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^{14}N Nuclear Quadrupole Relaxation in Sulfuric Diamide and Methanesulfonamide

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The ^{14}N nuclear quadrupole resonances (NQR) in sulfuric diamide (sulfamide), $H_2NSO_2NH_2$, and methanesulfonamide, $CH_3SO_2NH_2$, were studied by the pulse method. The resonance frequency and the spin-lattice relaxation time (T_1) were measured in the temperature range from liquid nitrogen temperature to room temperature. In the case of sulfuric diamide, T_1 decreases monotonously as the temperature rises, and is dominated by the thermal torsional motion below 140 K. On the other hand, T_1 is attributed to the reorientation of the amino group in the temperature range from 200 to 240 K, whereas it is due to the reorientation of the molecule above 240 K; the activation energies in these orientations are 43.5 and 61.5 kJ·mol^{-1} respectively. In the case of methanesulfonamide, the minimum of T_1 is found near 130 K. This is caused by the rotation of the methyl group. The activation energy for this motion is calculated to be 9.6 kJ·mol^{-1}. The dominant relaxation mechanism is attributed to the reorientation of the amino group from 200 to 240 K and to the reorientation of the molecule above 240 K. The activation energies for these motions are 19.2 and 40.6 kJ·mol^{-1} respectively.

Structural studies on sulfuric diamide (sulfamide), $H_2NSO_2NH_2$, and methanesulfonamide, $CH_3SO_2NH_2$, have been performed by various spectroscopic means. The ^{14}N nuclear quadrupole resonance (NQR) study on the former compound was recently reported by our group.[1] We hope to obtain further information on the dynamical properties of the two materials from ^{14}N nuclear quadrupole relaxation. We have measured the spin-lattice relaxation time (T_1) by the pulse method and will discuss the molecular motions in these compounds.

Experimental

^{14}N NQR measurements were carried out using a pulse spectrometer, consisting of a Matec gating modulator Model 5100, a R. F. gated amplifier Model 515, and a tuned receiver Model 615, which was designed by Petersen.[2,3] The resonance frequency and the spin-lattice relaxation time were measured in the temperature range from liquid nitrogen temperature to room temperature by the repeating 90° pulse method.[4] The pulse width was about 25—50 μs. The free induction decay signal was averaged in a Nicolet Instrument Model 527 signal averager. The temperature was controlled by the method of Abe[5] or Petersen.[2,3] The temperature was measured by the use of a copper-constantan thermocouple and stabilized within ± 0.1 K. The frequency was checked by means of a frequency counter, TR-5104, from the Takeda Riken Co.

The sulfuric diamide was obtained by the reaction of sulfuryl chloride with liquid ammonia and was purified by recrystallization from acetone.[6] On the other hand, the methanesulfonamide was prepared by the reaction of methanesulfonyl chloride with liquid ammonia and was purified by recrystallization from 1:2 ethanol–benzene.[7] In the present measurements, we used about a 20-g portion of each sample melted in a glass ampoule.

Results and Discussion

Generally a pair of ^{14}N NQR frequencies, ν_- and ν_+, are observed for a species of nitrogen atom:

$$\nu_\pm = \frac{|e^2Qq|}{4h}(3\pm\eta), \tag{1}$$

where $|e^2Qq/h|$ and η are the quadrupole coupling constant and the asymmetry parameter, respectively. In methanesulfonamide, a pair of resonance lines were found: $\nu_-=2442.1$ kHz and $\nu_+=3400.2$ kHz (at liquid nitrogen temperature). The quadrupole coupling constant and asymmetry parameter derived from these frequencies are as follows: $|e^2Qq/h|=3894.9$ kHz and $\eta=49.20\%$. These values are to be compared with those for sulfuric diamide: $|e^2Qq/h|=3905.3$ kHz and $\eta=50.82\%$.[1]

The temperature dependence of the resonance frequencies, ν_- and ν_+ lines, in sulfuric diamide and methanesulfonamide is shown in Fig. 1. The temperature dependence in sulfuric diamide is smaller than that in methanesulfonamide. This fact may be explained by the intermolecular interaction, probably by the difference in the number of the hydrogen bonds between sulfuric diamide and methanesulfonamide. That is, the vibration of the nitrogen atom in sulfuric diamide is more suppressed than in methanesulfonamide.

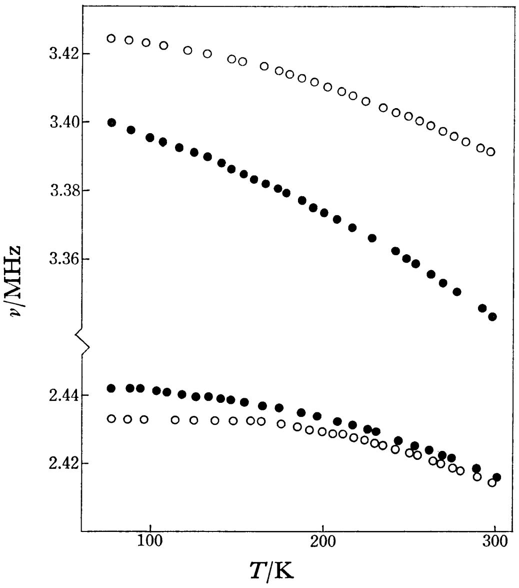

Fig. 1. The temperature dependence of the resonance lines in sulfuric diamide (○) and methanesulfonamide (●).

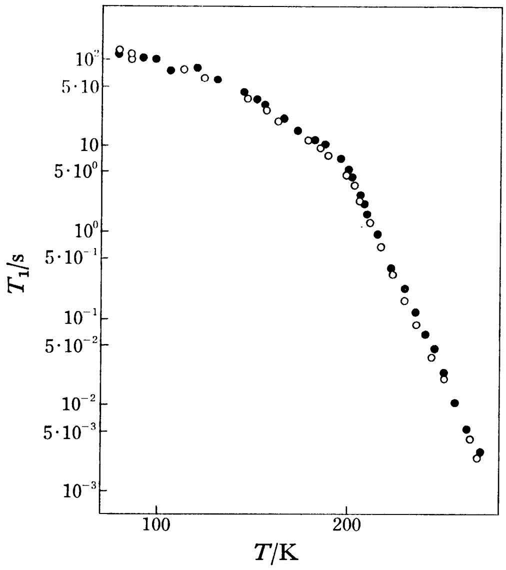

Fig. 2. The temperature dependence of the spin-lattice relaxation times in sulfuric diamide. ○: ν_- line; ●: ν_+ line.

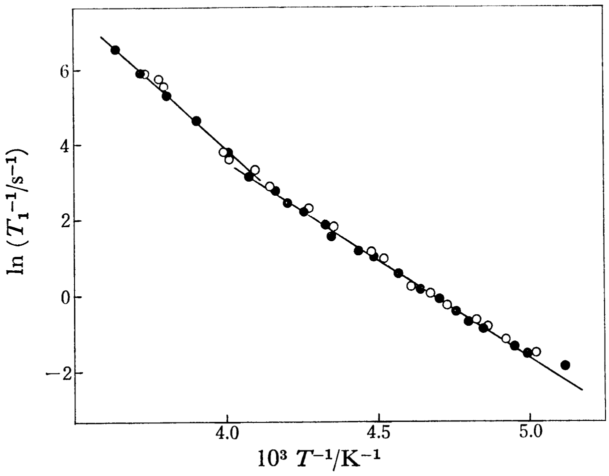

Fig. 3. $\ln(1/T_1)$ *vs.* $10^3/T$ in sulfuric diamide. ○: ν_- line; ●: ν_+ line.

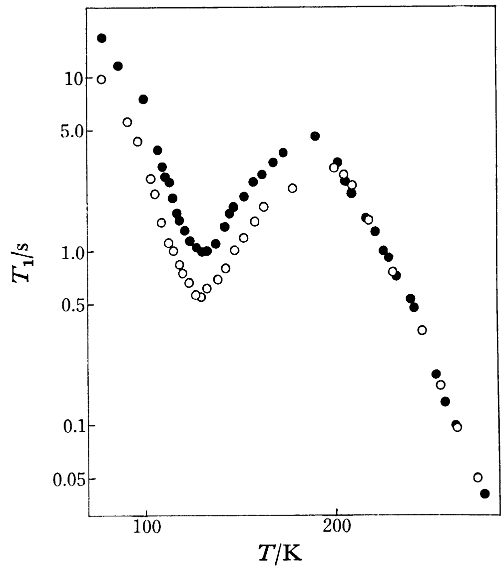

Fig. 4. The temperature dependence of the spin-lattice relaxation times in methanesulfonamide. ○: ν_- line; ●: ν_+ line.

The temperature dependence of the spin-lattice relaxation times (T_1) for ν_- and ν_+ lines in sulfuric diamide is shown in Fig. 2. Both curves are coincident within the experimental error. This fact suggests that the molecular motions equally contribute to T_1 for ν_- and ν_+ lines.

Below 140 K, the spin-lattice relaxation time is determined by torsional lattice vibration and is dominated by indirect two-phonon processes so that $1/T_1 \propto T^2$.

Above 200 K, the spin-lattice relaxation time drops exponentially as the temperature rises. This process can probably be attributed to the reorientation of the amino group around the S–N bond or to the reorientation of the molecule. In this case, the relaxation time is given by the following equation:[8]

$$1/T_1 = C\tau/(1+\omega_i^2\tau^2) \qquad (i=+,\ -,\ \Delta), \tag{2}$$

where C is a constant related to the intrinsic nature of the molecular motion, τ is the correlation time, and ω_i is the resonance angular frequency. In the low temperature region of the T_1 minimum, $\omega_i\tau \gg 1$, and assuming the Arrhenius' relation for the correlation time, the following equation holds:

$$\tau = \tau_0 \exp(E_a/RT), \tag{3}$$

where τ_0 is the inverse frequency factor and E_a is the activation energy of the motion. Accordingly, we get

$$1/T_1 = f(\omega_i)\cdot\exp(-E_a/RT). \tag{4}$$

Equation 4 can be rewritten as follows:

$$\ln(1/T_1) = -E_a/RT + f'(\omega_i) \tag{5}$$

where $f'(\omega_i)$ is a function of ω_i, whose temperature dependence is negligible. In Fig. 3, the $\ln(1/T_1)$ value is plotted as a function of $1/T$. A break point is found near $10^3/T=4.2$/K (about 240 K) as is shown in Fig. 3. This suggests that T_1 above 240 K and T_1 below 240 K are dominated by different molecular motions. That is, the dominant relaxation mechanism below 240 K is considered to be caused by the reorientation of the amino group around the S–N bond, whereas that above 240 K is brought about by the reorientation of the molecule. In fitting Eq. 5 to the experimental T_1 values, the activation energies for these motions are determined: 43.5±4.3 kJ·mol^{-1} for the former motion and 61.5±6.2 kJ·mol^{-1} for the latter.

The temperature dependence of the spin-lattice relaxation times for ν_- and ν_+ lines in methanesulfonamide is shown in Fig. 4. In the temperature region from liquid nitrogen temperature to 200 K, T_1 for the ν_+ line, *i.e.*, $T_1(\nu_+)$, are longer than those for the ν_- line, *i.e.*, $T_1(\nu_-)$. However, above 200 K both relaxation times are coincident within the experimental error. This fact suggests that the molecular motion contributes differently to $T_1(\nu_-)$ and $T_1(\nu_+)$ below 200 K, but equally above 200 K.

In the temperature range from liquid nitrogen temperature to 170 K, a T_1 minimum is found near 130 K, as is shown in Fig. 4. This is caused by the introduction of the methyl group, and accordingly by the rotation of the group. The activation energy for this motion is calculated to be 9.6±0.9 kJ·mol^{-1} by

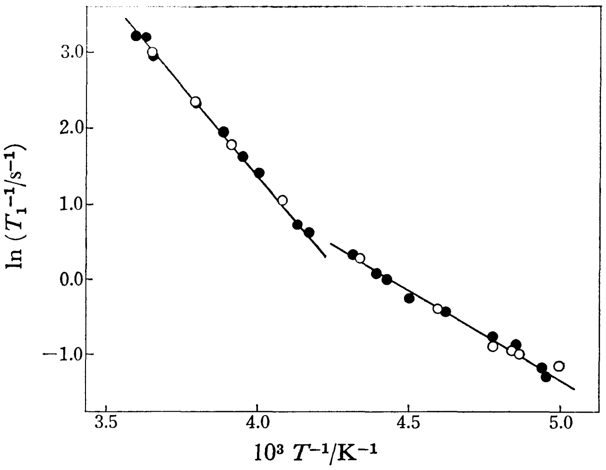

Fig. 5. ln(1/T_1) *vs.* $10^3/T$ in methanesulfonamide. ○: ν_- line; ●: ν_+ line.

the BPP theory.[9] This value is to be compared with 9.2 kJ·mol^{-1} for the rotation of the methyl group in acetonitrile.[10]

Above 200 K, T_1 drops exponentially as the temperature rises; this is shown in Fig. 4. As is shown in Fig. 5, in the ln(1/T_1) plot against 1/T, a break point is found near $10^3/T$=4.2/K (about 240 K). This fact is explained in the same manner as for sulfuric diamide. That is, T_1 is dominated by the reorientation of the amino group around the S–N bond below 240 K and by the reorientation of the molecule above 240 K. In fitting Eq. 5 to the experimental T_1 values, the E_a values are determined: 19.2±1.9 kJ·mol^{-1} for the former motion and 40.6±4.1 kJ·mol^{-1} for the latter. These values are smaller than those in sulfuric diamide. This suggests that the intermolecular interaction in methanesulfonamide is weaker than that in sulfuric diamide, that is, the number of the hydrogen bonds per molecule in the former compound is smaller than that in the latter.

Takagi *et al.*[11] calculated the energy of the hydrogen bonds in sulfuric diamide to be 19.7 kJ·bond^{-1}, assuming that there are only two N–H···O hydrogen bonds per molecule, although there are other weak N–H···N hydrogen bonds.[12] Assuming that the activation energy (E_a) for the reorientation of the amino group comes mostly from breaking the hydrogen bonds, N–H···O, it is estimated to be 39.3 kJ·mol^{-1}, which is in good agreement with our experimental value, 43.5 kJ·mol^{-1}. In the case of methanesulfonamide, the E_a value for the reorientation of the amino group is 19.2 kJ·mol^{-1}, which is nearly equal to 19.7 kJ·bond^{-1}. Accordingly, it is concluded that there is one hydrogen bond, N–H···O, per molecule, although there may exist other weak hydrogen bonds, for example N–H···N.

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