Temperature Dependence of the Reorientational Potential and NMR Second Moment in $(PyH)AuBr_4$

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Z. Naturforsch. **60a,** 736 – 738 (2005); received July 1, 2005

In the analysis of the temperature dependence of the ^1H NMR second moment of $(PyH)AuBr_4$, it is shown to be important to take the variation of the potential of molecular motions with temperature into account.

Key words: Reorientation; NMR; Second Moment.

1. Introduction

Reorientational motion of the pyridinium ion in a low-symmetric crystal phase has been discussed by use of a model with nonequivalent potential wells [1 – 7]. Previously we have analyzed the temperature dependence of the ^1H NMR second moment M_2 of $(PyH)AuBr_4$ by assuming a nonequivalent potential for the pyridinium reorientation which is consistent with the site symmetry in the crystal. Taking a nonequivalence of the potential well into account, a gradual decrease of M_2 over a very wide temperature range with increasing temperature could be qualitatively explained [2]. However, the observed M_2 showed a more rapid decrease than that expected from the theory at high temperatures. This may be due to the temperature dependence of the potential for the pyridinium reorientation. Recently in $(PyH)AuBr_4$, we have revealed from the analysis of a Schottky-like heat anomaly the temperature dependence of the energy difference, which characterizes the nonequivalence of the potential wells, through a cooperative effect of pyridinium orientation [6]. Having the knowledge of the temperature dependence of the potential, we have attempted to explain the temperature dependence of the ^1H M_2 of $(PyH)AuBr_4$ more satisfactorily.

2. Theory

The intramolecular contribution $(M_2)_{\text{intra}}$ to the ^1H M_2 from the proton-proton dipolar interaction within the PyH^+ ion can be written [2] as

$$(M_2)_{\text{intra}} = (\Delta M_2)_{\text{intra}}\left[\frac{7a^2-2a+4}{3(1+2a)^2}+\frac{9a}{(1+2a)^2\pi}\tan^{-1}(\delta\omega_0\tau_{c1}) + \frac{3a}{(1+2a)\pi}\tan^{-1}(\delta\omega_0\tau_{c2})\right]. \quad (1)$$

Here, $(\Delta M_2)_{\text{intra}}$ is the M_2 difference of the intramolecular contributions between the rigid lattice value and the motionally narrowed one at a high enough temperature, $\delta\omega_0$ is the resonance line-width for the rigid lattice, and τ_{c1}, τ_{c2} are the correlation times of the motional process in question, which are written as follows by use of transition probability rates W_1, W_2, and W_3 defined in Figure 1:

$$\tau_{c1} = (2W_1+W_2)^{-1}, \quad (2)$$

$$\tau_{c2} = (W_2+2W_3)^{-1}. \quad (3)$$

The parameter a in (1) is given by

$$a = \exp[(E_B-E_A)/RT] = \exp(-\Delta\varepsilon/RT), \quad (4)$$

in terms of the activation energy defined in Figure 1. By use of these activation energies, the foregoing transition probability rates (expressed as jumps per unit time) can be written in accordance with the rate theory of elementary process [8 – 10] as follows:

$$W_1 = K\exp(-E_A/RT), \quad (5)$$

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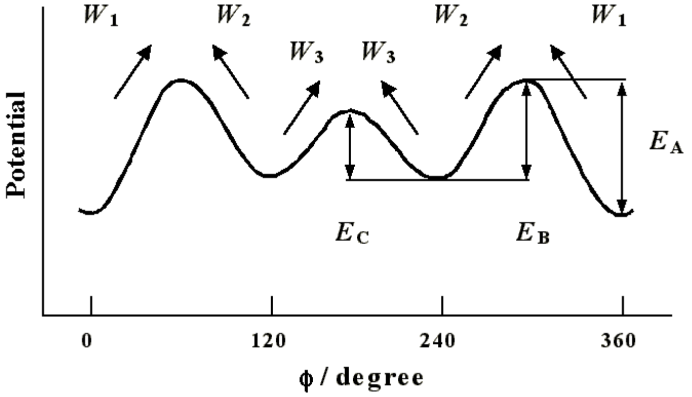

Fig. 1. Three-well potential model for the C_6' reorientation problem with disregarding the intermolecular magnetic dipolar interactions. The transition probabilities per unit time between different wells are defined by W_1, W_2, and W_3. A fictitious angle ϕ is used on the horizontal scale to represent the presence of the three nonequivalent orientations of the pyridinium ion (see [2]).

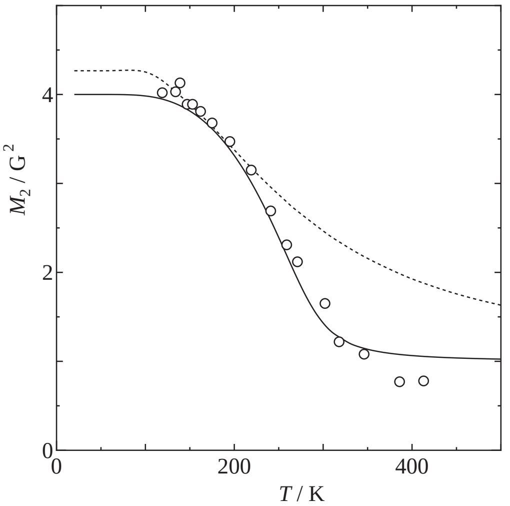

Fig. 2. Temperature dependence of ^{1}H NMR second moment M_2 of (PyH)AuBr$_4$. Circles indicate observed values. Solid and dotted curves show theoretical ones with and without taking into account temperature dependence of the reorientational potential, respectively.

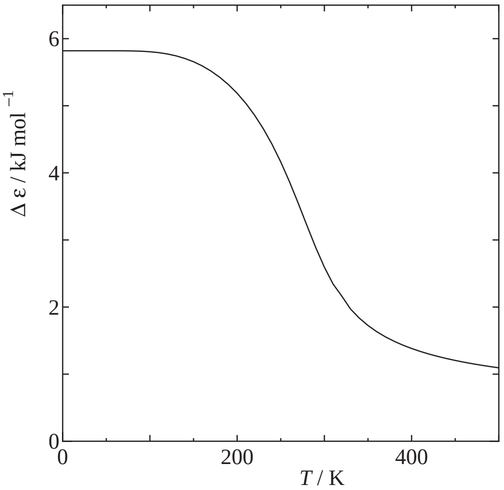

Fig. 3. Temperature dependence of the energy difference $\Delta\varepsilon = E_A - E_B$ of (PyH)AuBr$_4$ evaluated from the analysis of Schottky-like heat anomaly (see [6]).

$$W_2 = K \exp(-E_B/RT), \tag{6}$$

$$W_3 = K \exp(-E_C/RT). \tag{7}$$

3. Discussion

In [2] we have estimated the parameters in (1) for (PyH)AuBr$_4$ as follows: $E_A = 22.2$ kJ mol^{-1}, $E_B = 17.4$ kJ mol^{-1}, $E_C = 13.7$ kJ mol^{-1}, $K^{-1} = 7 \cdot 10^{-14}$ s, $\delta\omega_0 = 1.8 \cdot 10^5$ rad s^{-1}, $(\Delta M_2)_{\text{intra}} = 3.2$ G^2 (observed value). Putting these values into (1), $(M_2)_{\text{intra}}$ is calculated as shown by the dotted line in Figure 2. With the temperature independent values of these parameters, agreement between the observed values (circles) and the theoretically predicted values is poor above ca. 250 K.

On the other hand, in the analysis of the heat capacity we were able to estimate the energy difference $\Delta\varepsilon = E_A - E_B$ as a function of temperature as shown in Fig. 3 [6]. Using this $\Delta\varepsilon(T)$, determined at the respective temperature, we have estimated the first term of (1) as a function of temperature. The second and third terms in (1) can not be evaluated without knowledge of the activation energies E_A, E_B, and E_C as a function of temperature. However, in the foregoing calculations with the temperature independent parameters it was shown that the contribution from the second and the third terms is very small. Therefore it will be enough to evaluate only the first term of (1) in order to estimate $(M_2)_{\text{intra}}$ as a function of temperature.

The $(M_2)_{\mathrm{intra}}$ approximated by the first term is shown by the solid line in Figure 2. The temperature dependence of the observed M_2 is well explained over the wide temperature range for the first time by taking into account the temperature dependence of the potential wells (the activation energies). The present result emphasizes the importance of taking into account the variation of the potential with temperature for the molecular motion, even if no phase transition is concerned, when the molecular motion is taking place in a low-symmetric environment.

Acknowledgements

We thank Ayako Mogi for her collaboration in this study.

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