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The Chlorine Nuclear Quadrupole Resonance of Several Oxygen-chlorine Bonds

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It seemed that it would be of interest to investigate the chlorine electronic structure in the O–Cl bond by means of the nuclear quadrupole resonance (NQR), since the oxygen atom is more electronegative than the chlorine atom and since various coordination states of the chlorine atom appear in the compounds with O–Cl bonds. Although many reports have been published on NQR studies of the chlorates in which the chlorine atom is bound by three oxygen atoms, there have been few reports on the other compounds with O–Cl bonds. Therefore, we have observed the ^{35}Cl NQR frequencies of the O–Cl bonds in the following compounds: *t*-butyl hypochlorite, *t*-amyl hypochlorite, sodium chlorite and its trihydrate, and silver chlorite. In these compounds, the two organic hypochlorites contain a chlorine atom bound by only one oxygen atom, whereas the chlorine atom in the chlorite is bound by two oxygen atoms. Furthermore, we have measured the NQR Zeeman effect using the single crystal of $NaClO_2 \cdot 3H_2O$.

Experimental

The sodium chlorite trihydrate was obtained by recrystallization from an aqueous solution of commercial $NaClO_2$. The single crystal was grown from its saturated aqueous solution at about 35 °C. The anhydrate salts were obtained by drying $NaClO_2 \cdot 3H_2O$ over KOH in a desiccator *in vacuo*. The silver chlorite was prepared by the reaction of $NaClO_2$ with $AgNO_3$. The alkyl hypochlorites were prepared by bubbling chlorine gas through an aqueous solution of the relevant alcohol and sodium hydroxide.

The NQR spectrometer was a self-quenching, super-regenerative oscillator with frequency modulation; the ab-

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1) J. S. Rigden and S. S. Butcher, *J. Chem. Phys.*, **40**, 2109 (1964).

Table 1. ^{35}Cl nuclear quadrupole resonance frequencies of several O–Cl bonds

Compound	Resonance frequency, MHz[a]	
	77 K	299 K
t-BuOCl	55.278	—
	54.941	—
t-AmOCl	55.492	—
$AgClO_2$	55.160[3]	54.052[3]
$NaClO_2$	53.342	51.802[3]
$NaClO_2 \cdot 3H_3O$	53.502	51.121

a) Experimental error is within ±0.01 MHz.

sorption lines were displayed on an oscilloscope. A Zeeman magnetic field was applied by means of a Helmholtz coil.

Results and Discussion

Table 1 shows the resonance frequencies at the temperature of liquid nitrogen and at room temperature. It is noteworthy that all the resonance frequencies in Table 1 are quite high compared with those of the usual chlorine compounds.

If the asymmetry parameter of the field gradient at the chlorine atom in R–OCl is assumed to be negligible, referred to $\eta=0.04$ for gaseous CH_3OCl,[1] the quadrupole coupling constant of 110.22 MHz (average) is obtained for *t*-BuOCl, and that of 110.98 MHz, for *t*-AmOCl, at 77 K. These values are slightly higher than that of atomic chlorine. This is an expected tendency, taking into account the electronegativity difference between oxygen and chlorine. Assuming the s character of the O–Cl bond to be 0.12, as in the case of the N–Cl bond,[2] and no dπ-pπ bonding, the partial charge on the chlorine atom is $+0.16\,e$. This is in accordance with the fact that R–OCl is used as a chlorinating reagent in organic syntheses.

The resonance frequencies of $NaClO_2$ and $AgClO_2$ have been reported by Ragle;[3] they are in good agreement with our results, listed in Table 1. We have newly observed the resonance frequencies of $NaClO_2 \cdot 3H_2O$ and measured the Zeeman effect on its single crystal. Only one zero-splitting pattern was observed, as is shown in Fig. 1. This is consistent with the triclinic lattice of this compound. The asymmetry parameter of the field gradient was derived from the usual equation, using the least-squares method, as 0.52 ± 0.02. From this value, the quadrupole coupling constant was calculated to be 94.348 MHz.

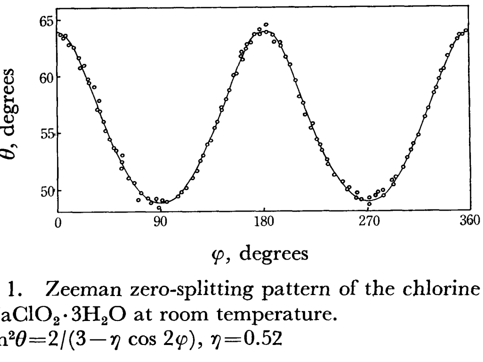

Fig. 1. Zeeman zero-splitting pattern of the chlorine atom in $NaClO_2 \cdot 3H_2O$ at room temperature.
$\sin^2\theta = 2/(3-\eta\cos 2\varphi)$, $\eta=0.52$

The bonding orbitals of the chlorine atom in the ClO_2^- ion may be presented as follows:[4]

$$\begin{aligned} \psi_1 &= \mathrm{p_x}, \\ \psi_2 &= (\cot\theta)s - (1-\cot^2\theta)^{1/2}\mathrm{p_y}, \\ \psi_3 &= \sqrt{\frac{1}{2}}(1-\cot^2\theta)^{1/2}\mathrm{s} + \sqrt{\frac{1}{2}}(\cot\theta)\mathrm{p_y} + \sqrt{\frac{1}{2}}\mathrm{p_z}, \\ \psi_4 &= \sqrt{\frac{1}{2}}(1-\cot^2\theta)^{1/2}\mathrm{s} + \sqrt{\frac{1}{2}}(\cot\theta)\mathrm{p_y} - \sqrt{\frac{1}{2}}\mathrm{p_z}, \end{aligned} \tag{1}$$

where 2θ represents the ∠O–Cl–O bond angle. The *x* axis lies perpendicularly to the plane of the ClO_2^- ion and the *y* axis is directed along the twofold axis of the ion. We will express the electron population of the two bonding orbitals, ψ_3 and ψ_4, of the chlorine atom by *A*, and those of the orbitals occupied by the lone pair, ψ_1 and ψ_2, by *B* and 2 respectively. Using the Townes-Dailey theory, the electric-field gradients at the chlorine atom can be expressed as functions of θ, *A*, and *B*:

$$\begin{aligned} q_\mathrm{x}/\mathrm{q_0}(1+\varepsilon)^\mathrm{n} &= (1-\cot^2\theta)(A-2)/2 + B - A, \\ q_\mathrm{y}/\mathrm{q_0}(1+\varepsilon)^\mathrm{n} &= (1-\cot^2\theta)(2-A) + (A-B)/2, \\ q_\mathrm{z}/\mathrm{q_0}(1+\varepsilon)^\mathrm{n} &= (1-\cot^2\theta)(A-2)/2 + (A-B)/2, \end{aligned} \tag{2}$$

where ε is 0.15 for the chlorine atom and where eq_0 is the field gradient of atomic chlorine. The symbol, *n*, represents the charge on the chlorine atom. The observed quadrupole coupling constant and asymmetry parameter are $|e^2Qq_i/h|$ and $(eq_k-eq_j)/eq_i$ when $|q_i|>|q_j|>|q_k|$.

The value of 2θ is in the range between 90° and 180°. If $B=2$, it can readily be found that q_x has the maximum absolute value of the field gradient when 2θ is between 90° and 109°28′. This is the case with the halogen bridge in the dimer molecule of the Group IIIb element or in the layer lattice as ScI_3, if the oxygen atom is replaced by the metal atom.[5] When 2θ is over 109°28′ and when $B=2$, the maximum field gradient becomes q_z.

The crystal structures of NH_4ClO_2 and $AgClO_2$ have been confirmed by means of X-ray diffraction.[6] The 2θ angles are found to be 110.5°±1.4° for NH_4ClO_2 and 111°±3° for $AgClO_2$. These angles are both larger than 109°28′. Also, the maximum field gradient at the chlorine atom in ClO_2 has been shown to be oriented along the axis of q_z.[7] Therefore, it seems reasonable to analyze the present data, by assuming that q_z is the maximum component of the field gradient.

As it is impossible to determine the three variables from the observed NQR parameters, we first assume the bond angle in this compound to be 111°. Substituting this value into Eq. (2), the following values

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[2] R. M. Hart and M. A. Whitehead, *Trans. Faraday Soc.*, **67**, 1569 (1971).

[3] J. L. Ragle, *J. Chem. Phys.*, **32**, 403 (1960).

[4] E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press Inc., New York (1969).

[5] See Ref. 4; P. A. Edwards and R. G. Barnes, *J. Chem. Phys.* **55**, 4664 (1971).

[6] R. B. Gillespie, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr.*, **12**, 867 (1959); J. Cooper and R. E. Marsh, *ibid.*, **14**, 202 (1961).

[7] R. F. Curl, *J. Chem. Phys.*, **37**, 779 (1962).

are obtained: $A=0.90$ and $B=1.73$. The decrease in B from 2 may be attributed to the presence of the dπ-pπ bonding in the O–Cl bond. The value of A, 0.90, indicates that the charge of 0.60 e is transferred to the oxygen atom from the chlorine atom in the σ bond of the O–Cl. The total charge on the chlorine atom is found to be $+1.47\,e$.

Taking 2θ to be larger than 111°, A becomes larger, whereas B becomes smaller. When $2\theta=123°$, $A=1.10$ and $B=2$, so the total charge on the chlorine atom is $+0.80\,e$. Actually, it may take an intermediate value between $+1.47\,e$ and $+0.80\,e$.

The temperature dependences were measured between 77 K and room temperature for $AgClO_2$, $NaClO_2$, and $NaClO_2 \cdot 3H_2O$. All the frequency *vs.* temperature curves decrease steadily as the temperature is raised.