

Influence of Rotational Levels on Slow-Neutron Scattering by Linear Gases*

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Calculations of slow-neutron partial differential scattering cross sections are reported for molecules with linear symmetry in which the quantum-mechanical nature of the rotational levels is taken explicitly into account. The method used is an extension of Griffing's results to nonspherical molecules. The calculations for HF, HCl, N₂, and HCN gases are compared to calculations based on the Krieger-Nelkin approximation, and the failure of the latter method to account correctly for rotational-energy transfers is pointed out.

INTRODUCTION

SLOW-neutron scattering by molecular gases has proved to be a useful tool in the study of molecular dynamics. In this context, theoretical calculations of the cross section for the scattering of neutrons by rotating molecules have become important. Exact calculations are not yet tractable, even with present digital computers, except in special cases. The early Sachs-Teller mass tensor concept¹ provided an approximation of the total cross section for rotating molecules. Krieger and Nelkin² applied this same idea within the exact Zemach and Glauber formalism³ and made a further approximation involving an average over orientations of the molecules. Although it has been well understood that both these treatments are approximations which do not take into account the details of the rotational motion (i.e., the discrete nature of the energy levels), their simplicity and their surprising success, even in regions where agreement is not expected, have led many authors⁴ to utilize these approximations in order to compare with experiment.

Improved measurements of the partial differential cross sections demonstrated the need for a better theory and a better understanding of when the Krieger-Nelkin (hereafter KN) and mass tensor theories can be applied. An essentially exact theory has become available which considers the quantum-mechanical nature of rotations.^{5,6} Unfortunately, calculations based on this theory are practical only for a limited number of molecules, those with spherical symmetry and those with linear symmetry. Since the exact theory is restricted to so few molecules, there has been a great deal of interest in recent years⁷⁻⁹ in trying to under-

stand and possibly improve the approximate theories as far as possible.

Using the quantum-mechanical theory, numerical calculations of the partial differential cross section for spherically symmetric molecules were first reported by Griffing.¹⁰ His calculations were for methane and excellent agreement was found with experiment. Calculations of the cross section for the second class of molecules, those with linear symmetry, are reported here.¹¹

ANALYTICAL EXPRESSION FOR THE CROSS SECTION

It is desired to obtain an expression for the partial differential scattering cross section for slow neutrons scattering from a gas of rigid linear molecules undergoing translation of the center of mass and free rotation. The problem is as follows: A neutron of momentum \mathbf{k}_i undergoes a collision with a molecule which is in the initial state Ψ_i having a total molecular energy E_i . In the Fermi pseudopotential approximation, the expression for the partial differential cross section for scattering with momentum gain $\mathbf{\kappa}$ to the neutron and energy gain ϵ while the molecule undergoes a transition from initial state Ψ_i to final state Ψ_f has been given by Zemach and Glauber³ as¹²

$$\frac{\partial^2 \sigma}{\partial \epsilon \partial \Omega} = \frac{k_f}{k_i} \frac{1}{2\pi N} \int_{-\infty}^{\infty} dt \exp(-i\epsilon t) \sum_{\nu\nu'} \langle \chi_{\nu\nu'} \rangle_T, \quad (1)$$

where \mathbf{k}_i and \mathbf{k}_f are the initial and final wave vectors of the neutron, and N is the number of molecules in the system. The intermediate scattering function is summed over all final states and the thermal average is taken over all initial states. Thus

$$\langle \chi_{\nu\nu'} \rangle_T = \sum_{f,i} P_i a_{\nu\nu'} \langle \Psi_i | \exp(iHt) \exp(i\mathbf{\kappa} \cdot \mathbf{r}_\nu) | \Psi_f \rangle \times \langle \Psi_f | \exp(-iHt) \exp(-i\mathbf{\kappa} \cdot \mathbf{r}_{\nu'}) | \Psi_i \rangle, \quad (2)$$

with $a_{\nu\nu'} = A_\nu A_{\nu'} + \delta_{\nu\nu'} C_\nu C_{\nu'}$, and where H is the Hamil-

¹⁰ G. W. Griffing, *Inelastic Scattering Neutrons Solids Liquids*, Proc. Symp. Chalk River, Can. 1962, I, 435 (1963).

¹¹ Calculations for the special cases of hydrogen and deuterium have been reported by J. A. Young and J. U. Koppel, *Phys. Rev.* **135**, A603 (1964).

¹² Note that t is in units of reciprocal energy so that $\hbar = 1$.

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¹ R. G. Sachs and E. Teller, *Phys. Rev.* **60**, 18 (1941).

² T. J. Krieger and M. S. Nelkin, *Phys. Rev.* **106**, 290 (1957).

³ A. C. Zemach and R. J. Glauber, *Phys. Rev.* **101**, 118 (1956).

⁴ See, for example, the review by J. A. Janik and A. Kowalska in *Thermal Neutron Scattering*, P. A. Egelstaff, Ed. (Academic Press Inc., New York, 1965).

⁵ A. Rahman, *J. Nucl. Energy* **13**, 128 (1961).

⁶ S. Yip, thesis, University of Michigan, 1962 (unpublished).

⁷ G. Kosály and G. Solt, *Phys. Letters* **6**, 51 (1963); **13**, 223 (1964); *Physica* **32**, 16 (1966).

⁸ L. J. Gannon and H. L. McMurry, U.S. Atomic Energy Commission Rept. IDO-17087, 1965 (unpublished).

⁹ P. Dzyub, *Soviet Physics—JETP* **22**, 347 (1966) [*Zh. Eksperim. i Teor. Fiz.* **49**, 493 (1965)].

tonian of the system. A , is the bound coherent scattering length and C , is the bound incoherent length of the ν th atom whose position is \mathbf{r}_ν , and P_i is the Boltzmann statistical weighting factor applied to the initial states. By removing the scattering length from the expectation value we have also ignored the effects of spin.

The intermediate scattering function can include effects of neutron interaction with all possible degrees of freedom of the molecular system. Here we choose to allow only two possible motions in the system, translation of the center of mass and free rotation. Furthermore, in a dilute gas these motions are independent and can be separated, and $H = H_T + H_R$. We also make the separation $\mathbf{r}_\nu = \mathbf{R} + \mathbf{b}_\nu$, where \mathbf{R} is the position of the center of mass and \mathbf{b}_ν is the displacement of the ν th nucleus from the center of mass. As

a result of the commutability of all the operators, the scattering function can be written as a product

$$\langle \chi_{\nu\nu'} \rangle_T = a_{\nu\nu'} \langle \chi_{\nu\nu'} \rangle_T^{\text{trans}} \langle \chi_{\nu\nu'} \rangle_T^{\text{rot}}. \quad (3)$$

The thermal average of the expectation value of the translational mode has been evaluated by Zemach and Glauber, with the following result:

$$\langle \chi_{\nu\nu'} \rangle_T^{\text{trans}} = \exp[(-i\mathbf{k}^2/2M) - (\ell^2 k_B T \mathbf{k}^2/2M)] \quad (4)$$

where M is the mass of the molecule, k_B is Boltzmann's constant, and T is the gas temperature. Note that the thermal average for the translation mode is independent of nuclear subscript. This is a result of neglecting the so-called "outer" scattering, or interference scattering between different molecules.

Let us now consider the rotational factor. It is necessary to perform the sum over final states and average over initial states. For this case, it is more convenient to perform the average first over initial states, and put off the summation over final states until later. The method used here follows the treatment of Yip.⁶

Since we are interested in linear molecules, we can make use of the Hamiltonian and wavefunctions for the linear rigid rotator with its center of mass fixed in space. Let L denote the rotator's angular momentum, and I the moment of inertia. Then

$$H_R = L^2/2I. \quad (5)$$

The wavefunctions are simply the spherical harmonics, and the corresponding energy eigenvalues are $E_J = B^J(J+1)$, where B is the rotational constant, $B = 1/(2I)$. The degeneracy for this system with only two degrees of freedom is $2J+1$. The appropriate thermal average to be evaluated is then

$$\begin{aligned} \langle \chi_{\nu\nu'} \rangle_T^{\text{rot}} &= \sum_{JM} P_{JM} \sum_{J'M'} \Gamma \exp[i\ell(E_J - E_{J'})] \\ &\times \langle JM | \exp(i\boldsymbol{\kappa} \cdot \mathbf{b}_\nu) | J'M' \rangle \\ &\times \langle J'M' | \exp(-i\boldsymbol{\kappa} \cdot \mathbf{b}_{\nu'}) | JM \rangle, \quad (6) \end{aligned}$$

where

$$P_{JM} = \frac{\exp(-E_J/k_B T)}{\sum_J (2J+1) \exp(-E_J/k_B T)}.$$

Note that $\boldsymbol{\kappa}$ is measured in the space-fixed system of axes, whereas \mathbf{b} is most conveniently expressed in terms of the molecular coordinates.

The above matrix elements are evaluated by a somewhat involved but otherwise straightforward calculation similar to that of Ref. 5, which is merely outlined here. The plane waves $\exp(i\boldsymbol{\kappa} \cdot \mathbf{b}_\nu)$ are expanded in spherical harmonics. Assuming the direction of $\boldsymbol{\kappa}$ along the space Z axis, and introducing the rotation matrices,

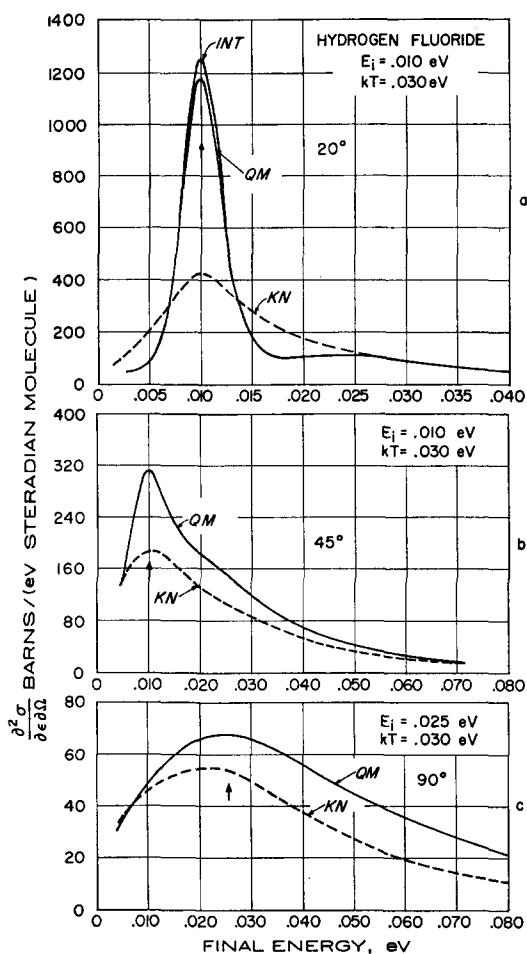


FIG. 1. Partial differential cross section for HF gas at 0.030 eV (348°K) as a function of final neutron energy. Dashed curve is the Krieger-Nelkin calculation (labeled KN), the smooth curve (labeled QM) is the quantum-mechanical calculation, and the curve labeled INT is the quantum-mechanical calculation with interference included. (a) Incident energy 0.010 eV and scattering angle 20°; (b) incident neutron energy 0.010 eV and scattering angle 45°; (c) incident neutron energy 0.025 eV and scattering angle 90°. The small arrow indicates the incident energy.

D_{0,k^l} , of Rose¹³ which are functions of molecular orientation angles

$$\exp(i\mathbf{k} \cdot \mathbf{b}_\nu) = \sum_{l=0}^{\infty} \sum_{k=-l}^l i^l [4\pi(2l+1)]^{1/2} j_l(\kappa b_\nu) Y_l^{k*}(\hat{\mathbf{b}}') D_{0,k^l}. \quad (7)$$

The wavefunctions are expressed in terms of the D 's, and the resulting integral is a product of three rotation matrices which can be evaluated making use of the symmetry and orthogonality relations of the rotation matrices.¹⁸

One of the resulting matrix elements is

$$\langle JM | \exp(i\mathbf{k} \cdot \mathbf{b}_\nu) | J'M' \rangle = \sum_{l=0}^{\infty} i^l j_l(\kappa b_\nu) \left[\frac{4\pi(2l+1)(2J+1)}{2J'+1} \right]^{1/2} (-1)^{M+M'} Y_l^{0*}(\hat{\mathbf{b}}_\nu) C_{M0}^{J1J'} C_{00}^{J1J'} \delta_{MM'}, \quad (8)$$

where the C 's are the Clebsch-Gordan coefficients. Using Eq. (8) in (6), and applying the closure relation for the C 's, we have for the thermal average of the intermediate scattering function for rotations,

$$\begin{aligned} \langle \chi_{\nu\nu'} \rangle_T^{\text{rot}} = & \left[\sum_J (2J+1) \exp(-\beta E_J) \right]^{-1} \sum_J (2J+1) \exp(-\beta E_J) \sum_{J'} \exp[i\ell(E_J - E_{J'})] \\ & \times \sum_{l=|J-J'|}^{J+J'} (2l+1) (\hat{\mathbf{b}}_{\nu'} \cdot \hat{\mathbf{b}}_{\nu'})^l j_l(\kappa b_\nu) j_l(\kappa b_{\nu'}) (C_{00}^{J1J'})^2, \quad (9) \end{aligned}$$

where $\beta = 1/k_B T$. Note that the l sum is restricted by the Clebsch-Gordan coefficients.

We are now in a position to write down the cross section. For direct scattering, using Eqs. (1), (3), (4), and (9) with $\nu = \nu'$,

$$\begin{aligned} \left(\frac{\partial^2 \sigma}{\partial \epsilon \partial \Omega} \right)^{\text{direct}} = & \sum_{\nu} a_{\nu\nu} \eta_{\nu} \frac{k_f}{k_i} \frac{(4\pi E_R/\beta)^{-1}}{\sum_J (2J+1) \exp(-\beta E_J)} \sum_J (2J+1) \exp(-\beta E_J) \\ & \times \sum_{J'} \exp \left[- \frac{(\epsilon + E_{J'} - E_J + E_R)^2 \beta}{4E_R} \right] \sum_l (2l+1) j_l^2(\kappa b_\nu) (C_{00}^{J1J'})^2, \quad (10) \end{aligned}$$

where $E_R = \kappa^2/2M$, and the sum over ν is now over distinct types of atoms. The number η_{ν} is the ratio of the number of atoms of the type¹⁴ ν in the system to the number of molecules (N) in the system; i.e., it is the number of ν -type atoms in each molecule.

The cross section for interference is easily obtained by considering the thermal average of the intermediate scattering function for $\nu \neq \nu'$

$$\begin{aligned} \left(\frac{\partial^2 \sigma}{\partial \epsilon \partial \Omega} \right)^{\text{int}} = & \sum_{\nu \neq \nu'} a_{\nu\nu'} \eta_{\nu\nu'} \frac{k_f}{k_i} \frac{(4\pi E_R/\beta)^{-1}}{\sum_J (2J+1) \exp(-\beta E_J)} \sum_J (2J+1) \exp(-\beta E_J) \sum_{J'} \exp \left[- \frac{(\epsilon + E_{J'} - E_J + E_R)^2 \beta}{4E_R} \right] \\ & \times \sum_l (2l+1) (\hat{\mathbf{b}}_{\nu'} \cdot \hat{\mathbf{b}}_{\nu'})^l j_l(\kappa b_\nu) j_l(\kappa b_{\nu'}) (C_{00}^{J1J'})^2, \quad (11) \end{aligned}$$

where $\eta_{\nu\nu'}$ is the number of pairs of the type $\nu\nu'$ and the sum is over all possible types of pairs.

The complete cross section is then

$$\frac{\partial^2 \sigma}{\partial \epsilon \partial \Omega} = \left(\frac{\partial^2 \sigma}{\partial \epsilon \partial \Omega} \right)^{\text{direct}} + \left(\frac{\partial^2 \sigma}{\partial \epsilon \partial \Omega} \right)^{\text{int}}. \quad (12)$$

CALCULATIONS

Numerical calculations of the cross sections using the formulas above were made and compared with the corresponding calculations based on the Krieger-Nelkin method. Calculations of the cross section are given here for four molecules: HF, HCl, N₂, and HCN.

¹³ M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

¹⁴ Classified as to environment as well as nuclear species.

These example calculations illustrate the kinds of results one might expect to find. The calculations for HF and HCl at several choices of incident energy and scattering angle (Figs. 1 and 2) do not include the interference scattering except for HF at a scattering angle of 20°. As can be seen by this result [Fig. 1(a)], the interference is quite small, as expected. Similar calculations for HCl indicate that the interference contributes only about 6%. Results for molecular nitrogen and hydrogen cyanide are given in Figs. 3

and 4. The cross sections shown here include interference. The direct part only is also shown for comparison. For triatomic or polyatomic linear molecules care must be taken to include the vibrations if the results are to be interpreted realistically.

A few comments on the techniques of computation are appropriate. All calculations were performed on The University of Michigan IBM-7090. The parity Clebsch-Gordan coefficients were calculated according to the well-known formulas.¹³ Spherical Bessel functions were generated using a subroutine developed by Erickson,¹⁵ and agreement with tabulated values was verified. The range of rotational quantum numbers used in the calculations was determined by inspecting

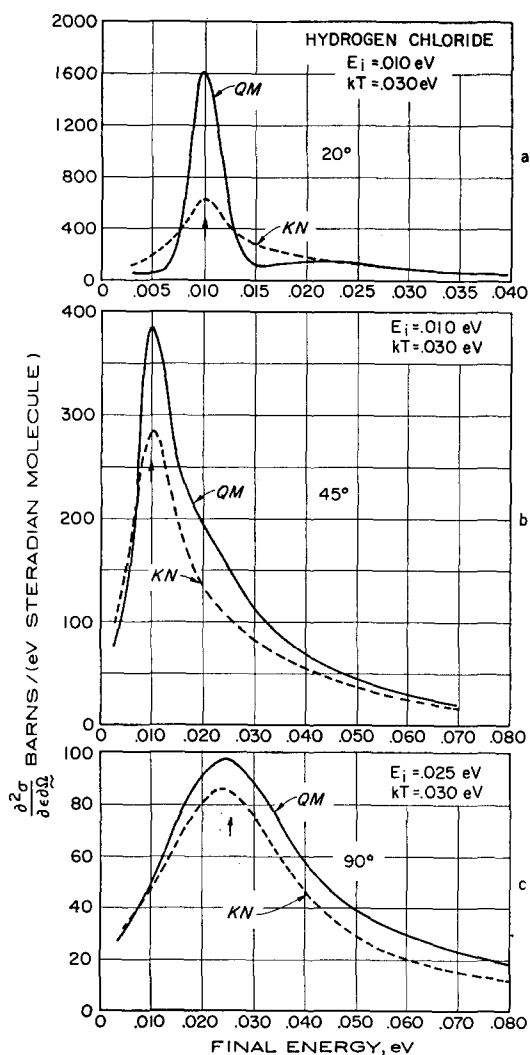


Fig. 2. Cross section for HCl gas at 0.030 eV (348°K). (a) Incident energy 0.010 eV, scattering angle 20°; (b) incident energy 0.010 eV, scattering angle 45°; (c) incident energy 0.025 eV at 90°.

¹⁵ J. D. Erickson (private communication).

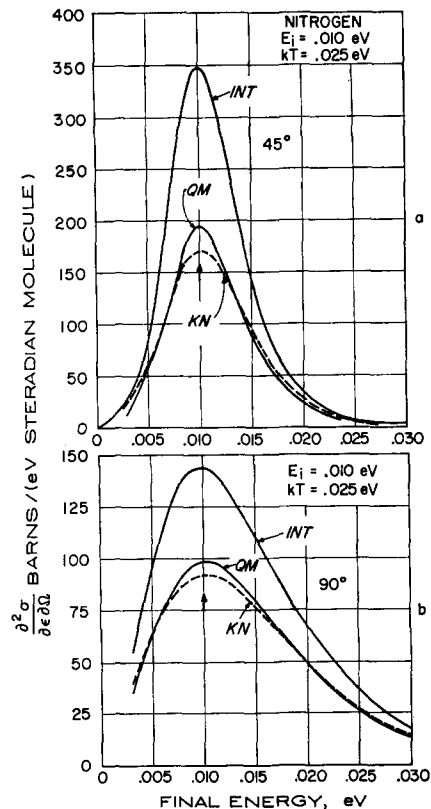


Fig. 3. Cross section for N₂ gas at 0.025 eV. (a) Incident energy 0.010 eV, scattering angle 45°; (b) incident energy 0.010 eV, scattering angle 90°.

the relative population of initial levels of the molecule at the given temperature. For most of these calculations they ranged from 0 to 20. The inner sum (on l), taken over limited combinations of initial and final quantum numbers, was truncated when the spherical Bessel function was sufficiently small. The molecular parameters used in the calculations are given in the Appendix.

DISCUSSION

Examination of the figures shows that inclusion of the discrete rotational levels gives a result that is distinctly different from that of the Krieger-Nelkin method, as expected. Furthermore, the difference becomes more pronounced as the incident neutron energy is reduced and the scattering angle decreases. This agrees qualitatively with Griffing's result¹⁰ for spherically symmetric molecules. Unfortunately, however, experimental data on linear molecules are not available at the present time. It is hoped that experimental data on gases with linear symmetry will become available so that comparison can be made.

Of particular interest for HF and HCl is the bump

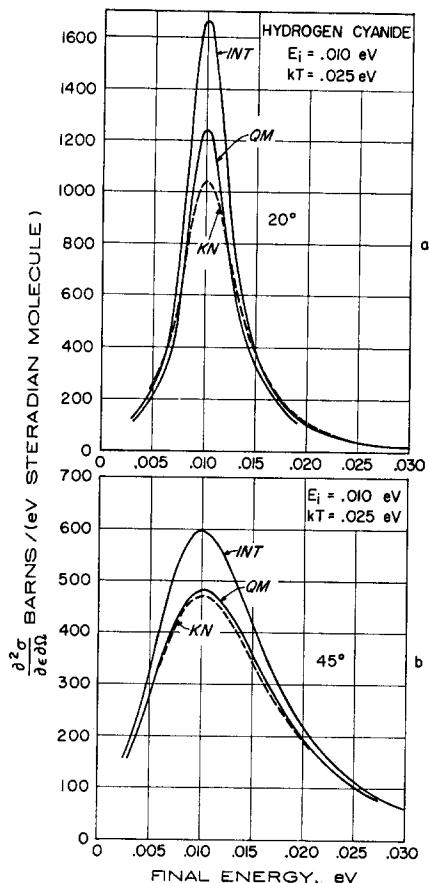


FIG. 4. Cross section for HCN gas at 0.025 eV and incident energy 0.010 eV. (a) Incident energy 0.010 eV, scattering angle 20° ; (b) incident energy 0.010 eV, scattering angle 45° .

in the cross section due to energy gain of the neutron from rotational levels of the molecules. As first pointed out by Griffing¹⁰ in his work on methane, this is a

composite of contributions of transitions from various initial to various lower final rotational states of the molecule. These are, of course, broadened by the translational motion and recoil of the molecule as a whole. One can also see that as the momentum transfer is increased, the bump is gradually washed out by the broadened translation-rotation peak. Thus, the most interesting experiment from the standpoint of testing this theory of rotations would be a small-angle scattering experiment at low incident energy.

Also worth noting is the difference in amplitudes of the two calculations. No resolution effects were applied to either calculation, and both were performed with absolute normalization.

The results for nitrogen illustrate a case for which the interference scattering is significant. This is to be expected since nitrogen is mostly a coherent scatterer. The Krieger-Nelkin calculation gives a fairly good representation of the direct scattering except near the elastic peak. HCN shows less significant interference effects and the KN result is very close to the direct scattering.

In conclusion, we can say that these calculations demonstrate the feasibility of performing numerical calculations using the quantum-mechanical theory for the class of molecular gases which possess linear symmetry and which have many rotational levels populated.

ACKNOWLEDGMENTS

The author is indebted to Dr. J. D. Erickson for the use of his subroutine to calculate spherical Bessel functions, and Professor J. M. Carpenter for many valuable discussions and criticisms. The author would also like to thank Dr. E. A. Straker for suggesting the problem and for his continued encouragement and assistance.

APPENDIX

The following parameters were used in the numerical calculations:

	HF	HCl	N ₂	HCN
Bond length (Å)	$2b = 1.10$	$2b = 1.2747$	$2b = 1.098$	$b_H = 1.620$ $b_C = 0.561$ $b_N = 0.596$
Moment of inertia ($g \text{ cm}^2 \times 10^{-40}$)	$I = 1.92$	$I = 2.64$	$I = 14.09$	$I = 19.05$
Rotational constant (eV)	$B = 0.00181$	$B = 0.00131$	$B = 0.000246$	$B = 0.000182$
Bound coherent scattering length (10^{-12} cm)	$A_H = 0.367$ $A_F = 0.560$	$A_H = 0.367$ $A_{Cl} = 0.99$	$A_N = 0.914$	$A_H = 0.367$ $A_C = 0.664$ $A_N = 0.914$
Bound incoherent scattering length (10^{-12} cm)	$C_H = 2.516$ $C_F = 0$	$C_H = 2.516$ $C_{Cl} = 0$	$C_N = 0.27$	$C_H = 2.516$ $C_C = 0$ $C_N = 0.27$
Sachs-Teller effective masses (amu)	$M_{ST}^H = 1.46$ $M_{ST}^F = 19.30$	$M_{ST}^H = 1.48$ $M_{ST}^{Cl} = 35.8$	$M_{ST}^N = 16.8$	$M_{ST}^H = 5.24$ $M_{ST}^C = 18.05$ $M_{ST}^N = 17.30$