therefore, in making calculations it is generally wise to include it at all energies in calculating σ^0 .

In addition to the conclusions based on Figs. 1, 2, and 3 an examination of the calculated results shows

1. The contributions of the interference terms ($v \neq v'$) decreases with increasing energy E_0 . In CH_4 they will be negligible for energies E_0 capable of exciting vibrations. Their contributions are greatest near the maxima of the σ vs. Z curves. However, they never contribute more than about 5% of the total. Sometimes their contribution is negative and at 0.015 ev it sometimes overrides the direct scattering from the carbon.

FIG. 1 Calculated total differential cross-section of CH_4 for 0.015 eV neutrons. Vibrations do not contribute. See Table I.

FIG. 2 Calculated total differential cross-section of CH_4 for 0.10 eV neutrons. Vibrations do not contribute. See Table I.

FIG. 3A Calculated partial differential cross-section σ^0 of CH_4 for 0.306 eV neutrons. Vibrational transitions are excluded from σ^0 . See Eq. I & Table I.

FIG. 3B Calculated partial differential cross-sections associated with lowest energy vibrational transitions in CH_4 for 0.306 eV neutrons. See Eq. I & Table I. Note: Scales are magnified over those in Figs. 3A & 3C.

FIG. 3C Calculated total differential cross-section of CH_4 for 0.306 eV neutrons.

In view of their relatively small contribution it is safe to omit interference terms in calculations on hydrocarbons except possible where unsaturation is large (low H/C ratio) so that carbon scattering is emphasized, or if a very exact result is needed.

2. The carbon contributes very little to the vibrational terms $\sigma_7^1 + \sigma_8^1 + \sigma_9^1$ and $\sigma_2^1 + \sigma_3^1$. It is only about 3% at 163.7° and is entirely negligible at the forward angles.

3. The peak scattering cross sections $\sigma_7^1 + \sigma_8^1 + \sigma_9^1$ and $\sigma_2^1 + \sigma_3^1$ decrease with increasing scattering angle, although not as sharply as σ^0 . Thus for the 0.306 ev neutrons the peak magnitudes at 16.3° , 84.7° and 163.7° are 6, 2.5 and 0.5 barns for steradian per angstrom as compared to peak σ^0 values of 600, 13.5 and 1.1 .

IV DISCUSSION

A. Results on CH₄

The K.N. method is accurate at low energies partly because the factor in the exponential of the vibrational expectation $\langle \chi_{vv'v} \rangle_T$ (Eqs.(4), (13)) is then small so that this expectation is near unity. Under these conditions different ways of averaging over orientation will not influence the result significantly.

The expansion of each factor in the vibrational expectation followed by averaging each term in the series separately (cf Eq.(21)) fails to give improved results at higher energies E_0 possibly because it is incorrect to assume that averages over orientation of the separate vibrational factors can be carried out independently. Thus, both of the Eulerian angles θ and χ generally appear in each term of the series in the exponent of Eq.(4) for the vibrational expectation. Any approximations like those in Eqs.(12) and (13), or the more elaborate expansion leading to Eq.(21) are quite artificial and can be expected to break down when E_0 is high enough so that the exponent in Eq.(4) is large.

The fact that the scattering from the carbon increases relative to that from the hydrogens as E_0 increases, and at high E_0 becomes relatively very important at the backward scattering angle, stems from several sources. First, high energy neutrons colliding with protons must transfer large amounts of energy if the simultaneous requirements of conservation of momentum and energy are to be met. The probability of such transfers turns out to be small since the cross section expression involves, among other quantities, a factor $Z^4 = (E/E_0)^2$ which is very small for large energy losses by the neutron. This effect is much less pronounced for impacts on carbon where the neutron sees a mass of 16 and momentum can be conserved with relatively small energy transfers. Second, a neutron moving with energy much larger than kT is scattered preferentially in the forward direction. The smaller the effective mass of the atom it strikes the greater is this anisotropy. Thus at high E_0 scattering from the hydrogens with

effective mass of $3.2 m_n$ is relatively weak in the backward directions, while it is quite isotropic for scattering from the carbon which has an effective mass of $16 m_n$. The hydrogens are more efficient in transferring energy to the vibrational modes since impacts of high energy neutrons on hydrogens favor large energy transfers such as are required to excite vibrations. Also the expressions for these contributions to σ involve the amplitudes of the motions of the atoms in such a way as to make the contributions of the atoms with the large amplitude important. The hydrogens have much larger amplitudes than the carbon in all modes in CH_4 .

B. Relation to Scattering in Other Hydrocarbons

The heavier hydrocarbon gases like propane and the butane will have larger effective masses for their protons than is true in CH_4 . This will make the σ^0 vs. Z curves more peaked and the maxima will come closer to $Z = 1$ for all energies and scattering angles. The dependence of σ^0 on scattering angle will be more isotropic at all energies.

Partial cross sections associated with vibrational excitations will also show sharper peaks when plotted against Z . These will come near values of $Z = \left(E_0 - \sum_l \frac{E_l}{E_0} \right)^{1/2} / E_0^{1/2}$; ie near those values of Z associated with the changes in vibrational energy. The excitations will be induced largely by collisions with hydrogens. The large molecules will have vibrational frequencies with energies around kT . Since transfers involving changes in translational and rotational energies will involve small energy changes it is possible that the excitations and de-excitations of vibrational modes will be important in determining the average energy transfer per collision. However, in large hydrocarbon molecules these low frequency modes involve rotational and translational motions of groups of atoms (like CH_3 , CH_2) and the probability for these energy transfers may be small just as they are in CH_4 for neutrons striking the carbon which has a large effective mass. Calculations now in progress on propane may throw light on the efficiency with which low frequency vibrations in hydrocarbons can be excited by neutrons.

Calculations which assume a harmonic force law for the vibrations may be too crude for excitation of low frequencies by high energy neutrons. The calculated results may be low because the density of states available to high energy transitions will be larger than is involved in a calculation based on a harmonic potential.

In liquid and solid hydrocarbons there will be no rotational degrees of freedom, but there will be energy changes associated with changes of configuration which can be achieved by rotations about C-C bonds. It is possible that energy transfers associated with changes of configuration will become important.

V REFERENCES

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APPENDIX

Derivation of Normal Coordinates and Associated Quantities

Pope⁽⁴⁾ has derived a set of normal coordinates for CH_4 which can be used to compute the elements in the $T_{v\ell}$ matrices. Once these are obtained the $\langle X_{vv';v} \rangle_T$, $f_{vv';\ell}$, etc. may be calculated.

Pope's normal coordinates are in terms of the axes shown in Fig. A-1 while the $\langle X_{vv';v} \rangle_T$ etc. have their simplest forms in terms of the axes in Fig. A-2.

Fig.A-1. Pope's Axes

Fig.A-2. Present Axes

Therefore, it is necessary to transform the normal coordinates as given by Pope in terms of the axes in Fig.A-1 so they are in terms of the axes in Fig.A-2. The procedure can be systematized as follows.

Define

$$\begin{bmatrix} q'_v \end{bmatrix} = \sqrt{m_v} \begin{bmatrix} \Delta x'_v \\ \Delta y'_v \\ \Delta z'_v \end{bmatrix}$$

A - 1

$$[q_v] = \sqrt{m_v} \begin{bmatrix} \Delta x_v \\ \Delta y_v \\ \Delta z_v \end{bmatrix} \quad A - 2$$

where $\Delta x_v'$ etc. are displacements of atom v relative to the axes in Fig. A-1 and Δx_v etc. are displacements relative to axes in Fig. A-2.

Furthermore, define

$$[Q] = \begin{bmatrix} Q_1 \\ Q_2 \\ - \\ Q_9 \end{bmatrix}; [q'] = \begin{bmatrix} q'_C \\ q'_1 \\ - \\ q'_4 \end{bmatrix}; [q] = \begin{bmatrix} q_C \\ q_1 \\ - \\ q_4 \end{bmatrix} \quad A - 3$$

The elements in $[Q]$ are the normal coordinates. The elements in $[q']$ and $[q]$ are defined in Eqs. A - 1 and A - 2 with subscripts 1,2,3,4 referring to the H atoms and C to the carbon.

The column matrices $[Q]$ and $[q']$ are related by the equation

$$[Q] = \tilde{B} [q'] \quad A - 4$$

The elements in $\tilde{B}$ are those in Table III of Pope's article (4). This table is reproduced in Table A-I in such a form that applications to CD_4 are also possible. The $\tilde{B}$ has 9 rows and 15 columns and the rows are orthogonal to each other and are normalized.

To find the transformation from Q to q the relation of q to q' is needed. This is given in terms of the axes in Figs. A-1 and A-2 by

$$[q] = S [q'] = \begin{bmatrix} S_1 & 0 & 0 & 0 & 0 \\ 0 & S_1 & 0 & 0 & 0 \\ - & - & - & - & - \\ 0 & 0 & 0 & 0 & S_1 \end{bmatrix} \begin{bmatrix} q'_C \\ q'_1 \\ - \\ q'_4 \end{bmatrix} \quad A - 5$$

where

$$S_1 = \begin{bmatrix} \frac{-1}{\sqrt{6}} & \frac{-1}{\sqrt{6}} & \frac{2}{\sqrt{6}} \\ \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \end{bmatrix} \quad A - 6$$

then

$$[Q] = \tilde{BS}[q] \quad A - 7$$

The matrix $\tilde{BS}$ is rectangular (9 rows, 15 columns). However, when the six equations are added which express the fact that the vibrational motions exhibit no linear or angular momenta relative to the molecular axes the result is a 15 x 15 orthogonal transformation⁽⁵⁾:

$$\begin{bmatrix} Q \\ 0 \end{bmatrix} = \begin{bmatrix} \tilde{BS} \\ \tilde{C} \end{bmatrix} [q] \quad A - 8$$

The result is

$$[q] = SB [Q] \quad A - 9$$

since

$$[q] = \left[\begin{array}{ccccc|c} \sqrt{m_C} & 0 & 0 & 0 & 0 & \Delta \vec{r}_C \\ 0 & \sqrt{m_P} & 0 & 0 & 0 & \Delta \vec{r}_1 \\ 0 & 0 & 0 & 0 & \sqrt{m_P} & \Delta \vec{r}_4 \end{array} \right] \quad A - 10$$

where

$$\Delta r_v = \begin{bmatrix} \Delta x_v \\ \Delta y_v \\ \Delta z_v \end{bmatrix}$$

the result for $[\Delta r]$ is

$$[\Delta r] = \begin{bmatrix} \frac{S_1 B_{C1}}{\sqrt{m_C}} & \frac{S_1 B_{C2}}{\sqrt{m_C}} & \dots & \frac{S_1 B_{C9}}{\sqrt{m_C}} \\ \frac{S_1 B_{11}}{\sqrt{m_p}} & \dots & \dots & \frac{S_1 B_{19}}{\sqrt{m_p}} \\ \dots & \dots & \dots & \dots \\ \frac{S_1 B_{41}}{\sqrt{m_p}} & \dots & \dots & \frac{S_1 B_{49}}{\sqrt{m_p}} \end{bmatrix} [Q] \quad A - 11$$

This yields

$$T_{v\ell} = \frac{S_1 B_{v\ell}}{\sqrt{m_v}} \quad A - 12$$

The $B_{v\ell}$ are three element column matrices which are found from the rows in Table A-1. Because of the equivalence of the hydrogens and the hydrogen pairs only the matrices with $v = 1, 2$, and C are needed in the present calculations.

These are:

$$[T_{11}] = \frac{1}{2\sqrt{m_p}} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} ;$$

$$[T_{21}] = \frac{1}{6\sqrt{m_p}} \begin{bmatrix} 2\sqrt{2} \\ 0 \\ -1 \end{bmatrix} ; [T_{C1}] = [0]$$

$$[T_{12}] = \frac{1}{2\sqrt{m_p}} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} ;$$

$$[T_{22}] = \frac{1}{2\sqrt{m_p}} \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix} ; [T_{C2}] = [0]$$

$$[T_{13}] = \frac{1}{2\sqrt{m_p}} \begin{bmatrix} -1 \\ 0 \\ 0 \end{bmatrix} ;$$

$$[T_{23}] = \frac{1}{6\sqrt{m_p}} \begin{bmatrix} -1 \\ 0 \\ 2\sqrt{2} \end{bmatrix} ; [T_{C3}] = [0]$$

$$[T_{14}] = \frac{1}{N_{iii}\sqrt{6m_p}} \begin{bmatrix} -(L - S_{iii}) \\ \sqrt{3}(L - S_{iii}) \\ \sqrt{2}(L + 2S_{iii}) \end{bmatrix} ; [T_{24}] = \frac{1}{N_{iii}\sqrt{6m_p}} \begin{bmatrix} -(L + 3S_{iii}) \\ \sqrt{3}(L - S_{iii}) \\ \sqrt{2}L \end{bmatrix} ; [T_{C4}] = \frac{N}{N_{iii}\sqrt{6m_c}} \begin{bmatrix} -1 \\ \sqrt{3} \\ \sqrt{2} \end{bmatrix}$$

$$[T_{15}] = \frac{1}{N_{iii}\sqrt{6m_p}} \begin{bmatrix} -(L - S_{iii}) \\ -\sqrt{3}(L - S_{iii}) \\ \sqrt{2}(L + 2S_{iii}) \end{bmatrix} ; [T_{25}] = \frac{1}{N_{iii}\sqrt{6m_p}} \begin{bmatrix} -(L + 3S_{iii}) \\ -\sqrt{3}(L - S_{iii}) \\ \sqrt{2}L \end{bmatrix} ; [T_{C5}] = \frac{N}{N_{iii}\sqrt{6m_c}} \begin{bmatrix} -1 \\ -\sqrt{3} \\ \sqrt{2} \end{bmatrix}$$

$$[T_{16}] = \frac{1}{N_{iii}\sqrt{6m_p}} \begin{bmatrix} 2(L - S_{iii}) \\ 0 \\ \sqrt{2}(L + 2S_{iii}) \end{bmatrix} ; [T_{26}] = \frac{1}{N_{iii}\sqrt{6m_p}} \begin{bmatrix} 2(L + S_{iii}) \\ 0 \\ \sqrt{2}(L - 2S_{iii}) \end{bmatrix} ; [T_{C6}] = \frac{1}{N_{iii}\sqrt{6m_c}} \begin{bmatrix} 2 \\ 0 \\ \sqrt{2} \end{bmatrix}$$

$$[T_{17}] , [T_{18}] , [T_{19}] , [T_{27}] , [T_{28}] , [T_{29}] , [T_{c7}] , [T_{c8}] , [T_{c9}]$$

are obtained from the corresponding quantities $[T_{14}] , [T_{15}] , [T_{16}] , \dots , [T_{c6}]$ by replacing S_{iii} by S_{iv} and N_{iii} by N_{iv} . The quantities L , S_{iii} , S_{iv} , N_{III} and N given for CH_4 by Pope as

$$L = -\frac{m_c}{4m_p + m_C} ; S_{iii} = 0.8187 ; S_{iv} = -0.4553$$

$$L = -0.75 ; N_{iii} = \left[\frac{4m_C}{4m_p + m_C} + 8(0.8187)^2 \right]^{\frac{1}{2}} = (8.3622)^{\frac{1}{2}}$$

$$N_{iv} = \left[\frac{4m_C}{4m_p + m_C} + 8(0.4553)^2 \right]^{\frac{1}{2}} = (4.6584)^{\frac{1}{2}}$$

$$N \equiv M \text{ of Pope} = \frac{4\sqrt{m_p m_C}}{4m_p + m_C} = \frac{\sqrt{3}}{2}$$

In using these relations to compute the quantities in Eqs.(4), (9) for CH_4 it is useful to use the relation

$$\left([\tilde{A}_Z][T_{v\ell}] \right) \left([\tilde{A}_Z][T_{v'\ell}] \right) = [\tilde{T}_{v\ell}][A_Z][\tilde{A}_Z][T_{v'\ell}] = [\tilde{T}_{v\ell}] \alpha [T_{v'\ell}] \quad A - 13$$

$$\alpha = [A_Z][\tilde{A}_Z] = \begin{bmatrix} \sin^2 \theta \cos^2 X & -\sin^2 \theta \sin X \cos X & -\sin \theta \cos \theta \cos X \\ -\sin^2 \theta \sin X \cos X & \sin^2 \theta \sin^2 X & \sin \theta \cos \theta \sin X \\ -\sin \theta \cos \theta \cos X & \sin \theta \cos \theta \sin X & \cos^2 \theta \end{bmatrix}$$

A - 14

Using this procedure the expressions for $\langle x_{HH,v}^o \rangle_T \equiv \langle x_{11,v}^o \rangle_T$;

$$\langle x_{HH,v}^o \rangle_T \equiv \langle x_{12,v}^o \rangle_T ; \langle x_{CC,v}^o \rangle_T ; \langle x_{CH,v}^o \rangle_T \equiv \langle x_{Cl,v}^o \rangle_T$$

$\langle x_{HC,v}^o \rangle_T \equiv \langle x_{1C,v}^o \rangle_T$ were derived, as well as the expression for

$$f_{HH,\ell} \equiv f_{11,\ell} , \text{ etc.}$$

Table A-1

Pope's Normal Coordinate Transformation for CH₄ and CD₄

$\bar{h}\omega$		Mode (i)	N_i^2	B_C			B_1			B_2			B_3			B_4		
CH ₄	CD ₄																	
0.361	0.259	1	12	0	0	0	1	1	1	-1	-1	1	-1	1	-1	1	-1	-1
0.188	0.135	2	8	0	0	0	1	-1	0	-1	1	0	-1	-1	0	1	1	0
		3	24	0	0	0	1	1	-2	-1	-1	-2	-1	1	2	1	-1	2
0.374	0.280	4	N_{iii}^2	N	0	0	L	S_{iii}	S_{iii}	L	S_{iii}	$-S_{iii}$	L	$-S_{iii}$	S_{iii}	L	$-S_{iii}$	$-S_{iii}$
		5	N_{iii}^2	0	N	0	S_{iii}	L	S_{iii}	S_{iii}	L	$-S_{iii}$	$-S_{iii}$	L	$-S_{iii}$	$-S_{iii}$	L	S_{iii}
		6	N_{iii}^2	0	0	N	S_{iii}	S_{iii}	L	$-S_{iii}$	$-S_{iii}$	L	S_{iii}	$-S_{iii}$	L	$-S_{iii}$	S_{iii}	L
0.162	0.123	7	N_{iv}^2	N	0	0	L	S_{iv}	S_{iv}	L	S_{iv}	$-S_{iv}$	L	$-S_{iv}$	S_{iv}	L	$-S_{iv}$	$-S_{iv}$
		8	N_{iv}^2	0	N	0	S_{iv}	L	S_{iv}	S_{iv}	L	$-S_{iv}$	$-S_{iv}$	L	$-S_{iv}$	$-S_{iv}$	L	S_{iv}
		9	N_{iv}^2	0	0	N	S_{iv}	S_{iv}	L	$-S_{iv}$	$-S_{iv}$	L	S_{iv}	$-S_{iv}$	L	$-S_{iv}$	S_{iv}	L

$$N_{iii}^2 = \left[\frac{4m_C}{4m+m_C} + 8S_{iii}^2 \right]; N_{iv}^2 = \left[\frac{4m_C}{4m+m_C} + 8S_{iv}^2 \right]; N = \frac{4\sqrt{mm_C}}{4m+m_C}; L = \frac{-m_C}{4m+m_C}$$

$\frac{1}{N_i}$ is a normalizing factor; $S_{iii} = 0.8187$; $S_{iv} = -0.4553$ for CH₄
 $S_{iii} = 0.6244$; $S_{iv} = -0.4805$ for CD₄
 The $\bar{h}\omega$ data for CH₄ are as given by Pope. Data for CD₄ are from J. K. Wilmshurst
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