^{14}N Nuclear Quadrupole Resonances of Sulfuric Diamide and Its Derivatives

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The study of ^{14}N nuclear quadrupole resonance (NQR) was performed on sulfuric diamide (sulfamide) and its methyl derivatives, such as *N,N*-dimethylsulfamide and tetramethylsulfamide. The ^{14}N NQR parameters for sulfuric diamide and tetramethylsulfamide were ($|e^2Qq|=3905.3$ kHz; $\eta=0.5082$) and ($|e^2Qq|=5325.9$ kHz; $\eta=0.1768$) respectively. In the case of *N,N*-dimethylsulfamide, the parameters were ($|e^2Qq|=4022.9$ kHz; $\eta=0.4799$) for the nitrogen atoms of NH_2 groups and ($|e^2Qq|=5125.0$ kHz; $\eta=0.2024$) for the nitrogen atoms of $N(CH_3)_2$ groups. From the temperature dependence of the resonance lines due to nitrogen atoms in sulfuric diamide, tetramethylsulfamide, and the NH_2 group of *N,N*-dimethylsulfamide, it is considered that the hydrogen bonds in sulfuric diamide are stronger than those in *N,N*-dimethylsulfamide. On the other hand, the electron densities for the N–S bond in sulfuric diamide and its methyl derivatives were derived from the corresponding NQR parameters.

The structural studies of sulfuric diamide have been performed by various spectroscopic means, but not by the nuclear quadrupole resonance (NQR). The NQR method is of especial interest in clarifying the charge distribution on the nitrogen atom. Therefore, we planned to examine ^{14}N NQR in sulfuric diamide and its methyl derivatives such as *N,N*-dimethylsulfamide and tetramethylsulfamide. On the basis of the ^{14}N NQR studies, the hydrogen bond in sulfuric diamide was compared with that in *N,N*-dimethylsulfamide, and the charge distributions on the nitrogen atoms in sulfuric diamide and its derivatives were compared with those in urea and tetramethylurea.

Experimental

The ^{14}N NQR spectra of these compounds were obtained by the use of a frequency-modulated spectrometer described previously.[1] The resonance frequencies were measured by a heterodyne-type frequency meter whose frequency was checked by means of a frequency counter, TR-5578, from the Takeda Riken Co. The Zeeman field was supplied by a Helmholz coil, 40 cm in diameter and 20 cm in gap width. Measurements were carried out at several temperatures between liquid nitrogen and room temperature. The temperatures were measured by the use of a copper-constantan thermocouple.

The sulfuric diamide and tetramethylsulfamide were obtained by the reactions of sulfuryl chloride with liquid ammonia[2] and liquid dimethylamine[3] respectively. The *N,N*-dimethylsulfamide was prepared by the reaction of dimethylsulfamyl chloride with liquid ammonia.[4] These samples were purified by recrystallization from organic solvents, such as acetone, ethyl ether, and ethyl alcohol. In the cases of sulfuric diamide and tetramethylsulfamide, about a 10-g portion of each sample was melted in a tube and used for measurements. In the case of *N,N*-dimethylsulfamide, about a 6-g single crystal was prepared by the Bridgman-Stockbarger method and examined.

Results and Discussion

Generally a pair of ^{14}N NQR frequencies, ν_I and ν_{II}, are observed for a species of nitrogen atoms:

$$\nu_I = |e^2Qq|(3-\eta)/4, \qquad \nu_{II} = |e^2Qq|(3+\eta)/4, \tag{1}$$

where $|e^2Qq|$ and η are the quadrupole coupling constant and the asymmetry parameter respectively. In sulfuric diamide and tetramethylsulfamide, a pair of resonance lines was found. The quandrupole coupling constants and asymmetry parameters derived from these frequencies are listed in Table 1. In *N,N*-dimethylsulfamide, four resonance lines were paired in two groups, depending upon the frequency shifts due to the influence of the Zeeman field. The two pairs of resonance frequencies due to NH_2 and $N(CH_3)_2$ in *N,N*-dimethylsulfamide are not very different from the corresponding pairs of the related compounds, sulfuric diamide and tetramethylsulfamide. The quadrupole coupling constants and asymmetry parameters observed are also listed in Table 1.

Table 1. NQR parameters in sulfuric diamide and its methyl derivatives

Compound	ν_I (kHz)	ν_{II} (kHz)	$\lvert e^2Qq\rvert$ (kHz)	η (%)
$O_2S(NH_2)_2$	2432.8	3425.1	3905.3	50.82
$O_2S(NH_2)N(CH_3)_2$	2534.5	3499.9	4022.9	47.99[a]
	3584.4	4103.1	5125.0	20.24[b]
$O_2S(N(CH_3)_2)_2$	3759.0	4229.8	5325.9	17.68

a) NQR parameters due to NH_2. b) NQR parameters due to $N(CH_3)_2$.

In the case of *N,N*-dimethylsulfamide, the temperature dependence of the ν_I of the NH_2 group was observed only in the temperature range from 148 K to 173 K. The other three resonance lines of the same compound were too weak to be found in this temperature range. Figure 1 shows the temperature dependence of the ν_I frequencies observed in sulfuric diamide, tetramethylsulfamide, and *N,N*-dimethylsulfamide. The absolute temperature coefficient of resonance frequencies in the NH_2 group can be expected to be larger than that in the $N(CH_3)_2$ group, because a hydrogen atom is much lighter than a methyl group. However, this is not the cases in sulfuric diamide and tetramethylsulfamide, as is shown in Fig. 1. This fact can be explained by the intermolecular

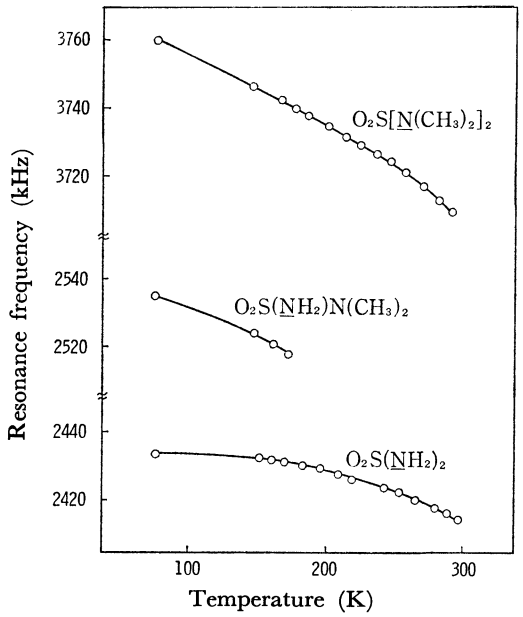

Fig. 1. Temperature dependence of resonance line, ν_I, of the nitrogen atoms (marked by underlines) in sulfuric diamide, tetramethylsulfamide and *N,N*-dimethylsulfamide.

interaction by which the nitrogen atom in sulfuric diamide is fixed by three hydrogen bonds, N–H···O (3.02 Å), N–H···N (3.18 Å) and N···H–N (3.18 Å),[5] while there are no hydrogen bonds in tetramethylsulfamide.[6] That is, the vibration of the nitrogen atom in sulfuric diamide is more suppressed than in tetramethylsulfamide. On the other hand, Fig. 1 shows that the temperature dependence in *N,N*-dimethylsulfamide is nearly equal to that in tetramethylsulfamide. This suggests that the hydrogen bonds in *N,N*-dimethylsulfamide are weaker than in sulfuric diamide.

The ∠HNH bond angle in sulfuric diamide was recently determined by Pedersen to be 110.6°,[7] which is close to the tetrahedral angle (109.5°). However, as the S–N bond length determined by Trueblood and Mayer, 1.60 Å,[5] is appreciably shorter than the single-bond length predicted from the covalent atomic radii, about 1.73 Å, the shape of the NH_2 group may be considered to be nearly planar. Therefore, we assumed sp^2-hybridization for the nitrogen σ-bond orbitals. The crystal structure of tetramethylsulfamide was determined by Jordan *et al.*[6] Despite the ∠CNC bond angle, 112.9°, which is close to the tetrahedral angle, the three bonds around the nitrogen atom in the $N(CH_3)_2$ group lie in a plane. Therefore, we assumed that the nitrogen σ-bond orbitals are sp^2-hybrids. The structure of *N,N*-dimethylsulfamide, however, is not known; therefore, we assumed that both two non-equivalent nitrogen atoms form an sp^2-hybridization and that the ∠HNH and ∠CNC bond angles are 110.6° and 112.9° respectively.

The electron densities on nitrogen atoms in sulfuric diamide and its methyl derivatives were derived from the following equations by Lucken:[8]

Table 2. Electron densities in sulfuric diamide, urea and their methyl derivatives

Compound	Lone pair	σ_{NC} or σ_{NS}	σ_{NH} or σ_{NCH_3}
$OC(NH_2)_2$	1.68	1.21	1.33
$OC[N(CH_3)_2]_2$	1.76	1.21	1.22
$O_2S(NH_2)_2$	1.74	1.10	1.38
$O_2S(NH_2)N(CH_3)_2$	1.75	1.10	1.37[a]
	1.75	1.08	1.22[b]
$O_2S[N(CH_3)_2]_2$	1.78	1.10	1.22

a) Electron densities due to NH_2. b) Electron densities due to $N(CH_3)_2$.

$$2\eta\cdot|e^2Qq/e^2Qq_p| = 3(c-b)(1-\cot^2\gamma), \quad (2)$$

$$(1-\eta/3)\cdot|e^2Qq/e^2Qq_p| = a-c, \quad (3)$$

where a is the electron density in the lone-pair orbital; b and c, the σ-electron densities in the N–S bond and N–H or N–CH_3 bond respectively; 2γ, the ∠HNH or ∠CNC bond angle, and $|e^2Qq_p|$, the quadrupole coupling constant due to one 2p-electron of a nitrogen atom. In the cases of the $N(CH_3)_2$ groups of tetramethylsulfamide and *N,N*-dimethylsulfamide, it is assumed that $|e^2Qq_p|$ is 9 MHz and that the σ-electron density for the N–CH_3 bond is the same as that for the N–CH_3 bond in tetramethylurea (1.22);[9] therefore, the values of a and b parameters can be evaluated. In the cases of the NH_2 groups of sulfuric diamide and dimethylsulfamide, the σ-electron density in the N–S bond is assumed to be the same as in tetramethylsulfamide; therefore, the values of a and c can be evaluated. Table 2 lists the values obtained in sulfuric diamide, urea, and their methyl derivatives. It may be seen that the σ-electron densities for the N–S bonds in sulfuric diamide and its methyl derivatives are smaller than for the N–C bond in the amido group in urea and tetramethylurea. The ^{35}Cl NQR frequencies in sulfuryl chloride, O_2SCl_2, 37.822 MHz and 37.613 MHz,[10] are higher than those in phosgene, $OCCl_2$, 36.225 MHz and 35.081 MHz.[11] Accordingly, the Cl–S bond in sulfuryl chloride is more covalent than the Cl–C bond in phosgene. From these facts, it may be concluded that the electron-attracting ability of an SO_2 group is stronger than that of a CO group.

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