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_4SCN, NH_4NO_3, $(NH_4)_2S_2O_8$, $(NH_4)_2Cr_2O_7$ 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.Ü. Fen Fakültesi, Fizik Bölümü, Turkey.

0340-4811 / 79 / 0200-0239 $ 01.00/0

2. Experimental

The proton spin-lattice relaxation times T_1 have been measured at 60 MHz using an SxP type 4–100 MHz Bruker Pulse Spectrometer over a temperature range 100–500 K. The pure polycrystalline compounds were supplied from commercial sources, finely grained and filled into sample tubes 0.8 cm in diameter and 0.5 cm in hight. The experiments were also performed at 20 MHz to test the frequency independence of the spin-lattice relaxation times at above 200 K.

3. Results and Discussion

3.1. Ammonium-aluminum sulfate ($(NH_4)_2Al(SO_4)_2$)

The experimental results (Fig. 1) indicate that between 100 K and 200 K the intra dipolar H–H interaction leads to a spin-lattice relaxation. For the ammonium ion and the case $\omega \tau_c \ll 1$, where ω is the angular Lamor frequency and τ_c the reorientational correlation time, this relaxation rate can be

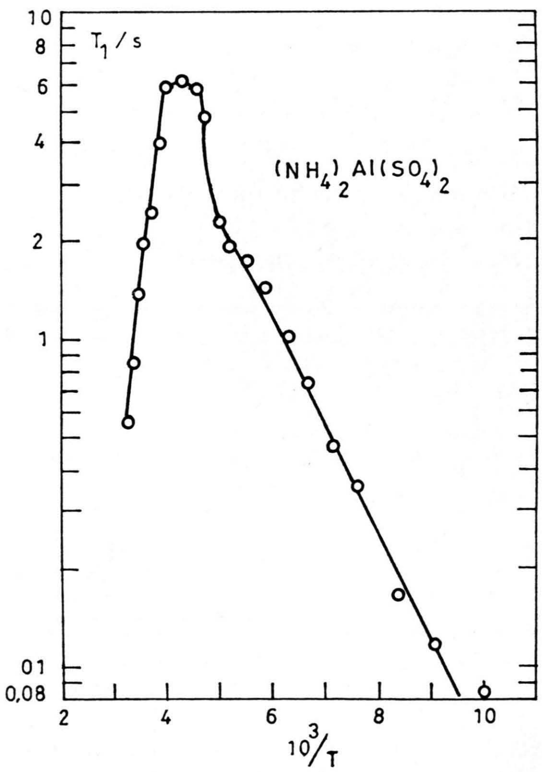

Fig. 1. ln T_1 vs $10^3/T\,(K^{-1})$ for ammonium-aluminum sulfate.

written as [14]

$$(1/T_1)_d = C_1 \tau_c \,. \qquad (1)$$

The activation law

$$\tau_c = \tau_c{}^0 \exp(E_a/RT) \qquad (2)$$

is supposed to be valid. From the linear portion of Fig. 1 we obtain the activation energy $E_a = 1.54$ 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

$$(1/T_1)_{sr} = C_2/\tau_c \,, \qquad (3)$$

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

$$C_2 = \tfrac{1}{3} I^2 C^2 \hbar^{-2} \,. \qquad (4)$$

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

$$1/T_1 = (1/T_1)_d + (1/T_1)_{sr} \,. \qquad (5)$$

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

$$T_1 = \tau_c/(C_2 + C_1 \tau_c{}^2) \,. \qquad (6)$$

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

3.2. Ammonium molybdate ($(NH_4)_2MoO_4$)

The experimental result for this compound, shown in Fig. 2, is almost the same as for $((NH_4)_2AlSO_4)_2$. From the linear portion of Fig. 2 we obtain $E_a =$ 1.56 kcal/mole and $\tau_c{}^0 = 1.51 \times 10^{-13}$ 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 $C^2 = 1.44 \times 10^{10}$ s^{-2}.

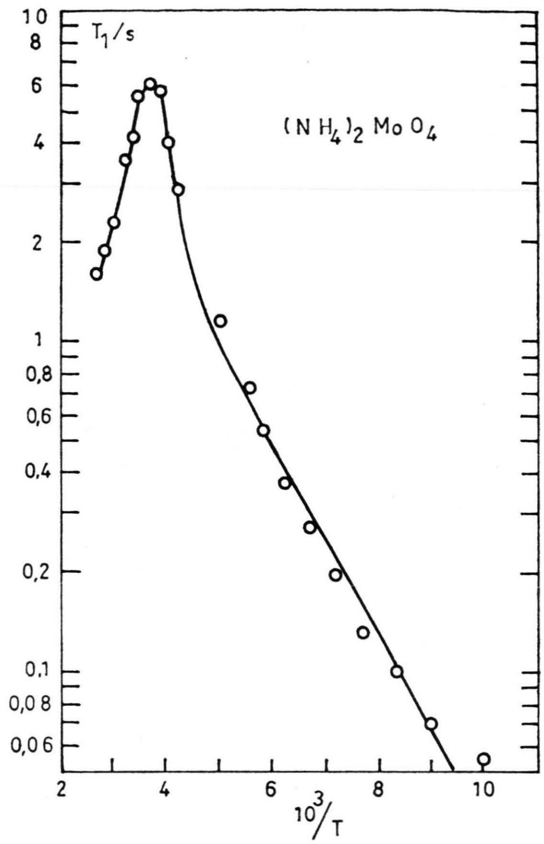

Fig. 2. ln T_1 vs $10^3/T$ (K^{-1}) for ammonium molybdate.

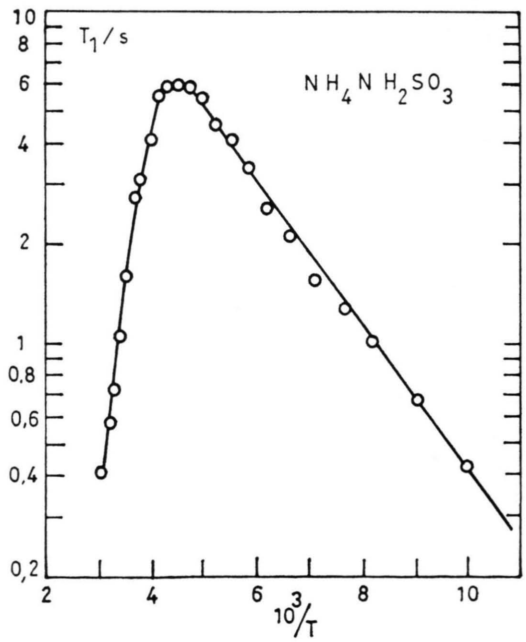

Fig. 3. ln T_1 vs $10^3/T$ (K^{-1}) for ammonium sulfamate.

3.3. Ammonium sulfamate ($NH_4NH_2SO_3$)

From the experimental results in Fig. 3 we obtain $E_a = 0.99$ kcal/mole and $\tau_c{}^0 = 1.42 \times 10^{-13}$ s. The spin-lattice relaxation time for this compound passes through a maximum at 222 K and $T_{1\,max} = 6.53$ s. Following the same way as above, C^2 was found to be 1.58×10^{10} s^{-2}.

3.4. Ammonium chloro-stannate ($(NH_4)_2SnCl_6$)

From the linear portion of Fig. 4 we obtain the activation energy $E_a = 0.91$ kcal/mole and $\tau_c{}^0 = 3.63 \times 10^{-13}$ s. The spin-lattice relaxation time passes through a maximum at 333 K and $T_{1\,max} = 6.16$ s. Using the experimental results as explained above, we obtain $C^2 = 1.25 \times 10^{10}$ 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 NH_4^+ 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 NH_4^+. 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 $T_{1\,max} \simeq 6$ s. This is almost 3 times shorter than the $T_{1\,max} \simeq 20$ s for the ammonium compounds

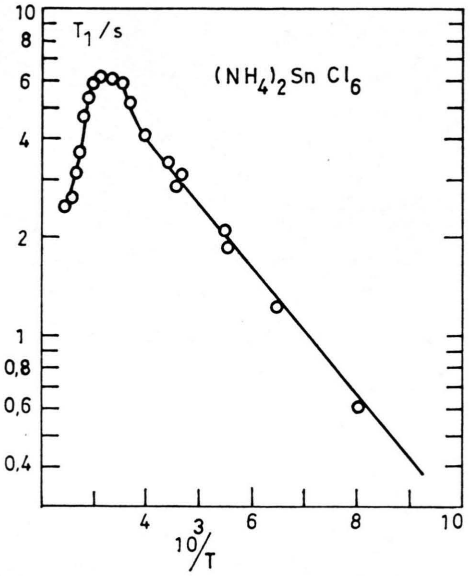

Fig. 4. ln T_1 vs $10^3/T$ (K^{-1}) for ammoniumchloro-stannate.

NH_4Br, NH_4SCN, $(NH_4)_2S_2O_8$, $(NH_4)_2Ce(NO_3)_6$, NH_4NO_3 and $(NH_4)_2Cr_2O_7$ reported lately [13]. 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 $C^2 = 1.42 \times 10^{10}$ s^{-2}. This is in good agreement with the experimentally obtained value of $C^2 = 1.27 \times 10^{10}$ s^{-2} in our previous work [13] and the calculated value $C^2 = 1.24 \times 10^{10}$ s^{-2} of Ikeda and McDowell's work [9].

Acknowledgement

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

[1] E.B. Wilson, Advan. Chem. Phys. **2**, 367 (1959).
[2] H.A. Levy and S.W. Peterson, Phys. Rev. **86**, 766 (1952).
[3] R.G.S. Morfee, L.A.K. Stavely, S.T. Walters, and D.L. Wigley, J. Phys. Chem. Sol. **13**, 132 (1960).
[4] E.L. Wagner and D.F. Hornig, J. Chem. Phys. 18, 296 (1950).
[5] D.E. Woessner and B.S. Snowden, Jr., J. Chem. Phys. **47**, 378 (1967).
[6] W. Gütler and J.W. Von Schütz, Chem. Phys. Letters **20**, 133 (1973).
[7] E.E. Ylinen, J.E. Touhi, and L.K.E. Niemela, Chem. Phys. Letters **24**, 447 (1973).
[8] M. Bonori and M. Terenzi, Chem. Phys. Letters **27**, 281 (1974).
[9] R. Ikeda and C.A. McDowell, Chem. Phys. Letters **14**, 389 (1972).
[10] A.R. Sharp and M.M. Pintar, J. Chem. Phys. **53**, 2428 (1970).
[11] K. Morimoto, J. Phys. Soc. Japan **40**, 804 (1976).
[12] J.H. Strange and M. Terenzi, J. Phys. Chem. Sol. **33**, 923 (1972).
[13] F. Köksal and S. Bahçeli, J. Chem. Soc. **74 A**, 1844 (1978).
[14] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford 1961.
[15] P.S. Hubbard, Phys. Rev. **131**, 1155 (1963).