Investigation of the $H^1$ Spin-Lattice Relaxation Times of Some Ammonium Compounds

F. Köksal

Department of Physics, Faculty of Sciences, Ankara University, Turkey

Z. Naturforsch. 34a, 239—241 (1979); received November 21 (1978)

The temperature dependence of the proton spin-lattice relaxation times of $(NH_4)_2Al(SO_4)_2$, $(NH_4)_2MoO_4$, $NH_4NH_2SO_3$ and $(NH_4)_2SnCl_6$ has been investigated in the temperature range 100—500 K. The experimental results indicate that intra H-H dipolar interaction, modulated by reorientational motion of the ammonium ion, is the dominant relaxation mechanism between 100 and 200 K. The activation energies for the reorientational motion of the ammonium ions were found to be 1.54, 1.56, 0.99, and 0.91 kcal/mole, respectively. Furthermore, it has been detected that above 200 K the spin-rotational interactions of the ammonium ions contribute to the spin-lattice relaxation. The average value of the mean-square spin-rotational interaction constant for $NH_4^+$ was found to be $C^2 = 1.42 \times 10^{10}$ s$^{-2}$.

1. Introduction

By now a considerable variety of experimental methods and theoretical procedures has been applied to study molecular rotation [1]. In particular in condensed phases pulsed NMR provides estimates of the motional rates and activation energies for internal rotation and as a result gives information complementary to that obtained by neutron scattering, specific heat and infrared techniques [2—4].

In the last years many ammonium salts have been investigated by NMR, mostly at low temperatures [5—12]. Lately in our study on $NH_4Br$, $NH_2SCN$, $NH_2NO_3$, $(NH_4)_2S_2O_3$, $(NH_4)_2Cr_2O_7$, and $(NH_4)_2Ce(NO_3)_6$ we have detected the spin-rotational interaction contribution to the spin-lattice relaxation times at elevated temperatures [13]. It is the purpose of this paper to investigate the reorientational and rotational motions of $NH_4^+$ in the ammonium compounds $(NH_4)_2Al(SO_4)_2$, $(NH_4)_2MoO_4$, $NH_4NH_2SO_3$ and $(NH_4)_2SnCl_6$ over the temperature interval 100—500 K. This work shows again that the spin-rotational interaction may operate as a spin-lattice relaxation mechanism also in solids.

Reprint requests to Dr. F. Köksal, A.U. Fen Fakültesi, Fizik Bölümü, Turkey.

0340-4811 / 79 / 0200-0239 $01.00/0
written as [14]

\[(1/T_1)_d = C_1 \tau_c . \] (1)

The activation law

\[\tau_c = \tau_c^0 \exp (E_a / RT) \] (2)

is supposed to be valid. From the linear portion of Fig. 1 we obtain the activation energy \(E_a = 1.54 \text{ kcal/mole} \) for the reorientational motion of the ammonium ion. The spin-lattice relaxation time passes through a maximum at 250 K after a discontinuity at 200 K. Since the spin-lattice relaxation time does not depend on the frequency we conclude that at 200 K the ammonium ion begins to rotate around the \( N \) nucleus and the spin-rotational interaction contributes to \( T_1 \). The spin-rotational interaction contribution to the spin-lattice relaxation rate is

\[(1/T_1)_{sr} = C_2/\tau_c , \] (3)

where \( C_2 \), according to the rotational diffusion model, is given as [15]

\[C_2 = \frac{1}{2} I^2 C^2 \text{ s}^{-2} . \] (4)

In (4) \( I \) is the moment of inertia of the rotating ammonium ion and \( C^2 \) is the mean-square spin-rotational interaction constant. In the presence of dipolar and spin-rotational interactions the effective spin-lattice relaxation rate becomes

\[1/T_1 = (1/T_1)_d + (1/T_1)_{sr} . \] (5)

Thus the effective value of the spin-lattice relaxation time is

\[T_1 = \tau_c / (C_2 + C_1 \tau_c^2 ) . \] (6)

At the maximum of \( T_1 \) in Fig. 1, \( (1/T_1)_d \) should equal \( (1/T_1)_{sr} \). By incorporating \( I = 4.8 \times 10^{-40} \text{ g cm}^2 \) and \( C_1 = 11.37 \times 10^{10} \text{ s}^{-2} \) for the ammonium ion [13], \( \tau_c^0 = 1.40 \times 10^{-13} \text{ s} \), \( T_{\text{max}} = 6 \text{ s} \) at 250 K, the correlation time discontinuity factor of 2 and \( E_a = 1.54 \text{ kcal/mole} \) in (2), (4) and (6) we obtain \( C^2 = 1.44 \times 10^{10} \text{ s}^{-2} \).

3.2. Ammonium molybdate ((NH₄)₂MoO₄)

The experimental result for this compound, shown in Fig. 2, is almost the same as for ((NH₄)₂Al₂O₄). From the linear portion of Fig. 2 we obtain \( E_a = 1.56 \text{ kcal/mole} \) and \( \tau_c^0 = 1.51 \times 10^{-13} \text{ s} \). The spin-lattice relaxation time passes through a maximum at 285 K. Using these and the correlation time discontinuity factor of 1.6 in (2), (4) and (6) we obtain \( C^2 = 1.44 \times 10^{10} \text{ s}^{-2} \).
3.3. Ammonium sulfamate (NH₄NH₂SO₃)

From the experimental results in Fig. 3 we obtain \( E_a = 0.99 \text{ kcal/mole} \) and \( r_c = 1.42 \times 10^{-13} \text{ s} \). The spin-lattice relaxation time for this compound passes through a maximum at 222 K and \( T_{1\text{max}} = 6.53 \text{ s} \). Following the same way as above, \( C^2 \) was found to be \( 1.58 \times 10^{10} \text{ s}^{-2} \).

3.4. Ammonium chloro-stannate ((NH₄)₂SnCl₆)

From the linear portion of Fig. 4 we obtain the activation energy \( E_a = 0.91 \text{ kcal/mole} \) and \( r_c = 3.63 \times 10^{-13} \text{ s} \). The spin-lattice relaxation time passes through a maximum at 333 K and \( T_{1\text{max}} = 6.16 \text{ s} \). Using the experimental results as explained above, we obtain \( C^2 = 1.25 \times 10^{10} \text{ s}^{-2} \).

The present and the above mentioned studies on ammonium compounds [8—13] indicate that at low temperatures the reorientational motion of the ammonium ion provides the most effective spin-lattice relaxation mechanism. However, in a few of the previous studies it has been concluded that the spin-rotational interaction of NH₄⁺ may contribute to the spin-lattice relaxation. Our experimental results in the present and the previous study [13] indicate that generally the spin-rotational interaction contribution begins to be effective at lower temperatures the smaller the activation energy of the reorientational motion of NH₄⁺. This is an expected result since the smaller the hindering potential the more easily the ammonium ion will rotate.

The maximum values of the spin-lattice relaxation times of the compounds in this study are equal within the limits of experimental errors to \( T_{1\text{max}} \approx 6 \text{ s} \). This is almost 3 times shorter than the \( T_{1\text{max}} \approx 20 \text{ s} \) for the ammonium compounds

\[ \text{Fig. 4. } T_1 / s \text{ vs } 10^2 / T (K^{-1}) \text{ for ammoniumchloro-stannate.} \]

\[ \text{NH}_4\text{Br, NH}_4\text{SCN, (NH}_4\text{)_2S}_2\text{O}_8, (NH}_4\text{)_2Ce(NO}_3\text{)_6, NH}_4\text{NO}_3 \text{ and (NH}_4\text{)_2Cr}_2\text{O}_7 \text{ reported lately [13].} \]

\[ \text{This difference may be explained by the different lattice spacings, symmetry and charge distributions on the ions in the compounds. However the average value of the mean square spin-rotational interaction constant for the compounds in this study was found to be } C^2 = 1.42 \times 10^{10} \text{ s}^{-2}. \]

\[ \text{This is in good agreement with the experimentally obtained value of } C^2 = 1.27 \times 10^{10} \text{ s}^{-2} \text{ in our previous work [13] and the calculated value } C^2 = 1.24 \times 10^{10} \text{ s}^{-2} \text{ of Ikeda and McDowell's work [9].} \]

Acknowledgement

This research was supported in part by TBTAK (Turkish Scientific and Technical Research Council).