Low-Energy Neutron Scattering from Hydrogen Chloride*

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Measured double differential cross sections are reported for low-energy neutron scattering by gaseous hydrogen chloride. Comparison of these data against a calculation based on a quantum mechanical treatment of rotations shows excellent agreement and thus provides the first experimental verification of this theory for the class of molecules with linear symmetry.

I. INTRODUCTION

Measurements of slow-neutron scattering by a variety of molecular gases[1-7] have evinced a fairly good understanding of the neutron interaction with molecular degrees of freedom in the gas phase. Particular attention in most of these studies has been focused on translational and rotational motions of the molecules since these are the motions most likely to affect slow-neutron interactions.

Although many approximate methods for treating rotations have been proposed,[8-14] unquestionably the best method involves no approximation and consists of an exact quantum mechanical calculation involving explicit summation on rotational states.[15,16] Unfortunately, the quantum mechanical result cannot be expressed in closed form, which means that numerical computations are not yet economical for most molecules even using the most advanced computers.

These computations are sufficiently complex and sufficiently different for each type of symmetry that experimental verification of the theoretical calculation for each symmetry class is important in order to allow one to confidently proceed to more complicated systems. So far computations using the exact theory have been reported for spherical,[17] linear,[18,19] and symmetric-top[20,21] molecules, but the only detailed comparisons with experiments are for methane[2,7,17] (spherical) and ammonia[2,4,21] (symmetric). Agreement for these two cases generally was good, although some minor discrepancies remained. The measurements on gaseous hydrogen chloride reported here provide the first experimental verification of the theory for the class of molecules with linear symmetry and show even better agreement.

II. EXPERIMENTS

Anhydrous hydrogen chloride 99.0% pure purchased from the Matheson Company was used without further purification, drying, or analysis. The largest impurity, stated by the manufacturer, was carbon dioxide, but the effect of all impurities was negligible. The gas was contained in a cylindrical anodized aluminum target holder which, in the region exposed to the neutron beam, had an outside diameter of 2.0 in., a wall thickness of 0.030 in., and a height of 2.25 in.

The portions of the holder not in the direct neutron beam were covered with 0.020 in. of cadmium to minimize the scattering from aluminum. The target holder was thoroughly dried before filling to reduce the possibility of chemical reaction.

The target was filled to a pressure of 166 psia at 20°C, which gave a measured transmission of 87.6% at an energy 18.4 meV. The mass of hydrogen chloride sample was independently determined by weighing the container before and after filling. No evidence of deterioration of the target was observed during the experiment.

Inelastic scattering measurements were made using the University of Michigan phased-rotor velocity selector and time-of-flight spectrometer.[5] The neutron detectors used in this system were Stedman-type ^{6}LiF–ZnS(Ag) scintillation detectors,[22] each 5 in.^{2} A bank of six such detectors was fixed along a segment of a ring at a scattering angle of 90°; a movable bank of three detectors was used for the smaller angle measurements. The size of the detectors introduced an angular uncertainty of 3.5° over a flight path of 2m.

The target and an identical air-filled dummy for background were cycled into the neutron beam by an automatic sample cycler in the ratio of about 6 to 2 min, respectively. Pulses resulting from detected neutrons were stored in the memory of a 1024 channel time-of-flight analyzer. Data from each scattering angle were allotted 256 channels, each 8 μsec wide. Each of these quarters of the memory was equally divided between signal and background.

Data taken at scattering angles of 22.1°, 47.5°, and 90°, all for an incident neutron energy of 18.4 meV, were converted to cross sections on the University of Michigan IBM system 360/67 computer. Background subtraction was made after linearly smoothing each background channel with four adjacent channels. All measurements were made at room temperature, 20±1°C.

The detector efficiency (the function describing the energy dependent detector efficiency in the data reduction computer program) was determined prior to the HCl measurements using a target of methane. The efficiency was adjusted so that the counting rate observed in the methane measurement corresponded to the calculated[17] absolute value of the methane cross section.
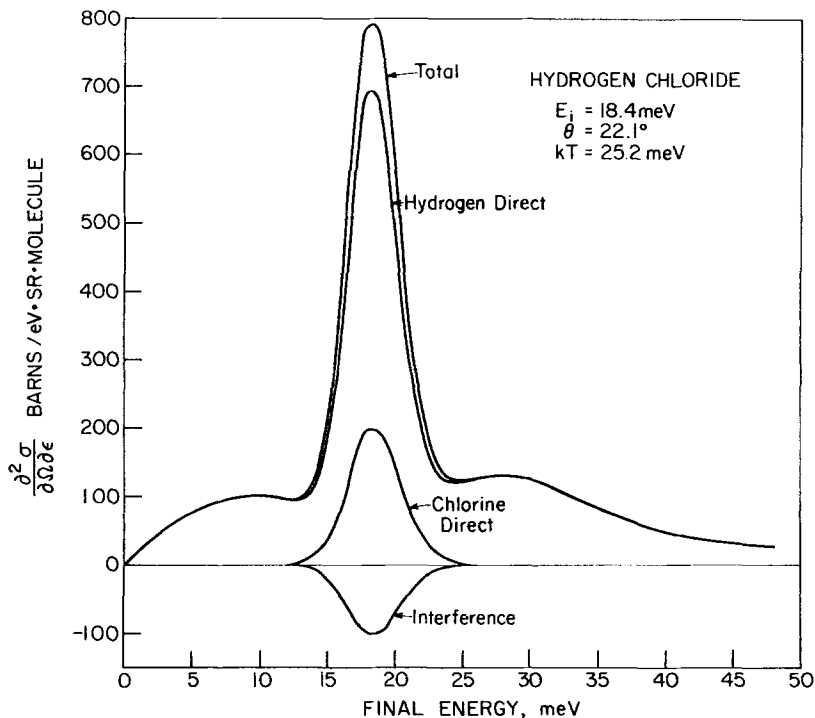
FIG. 1. Calculated cross sections for gaseous hydrogen chloride at an incident energy of 18.4 meV, temperature of 25.2 meV and scattering angle 22.1°.

In addition to the background and air scattering corrections, the large absorption cross section of chlorine necessitated an additional correction for attenuation of the neutron beam passing through the target. This was done using the procedure described by Carpenter.[23]

III. THEORY

Theoretical calculations of the scattering cross section for hydrogen chloride have previously been reported,[19] using as a dynamical model a freely translating rigid rotor. Inherent in the use of this model for gaseous hydrogen chloride are the assumptions that spin correlations, vibrations, and interactions between molecules can all be neglected. The first is known to be a good approximation.[24]

A more realistic model can be achieved by including the vibrational effects. Since the neutron energy in these experiments was too low to excite vibrational transitions and since virtually no excited levels are populated at room temperature, only zero-point vibrations need to be considered. The cross section based on such a model is

$$\partial^2\sigma/\partial\Omega\partial\epsilon = \sum_{\nu,\nu'} a_\nu a_{\nu'} (k_f/k_i)(\beta/4\pi E_R)^{1/2}$$

$$\times \exp(-2W_{\nu\nu'}) z^{-1} \sum_J (2J+1) \exp(-\beta E_J)$$

$$\times \sum_{J'} \exp\{-(\epsilon + E_{J'} - E_J + E_R)^2\beta/4E_R\} \sum_l (2l+1)$$

$$\times (2\delta_{\nu\nu'}-1)\,{}^l j_l(\kappa b_\nu) j_l(\kappa b_{\nu'})\,(C_{00}{}^{JlJ'})^2,$$

where

$$E_J = (\hbar^2/2I)J(J+1),$$

$$E_R = \hbar^2\kappa^2/2M,$$

$$2W_{\nu\nu'} = (\hbar^2\kappa^2/12\hbar\omega)(\gamma_\nu{}^2 + \gamma_{\nu'}{}^2)\coth(\hbar\omega\beta/2),$$

and where the γ's are the amplitude vectors of the normal coordinates which have the normalization

$$\sum_\nu M_\nu(\gamma_\nu)^2 = 1,$$

and the remaining symbols have the same meaning as in Ref. 19.

The zero-point vibrations have been treated here in an approximate way which involves averaging over the directions of κ to yield a Debye–Waller-type factor.[9] This is a very good approximation as long as the incident neutron energy is very small compared to the first vibrational level. For the range of momentum transfers and energies encountered in these measurements, the Debye–Waller factor for hydrogen direct scattering varies from about 0.9 to unity and is slowly varying. The Debye–Waller factor was included in the calculations.

We have also calculated the importance of the contribution due to one-quantum vibrational transitions. Employing a method which involves no approximation[25] we found that, for the conditions of these experiments, the one-quantum cross section is completely negligible. This is not surprising since almost no excited levels are populated at room temperature. Both the interference scattering and direct scattering

from chlorine were taken into account. Figure 1 shows the various contributions at the conditions of the experiment and a scattering angle of 22.1°.

The direct scattering from hydrogen is dominant, and its central peak has roughly the same width as the chlorine direct and interference scattering peaks. The peak primarily represents broadening due to center-of-mass, free-translational motion. The small bumps which appear in the inelastic regions of the spectrum are due to rotational motions but not to a particular rotational transition. Rather, they are a collective contribution from various rotational transitions which have nearly the same energy and are in addition broadened by the translational motion.

IV. DISCUSSION

A. Multiple Scattering

One of the most persistent problems plaguing inelastic neutron scattering experiments is multiple scattering. In order to relate the scattered intensity to a single-collision theory, we must either experimentally eliminate multiple scattering or find a procedure to correct the data. At the present time there exists no reliable, practical method for achieving either of these goals. There are, however, several methods which have been used with varying degrees of success for estimating the multiple scattering contribution.

One common experimental method is to measure the double differential cross section for various sample thicknesses. By reducing the thickness until the cross section remains unchanged, one presumably has eliminated multiple scattering. A difficulty here is that one may find that for the thinnest practical samples there are still considerable effects. Although without solid foundation, it is generally accepted that a sample such that approximately 10% of the incident beam will scatter is satisfactory. Also, it has been found[26] that there exists a range over which the multiple scattering corrections are insensitive to a change in the thickness.

Another procedure[27,28] is to reduce the scattering perpendicular to the horizontal plane (usually of larger dimensions than the thickness) by inserting spacers of absorbing material parallel to this plane at various separations. A simple comparison could be made, or one could plot the differences as a function of spacing for each energy interval and extrapolate to zero separation of the spacers. This procedure has been used for a cylindrical sample of gaseous ethane by Strong and Brugger[27] and for a water target by Brugger.[28] The extrapolation was based on the assumption that the multiple scattering varies linearly with spacer separation. Strong and Brugger found that for their cylindrical gas target this type of scattering occurred in the wings of the elastic peak and that it varied with energy (decreasing at large energy transfers). They

also found that it depended on scattering angle (getting worse as the scattering angle decreases). The multiple scattering correction was a maximum of about 8% at their smallest angle (4.8°).

A computational procedure for determining the amount of multiple scattering has been used by Slaggie.[26] A criticism of this method, as for most calculational methods, is that one must assume a double differential cross section or scattering kernel in order to do the calculations, and Slaggie has found in his studies on slab geometry water targets that the results were very sensitive to the kernel.[26] Qualitatively, Slaggie found (in agreement with Strong and Brugger) that multiple scattering displaces neutrons from the elastic peak into the wings of the elastic peak, and the importance of multiple scattering decreases as the energy and scattering angle increase. Slaggie disagreed, however, with the magnitude of Brugger's multiple scattering measurements on water. In particular, he cast doubt on the assumption of the extrapolation procedure to yield the proper correction. Although this work was for a complicated slab geometry water sample, one might also have reservations about the extrapolation procedure for a gas target. Unfortunately no calculations have been performed for multiple scattering in a gas; although the cross sections are thought to be reasonably well known, they are too complicated to permit Slaggie-type calculations.

We have chosen to minimize the multiple scattering experimentally as much as possible realizing that it cannot be completely eliminated. We chose a cylindrical geometry with a moderately thin sample and with the cylinder height approximately the same as the diameter. Also our scattering angles are not particularly small. Even more importantly, however, we chose a sample with a substantial absorption cross section (33 b/H at 2200 m/sec). Provided one is able to correct the results for depletion of the incident beam and attenuation after scattering, a target with a uniformly distributed absorber is probably as ideal a situation as presently exists for minimizing multiple scattering.

B. Discussion of the Data

The corrected measured energy cross sections are shown along with the theoretical calculations in Fig. 2. The data have been smoothed over nine channels. No normalization of any kind was applied to the theory or data at 22.1° and 90°. The data at 47.5°, however, were taken without calibration against the methane standard. Therefore, these data were normalized so as to give the same area as the theory.

In the 22.1° data there are slight discrepancies at the elastic peak and in the wings of the elastic peak. These are the results of at least three factors. The resolution correction, which has not been made, will broaden the theory by about 2%. Since the data were
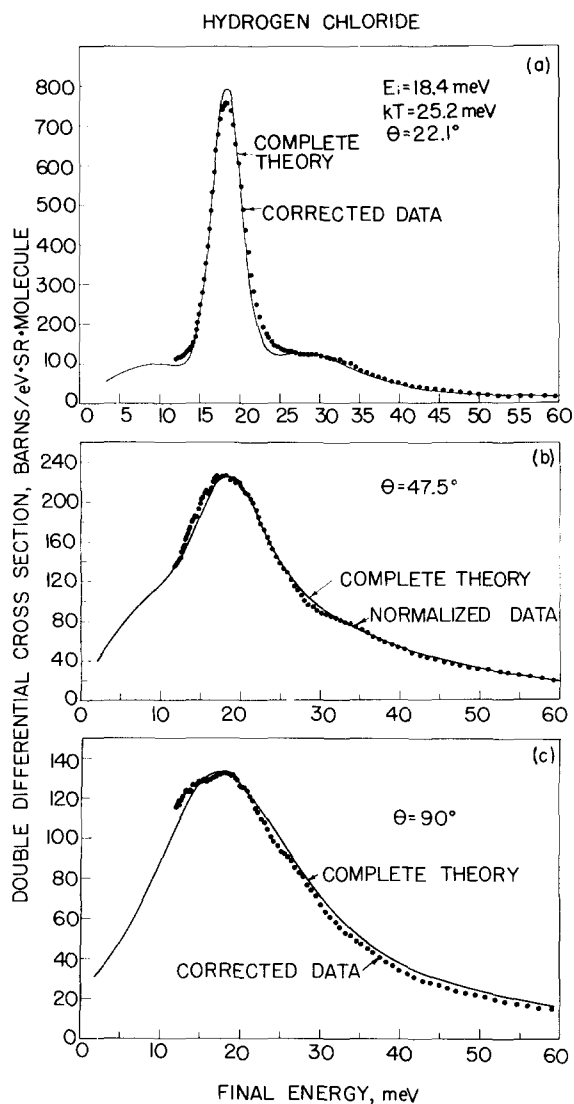
HYDROGEN CHLORIDE

FIG. 2. Measured and calculated double differential cross sections for hydrogen chloride at an incident energy of 18.4 meV, $kT = 25.2$ meV and scattering angles of (a) 22.1°, (b) 47.5°, and (c) 90°.

smoothed, additional broadening will result from this procedure and should be similarly applied to the theory (about 1%). Both of these effects are only important in the 22.1° data. These contributions, however, are not expected to completely explain the discrepancy at the wings of the elastic peak. The disagreement here is thought to be due mostly to multiple scattering. The estimates of both Brugger[28] and Slaggie[26] suggest that the wings of the elastic peak are precisely where multiple scattering is expected to contribute.

The data and theory at 47.5° show no prominent disparity. For the data at a scattering angle of 90° the measured points lie slightly below the theory at large final energies and slightly above the theory near the incident energy. This we attribute to the error

in the determination of the energy dependence of the detector efficiency. Other energy dependent corrections such as the attenuation correction cannot be excluded from also contributing to the discrepancy.

The excellent agreement between theory and the measurements reported here justifies the conclusion that the free molecular gas model appropriately describes hydrogen chloride under the conditions of the experiments. In particular, intermolecular effects such as collisions, dipole interactions, and formation of dimers or polymers do not appear in the data. Multiple scattering appears to be most important in the 22.1° data, and there to contribute between 5% and 10% in the wings of the elastic peak. However, final and absolute judgment of these effects must be reserved until a workable procedure for multiple scattering corrections has been formulated or suitable calculations have been done.

The so-called quantum mechanical calculations are believed to be sufficiently well verified to provide a point of reference against which approximate theories can be compared. These calculations could also serve as a basis of comparison for study of intermolecular effects in systems of dense linear gases. Any theory describing denser forms should conform to the dilute gas results in the limit of low density.

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Optical and Microwave Spectra of Cr^{3+} in the Spinel $ZnGa_2O_4$*

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The EPR, optical absorption, and fluorescence spectra of Cr^{3+} in the spinel $ZnGa_2O_4$ have been measured and interpreted using a crystal-field model. The EPR experiments can be described by a spin Hamiltonian whose parameters are: $2D=+1.048\pm0.001$ cm^{-1}, $g_{||}=1.9774\pm0.0005$, $g_{\perp}=1.9761\pm0.0005$. The broad band transitions to the $^4T_2$ and lower $^4T_1$ terms show a trigonal field splitting of <500 and 1500 cm^{-1} respectively. The zero field splittings of the $^4A_2$ level (1.048 cm^{-1}) and ^2E level (40.0 cm^{-1}) are considerably different than in the two other spinel systems which have been reported, i.e., $ZnAl_2O_4$ and $MgAl_2O_4$. The model parameters used in the numerical calculations are: $\Delta=18\,000$ cm^{-1}, $B=670$ cm^{-1}, $C=3230$ cm^{-1}, $\zeta=250$ cm^{-1}, $v=-650$ cm^{-1}, $v'=-1100$ cm^{-1}, $k=0.7$. The detailed structure of the phonon sidebands and fluorescence, which is tentatively assigned to exchange-coupled Cr^{3+} pairs, are significantly different from other spinels.

I. INTRODUCTION

This paper is concerned with crystalline fields in the spinel $ZnGa_2O_4$. A large class of compounds exhibit the spinel structure, the most interesting of which are the various magnetic insulators known as the spinel ferrites. While electron spin resonance, optical absorption, and fluorescence measurements of paramagnetic impurities have been the subject of many investigations in a wide variety of lattices, similar studies in the spinel system have only become possible in recent years with the availability of laboratory-grown diamagnetic spinel single crystals. Until the work of Wood et al.,[1] only a few sketchy and sometimes misleading reports on the microwave and optical spectra of Cr^{3+} ions in spinels had been made and then only in natural crystals. A consistent interpretation of the internal crystalline field in a solid should make use of all the information obtainable from both microwave and optical spectra of the same crystal and seldom does one find such a complete set of data. This latter point is especially important in the spinel system because of the many different cation distributions and cation orders which may exist in crystals of this structure.

Using a crystal-field model, we have made a relatively complete analysis of the electron spin resonance, optical absorption, and fluorescence spectra of Cr^{3+} as a dilute impurity in the spinel $ZnGa_2O_4$. While the general features of the spectra are qualitatively similar to recently reported results for Cr^{3+} in the aluminate spinels $ZnAl_2O_4$ and $MgAl_2O_4$,[1] the zero field splittings of the $^4A_2$ ground state and ^2E excited state are considerably different. This emphasizes the sensitivity of these quantities to the details of the B site geometry. The parameters determined from our analysis provide reliable values with which to test model calculations of the crystal field.

II. CRYSTAL STRUCTURE AND PREPARATION

The mineral spinel ($MgAl_2O_4$) has given its name to a large class of compounds of general formula AB_2O_4 having the crystal structure O_h^7 with eight formula units in a unit cell. The 32 oxygen ions are in C_{3v} sites arranged in a close-packed cubic formation leaving 64 tetrahedral (T_d) and 32 distorted octahedral (D_{3d}) sites as possible cation locations. Of these only 8 tetrahedral (8A) and 16 octahedral (16B) positions are occupied. The 24 cations (8A, 16B) and 32 oxygen ions constitute an fcc cell with an edge dimension a_0 of about 8 Å depending on the composition, and distribution of cations in the A and B sites. The spinel $ZnGa_2O_4$ is a normal spinel with all of the Zn ions in A sites, the Ga ions in B sites, and $a_0=8.37$ Å.[2]

Crystals of chromium-doped $ZnGa_2O_4$ were grown by slow cooling from a PbO–PbF$_2$ flux. The starting