Structural Phase Transition of N,N-Dimethylnitramine as Studied by ^{14}N Nuclear Quadrupole Resonance *

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The ^{14}N nuclear quadrupole relaxation time T_{1Q} and resonance frequencies ν_+, ν_-, and ν_d of N,N-dimethylnitramine were measured between 14 and 313 K. The frequency increase of ν_+ and ν_- observed below T_c (108 K) is explained by the increase of pπ electrons in the amino nitrogen caused by the deformation of the molecular skelton, which is planar above T_c. The sharp T_{1Q} minima for ν_+ and ν_- observed at T_c are attributed to the softening of vibration modes on both sides of T_c. The fluctuation of the nitrogen-hydrogen magnetic dipolar interaction due to CH_3 reorientation was detected as a broad T_{1Q} minimum observed around 84 K. A logarithmic divergence of T_{1Q}^{-1} observed on the high-temperature side of T_c suggests the presence of a diffusive or overdamped-type soft mode.

Key words: Molecular crystal; Phase transition; Soft mode; NQR; Spin-lattice relaxation.

Introduction

N,N-Dimethylnitramine (DMN), $(CH_3)_2NNO_2$, shows a displacive phase transition at $T_c = 107$ K, accompanied by a very small transition entropy ($\Delta S = 0.17$ J K^{-1} mol^{-1}) [1, 2]. A soft mode was detected by Raman spectroscopy in the low-temperature phase (space group P2$_1$/c, $Z = 4$) [3] with its nonplanar structure of the $C_2N_2O_2$ skelton, while a planar structure was found in the high-temperature phase (space group P2$_1$/m, $Z = 2$). The structural change from the high- to low-temperature phase can essentially be described by a rotation of the whole molecule (ca. 4° at $(T_c - 20)$ K) and the molecular deformation which changes the angle between the N–N bond and the C–N–C plane from zero to ca. 10° at $(T_c - 20)$ K [4]. This soft mode is, accordingly, expected to be of a composite type, assignable to an internal mode coupled with a molecular rotation.

In molecular crystals, soft mode behaviour has so far been observed only in a few systems: chloranil [5–7], biphenyl [8–10], and s-triazine [11, 12] in which the symmetry-breaking distortion is rotation of the whole molecule, torsion about the central single bond, and ferroelastic distortion, respectively. For the study of the displacive phase transition in molecular crystals, the present compound offers another candidate with a complex combination of the intra- and intermolecular forces.

The present study intends to obtain information on the dynamical properties of the phase transition of DMN by measuring the spin-lattice relaxation time T_{1Q} of ^{14}N nuclear quadrupole resonance.

Experimental

The sample of DMN was supplied from Hitachi Chemical Co., Ltd. The ^{14}N NQR spin-lattice relaxation time T_{1Q} and resonance frequencies were measured using a pulsed spectrometer previously reported [13, 14], with accuracies of ca. ±10% and ±0.1 kHz, respectively. The NQR frequency was measured by directly matching the carrier frequency to the NQR signal. T_{1Q} was determined by the use of the steady state pulse method [15–17]. The sample temperature was controlled within ±0.2 K and measured with an accuracy of ±0.3 K using copper-constantan and gold + 0.07% iron-chromel thermocouples above and

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below 77 K, respectively. The ^1H NMR spin-lattice relaxation time T_1 was measured at the Larmor frequencies of 11.2, 35.8, and 44.2 MHz with a home-made spectrometer applying the inversion recovery method. A chromel-constantan thermocouple was used to determine the temperature within ± 1 K.

Results and Discussion

At room temperature (291 $\pm$ 1 K), a set of resonance lines ν_+, ν_-, and ν_d, assignable to the amino nitrogen, were detected at 4553 $\pm$ 0.5, 2891 $\pm$ 0.5, and 1662 $\pm$ 1 kHz, respectively ($e^2Qq/h = 4963 \pm 1$ kHz, $\eta = 0.6698 \pm 0.0005$). The temperature dependences of ν_+ and ν_- showed a cusp at $T_c = 108$ K as shown in Figure 1. No discontinuity in frequency was observed at T_c, indicating second order nature of the phase transition. Figure 2 shows the temperature dependences of T_{1Q} of ν_+ and ν_-, both exhibiting a sharp minimum at T_c. This enhancement of the relaxation rate indicates the existence of a soft mode in the high- and low-temperature phases. A broad minimum was observed at ca. 84 K, suggesting that the contribution from another relaxation mechanism is operative in the low-temperature region. Above ca. 170 K, the main relaxation mechanism may be due to lattice vibrations and other molecular motions. In the whole temperature range studied, no remarkable difference in T_{1Q} was observed for ν_+ and ν_-. In Table 1 the resonance frequencies and T_{1Q} values at selected temperatures are listed.

The temperature dependences of ^1H NMR T_1 are shown in Figure 3. The T_1 showed broad minima around T_c. Above the T_1 minimum temperature, the only long component of T_1 is plotted in Fig. 3, since the magnetization recovery was appreciably nonexponential.

Molecular Deformation and NQR Frequency Shift below T_c

The marked increase of both ν_+ and ν_- frequencies upon cooling below T_c is attributable to the structural change associated with the phase transition. According to X-ray and neutron diffraction analyses [4], the major structural changes are the molecular rotation by the angle ω about an axis parallel to the crystal *a*-axis, the torsion of the NO_2 group by an angle ε around N–N bond axis, and the amino group deformation which is defined by the angle δ between the C–N–C plane and the N–N bond. Among these structural deformations, the deformation δ is expected to have the most important influence to the electronic state of the amino nitrogen. We tried to explain the change of the NQR parameters by the amino group deformation δ, applying the Townes-Dailey theory [18].

Here, we need expressions which can describe the electron population in the amino nitrogen through the

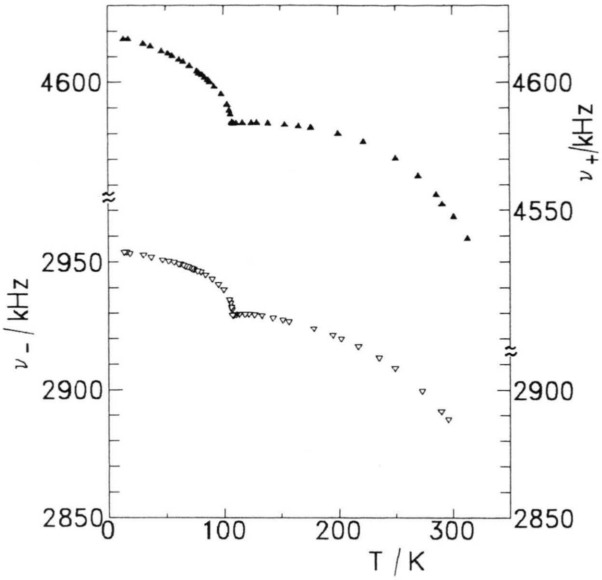

Fig. 1. Temperature dependences of ^{14}N NQR frequencies ν_+ (▲) and ν_- (▽) of N,N-dimethylnitramine.

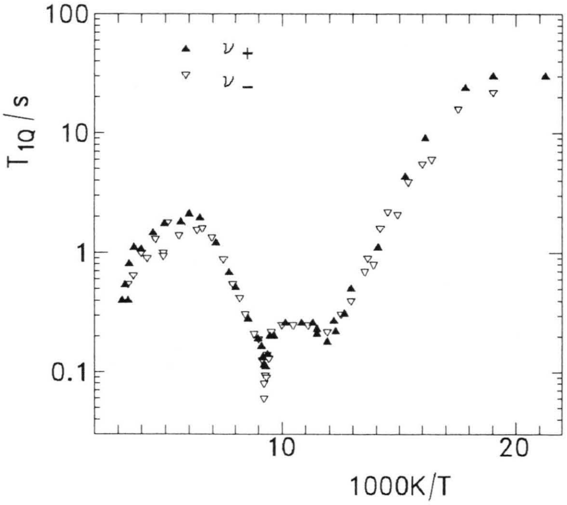

Fig. 2. Temperature dependences of ^{14}N NQR spin-lattice relaxation times T_{1Q} of N,N-dimethylnitramine.

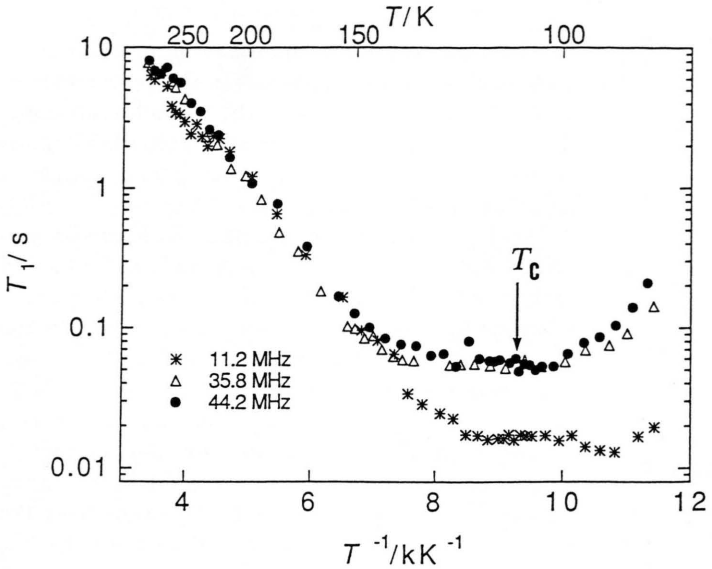

Fig. 3. Temperature dependences of ^{1}H NMR spin-lattice relaxation times T_1 of N,N-dimethylnitramine measured at the Larmor frequencies of 11.2 (✳), 35.8 (△), and 44.2 (●) MHz.

continuous change from the planar sp^2 hybridization ($\alpha = 1$) to tetrahedral sp^3 hybridization ($\alpha = 3/4$) by changing the hybridization parameter α. For this purpose we employ valence orbitals of the amino nitrogen given by [19, 20]

$$\psi_\pi \;= (1-\alpha)^{1/2}\,\phi_s + \alpha^{1/2}\,\phi_{pz}\,, \tag{1}$$

$$\psi_{NN} = (\alpha/3)^{1/2}\,\phi_s - ((1-\alpha)/3)^{1/2}\,\phi_{pz} - (2/3)^{1/2}\,\phi_{py}\,, \tag{2}$$

$$\psi_{NC1} = (\alpha/3)^{1/2}\,\phi_s - ((1-\alpha)/3)^{1/2}\,\phi_{pz} + (1/2)^{1/2}\,\phi_{px} + (1/6)^{1/2}\,\phi_{py}\,, \tag{3}$$

$$\psi_{NC2} = (\alpha/3)^{1/2}\,\phi_s - ((1-\alpha)/3)^{1/2}\,\phi_{pz} - (1/2)^{1/2}\,\phi_{px} + (1/6)^{1/2}\,\phi_{py}\,, \tag{4}$$

where

$$\alpha = (1 - 3\cos^2\theta)/(1 - \cos^2\theta)\,. \tag{5}$$

θ denotes the angle between the z-axis of lone-pair orbital ψ_π and the three bonds of nitrogen assumed to make the same angle with the z-axis. This angle is in turn related to the deformation angle δ:

$$\cos\delta = (1 - 3\cos^2\theta)/(1 + 3\cos^2\theta)^{1/2}\,. \tag{6}$$

Denoting the occupation numbers of electron in the valence orbitals ψ_π, ψ_{NN}, ψ_{NC1}, and ψ_{NC2} by π, σ_{NN}, σ_{NC}, and σ_{NC}, respectively, the following equations are derived by Townes-Dailey analysis [21]:

$$\alpha\pi - \sigma_{NC} \;= (4/3\,A)\,\nu_-\,, \tag{7}$$

$$\sigma_{NC} - \sigma_{NN} = (2/A)\,(\nu_+ - \nu_-)\,, \tag{8}$$

Table 1. Temperature dependences of ^{14}N NQR frequencies ν_+ and ν_- and spin-lattice relaxation times T_{1Q} of amino nitrogen of N,N-dimethylnitramine.

T/K	ν_+/kHz	T_{1Q}/s	T/K	ν_-/kHz	T_{1Q}/s
14	4616.8	–	14	2953.6	–
31	4615.0	–	30.5	2952.7	–
52.5	4611.2	30 ± 10	52.5	2950.4	22 ± 10
56	4610.2	24 ± 10	57	2950.0	16 ± 10
62	4608.8	9	61	2949.2	6
77	4604.2	0.5	77	2946.6	0.4
84	4601.65	0.18	84	2945.0	0.22
98.5	4595.1	0.26	100	2939.2	0.25
105.5	4588.7	0.20	105.9	2934.1	0.13
107.5	4584.2	0.11	107.3	2931.4	0.09
111.5	4583.8	0.19	111	2929.5	0.19
125	4583.9	0.51	127	2929.4	0.55
166	4582.7	2.1	157	2926.7	1.55
222	4576.6	1.46	235	2912.5	0.9
270	4563.2	1.1	273	2899.6	0.65
301	4547.4	0.54	290	2891.6	0.55

where $A = e^2 Q\, q_p/\mathrm{h}$ is the quadrupole coupling constant of a single 2p electron. Since it is expected that the occupation number π is much more influenced by the amino group deformation δ than σ_{NC} or σ_{NN}, as a first approximation we assumed that σ_{NC} and σ_{NN} are constant. Then, the increase of ν_- below T_c leads to the increase of ν_+, and these increases are ascribable to the increase of π. The molecular deformation from the high-temperature planar structure causes a decrease of the π-bond character between the amino and nitro nitrogens, which increases the number of pπ electrons of the amino nitrogen.

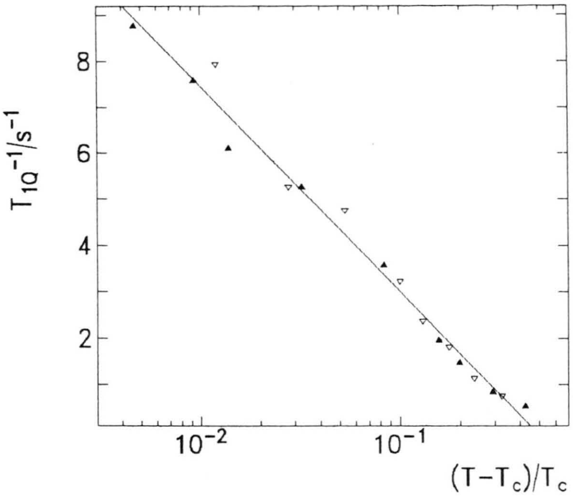

Fig. 4. Logarithmic divergence of spin-lattice relaxation rate T_{1Q}^{-1} of N,N-dimethylnitramine, in the temperature range $T_c < T < T_c + 35$. The solid line represents the fitted empirical expression $T_{1Q}^{-1}/s^{-1} = -1.9 \ln[(T-T_c)/T_c] - 1.4$.

Spin-Lattice Relaxation

As shown in Fig. 2, T_{1Q} becomes anomalously short in the range $7 < 10^3$ K$/T < 16$, contradicting the normal lattice vibrational model [22]. T_{1Q} of nitrogen located close to a methyl group often shows such anomalous behaviour, which can be interpreted by the fluctuation of the nitrogen-hydrogen magnetic dipolar interaction due to the methyl group reorientation [23–25].

Figure 3 shows ^{1}H NMR T_1 of DMN as a function of T^{-1} observed at the Larmor frequencies of 11.2, 35.8, and 44.2 MHz. Broad minima of ^{1}H T_1 were observed around T_c. Nonexponential behaviour was observed in the magnetization recovery above the T_1 minimum temperature. These ^{1}H T_1 data are explainable using the symmetry-restricted spin-diffusion theory [26, 27]. The preliminary calculations suggest that the observed broad minima result from the overlapping of the two minima each in the high- and low-temperature phases, in which the crystallographically nonequivalent methyl groups in a molecule [4] reorient with almost the same frequency, giving a single T_1 minimum at each phase.

The T_{1Q} minimum observed at ca. 84 K can be connected with one of the minima caused by the methyl reorientation. The T_{1Q} minimum corresponding to the other methyl reorientation seems to be masked by the fast relaxation mechanism associated with the soft mode transition at $T_c = 108$ K. The slope of the ^{1}H T_1 vs. T^{-1} plots gives the activation energy of 11.2 kJ mol^{-1} on the high-temperature side of the T_1 minimum, whereas T_{1Q} in $7 < 10^3$ K/T<9 gives 8.5 kJ mol^{-1}, implying a different T_{1Q} origin from the methyl reorientation. We therefore assigned the T_{1Q} decrease observed for $T > T_c$ to the lattice fluctuations due to the displacive phase transition.

As shown in Fig. 4, the observed relaxation rate T_{1Q}^{-1} fits to a logarithmic expression given by

$$T_{1Q}^{-1}/s^{-1} = -1.9 \ln[(T-T_c)/T_c] - 1.4 \qquad (9)$$

in the temperature range $T_c < T < T_c + 35$, where $T_c = 108$ K. This result suggests that the soft mode involved is of the diffusive or overdamped type with an anisotropic interaction [28].

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