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PROTON MOTIONS IN AMMONIUM HALIDES BY SLOW NEUTRON CROSS-SECTION MEASUREMENTS*

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The motions of ammonium ions and the order-disorder transitions in their salts have been investigated extensively by a variety of techniques. These include specific heat measurements,[1-4] crystal structure studies by neutron diffraction,[5] infrared spectroscopy,[6-8] and nuclear magnetic resonance.[9-11] The results of the investigations reported here show that cross-section measurements for neutrons of subthermal energy also provide a valuable criterion for determining the type of proton motion and the strength of chemical binding in the ammonium halides or other compounds of hydrogen.

Using a crystal spectrometer[12,13] at the Brookhaven reactor, total neutron cross-section measurements were made at room temperature for NH_3 gas at 115 psia and for the following ammonium halide salts: NH_4F, NH_4Cl, NH_4Br, and NH_4I. In Fig. 1 the cross sections per hydrogen atom, corrected for neutron absorption,[14] are plotted as a function of neutron wavelength. Since the scattering cross section for hydrogen is large and primarily incoherent, Bragg interference effects are relatively small and do not contribute significantly to the total cross section. A series of closely spaced cross-section measurements in the neighborhood of the most intense Bragg peak for NH_4Br indicated that the Bragg effects were small and could be neglected.

At short wavelengths ($\lambda_n \to 0$) the scattering cross sections approach the values for the free atoms. At long wavelengths the predominant inelastic scattering process is one in which the neutron gains energy from the crystal or molecule. The scattering cross section then becomes proportional to the wavelength, λ_n, and may be represented by $\sigma_s = a + b\lambda_n$. The slopes, b, of the cross-section curves in Fig. 1 were determined in the long-wavelength range by a least-squares fit to the data. The dashed line is the theoretical

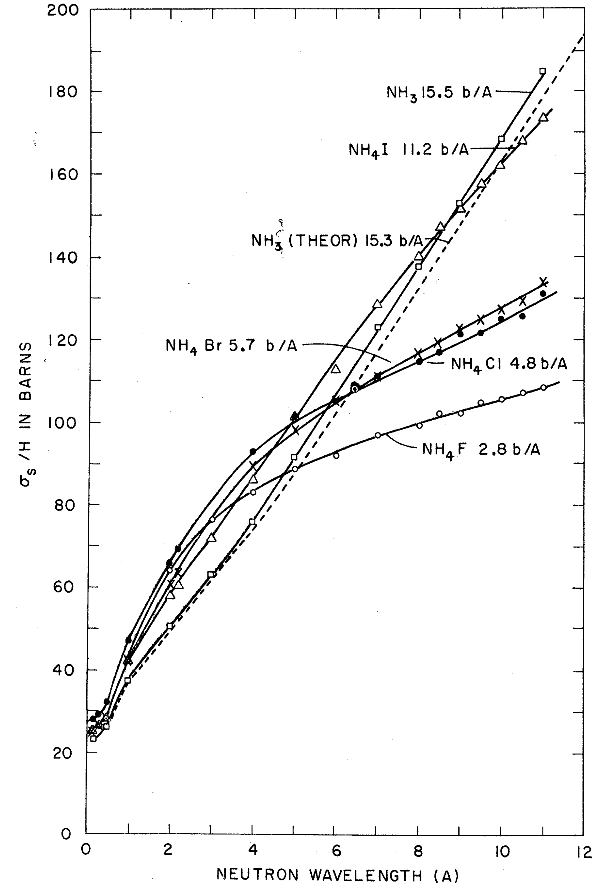

FIG. 1. Neutron scattering cross section per hydrogen atom for ammonia and the ammonium halides.

cross section per proton in NH_3 calculated using the Krieger-Nelkin method.[15]

The slopes from Fig. 1 together with other properties of the ammonium halides are summarized in Table I. Previous work referred to above has established that the ammonium ions in phases II and III may be considered torsional oscillators with the frequencies listed and with barriers to rotation[9] well above kT_λ. The transition from phase III to phase II at T_λ is a cooperative order-disorder process involving reorientation of the ammonium ions. At room temperature NH_4I is in phase I where the ammonium ions are thought to be freely rotating around the $N-H--I^-$ axes with a potential barrier to rotation of approximately 35 cm^{-1}.[7]

The slopes and the absolute magnitudes of the scattering cross sections show a definite correlation with the proton dynamics and hydrogen bonding in the ammonium halide salts. As shown in Table I, the slopes decrease with increasing torsional frequencies, although a more detailed comparison would involve consideration of the entire fundamental and lattice vibrational spectrum. The order of the torsional frequencies and the slopes is that expected from the abilities of the halide ions to form hydrogen bonds, i.e., $F^- > Cl^- > Br^- > I^-$. Thus, the strong hydrogen bonds in ammonium fluoride result in a relatively high torsional frequency with fewer states excited and a low slope (2.85 barns/A). The weaker bonds in the other ammonium halides and a structure which allows reorientation of the ammonium ions result in higher slopes.

The slope of the scattering cross-section curve for NH_4I at room temperature approaches that for NH_3 gas. This is consistent with the model in which the ammonium ion in phase I of NH_4I is relatively free to rotate about one axis, as established from other evidence. Preliminary measurements of the slope of the cross-section curve for NH_4I at 0°C and -20°C result in values of 11 and 6 barns/A, respectively. Thus, there is a marked change in slope in passing from phase I in which the ammonium ion is freely rotating to phase II in which it is a torsional oscillator. Relatively little change was observed in passing through the order-disorder transition from phase III to phase II for NH_4Cl. It is interesting to note that the slopes for NH_4Br and NH_4Cl are measurably different even though the difference in their torsional frequencies is small. The limiting slope of the scattering cross-section curve appears to be correlated with the number of excited states and therefore the freedom of motion of the hydrogen atoms.

Table I. Limiting slopes of the scattering cross-section curves for the ammonium halides compared with other properties. The errors listed include those due to counting and to uncertainty in the absorption cross sections.[a]

	NH_4F	NH_4Cl	NH_4Br	NH_4I
Slope, barns/A, 23°C	2.85 ±0.21	4.83 ±0.18	5.71 ±0.09	11.21 ±0.18
Wavelength range, A	8–11	6–11	6–11	7–11
Cross section per proton at 10 A, barns	105	125	128	162
Motion of NH_4^+ at 23°C	osc.	osc.	osc.	rot.
Transition temperatures, °C				
Phase I (NaCl) ⟷ Phase II (CsCl)	...	184.3	137.8	-17.6
Phase II (CsCl) ⟷ Phase III[b]	...	-30.5	-38.1	-41.6
Torsional frequency, cm^{-1} [c]				
Phase III	523[b]	391	319	279
Phase II	...	359	311	...
Potential barrier to rotation[d] kcal/mole (Phase II)	...	5.3	4.2	2.9

[a] See reference 14.

[b] Phase III for NH_4Cl has the cubic CsCl structure, while that for NH_4Br and NH_4I is slightly distorted to a tetragonal structure. NH_4F has a hexagonal structure in which each NH_4^+ ion is surrounded tetrahedrally by four F^- ions. The only observed thermal transition is a small one about -30°C (references 1 and 7).

[c] See references 6 and 7.

[d] See reference 9.

The data presented here show that total cross-section measurements can give valuable evidence concerning the dynamics and chemical binding of hydrogen in molecules and crystals. Measurements are now being extended to other ammonium salts and hydrogen compounds.

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ROTATING SELF-CONSISTENT FIELDS AND ROTATIONAL STATES OF NUCLEI

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Moments of inertia of rotating nuclei have been calculated by means of the cranking model[1-3] in which the particle motion is investigated in a potential rotating with a given angular velocity. The aim of the present work is to show that the self-consistent equations of the time-dependent Hartree-Fock method have such rotating solutions. The rotating potential is produced by the particles themselves and the particles move in this potential. Similar considerations hold for the generalized Hartree-Fock equations which take into account the pairing correlations.

The time-dependent Hartree-Fock equations can be written as[4]

$$i\partial\rho/\partial t=[\nu,\rho], \tag{1a}$$

where ρ is the density matrix which satisfies the condition $\rho^2=\rho$, and ν is the self-consistent energy. The matrix elements of ν are given by

$$\nu(x,x')=-\frac{1}{2m}\nabla^2\delta(x-x')$$
$$+\int dx_1dx_1'[(xx_1|V|x'x_1')-(xx_1|V|x_1'x')]\rho(x_1',x_1). \tag{1b}$$

For a system with translational invariance, the solutions of the time-independent equation

$$[\nu,\rho]=0 \tag{1c}$$

are degenerate, because the center of the self-consistent potential may be moved to any position. This degeneracy permits solutions of the time-dependent equation (1a) to be constructed, which represent a translational motion of the system with constant velocity.[5] The simplest way to obtain these solutions is to transform the equations to a reference system moving with a constant velocity v. Since there are no inertial forces acting in this system, the stationary solutions in the moving system can be obtained explicitly in terms of the solutions with $v=0$.

For a nucleus with a nonspherical equilibrium shape, the solutions of (1c) are degenerate because of an arbitrary orientation of the axes of the system. The time-dependent equation (1a) has accordingly solutions corresponding to a rotation of these axes. They can be investigated by transforming the equation to a rotating reference system. Time-independent solutions in the rotating frame represent rotating solutions in the rest system, except in the case of rotation about a symmetry axis. Transforming (1a) to a reference system rotating with uniform angular velo-