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Dipole Moments of Molecules Containing Single Chlorine Atoms

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Synopsis. The dipole moments of CD_2ClF, CHDClF, CH_3CHClF, $CH_3CCl{=}CH_2$, and DCOCl have been determined from the $J=1\leftarrow0$ transitions of their microwave spectra. For the analyses of the Stark effects, the method of the intermediate field case proposed by Mizushima has been used.

In our laboratory the structures of halogeno-substituted hydrocarbons have been systematically investigated. These studies have clarified that the C–C, C–Cl, and C–F bond lengths are shortened regularly with further substitution of the chlorine or fluorine atoms for the hydrogen atoms,[1,2] and that the nuclear quadrupole coupling constants of Cl are mutually related to the bond lengths of C–Cl to a certain degree. It would be interesting to examine how the dipole moment of a molecule is influenced by the structure, whereas the informations on dipole moments are not enough for this purpose because of lack of the precise data for molecules containing atoms with nuclear quadrupoles. In the present work the dipole moments of some molecules containing single chlorine atoms are determined.

The Stark shift of the transition frequency was measured by using a d.c. voltage with a superimposed small a.c. voltage on the electrode plate inserted in the waveguide. Fluke 415B was used for the supply of a d.c. voltage, and the peak to peak height of an a.c. voltage was measured with Takeda TR-6334 digital voltmeter. The center frequency of a shifted spectral line was obtained as the zero-crossing point of the output of the phase-sensitive detector. The electrode spacing was calibrated by the Stark shift of the $J=2\leftarrow1$ transition of OCS[3] and determined to be 0.486±0.002 cm.

From the viewpoint of analysis it is desirable to determine the dipole moment from the Stark shift of the $J=1\leftarrow0$ transition in the case of a molecule which has a rotational spectrum with hyperfine structure. Since the $J=1\leftarrow0$ transitions of CD_2ClF, CHDClF, CH_3CHClF, and $CH_3CCl{=}CH_2$ fall into a suitable frequency region, their dipole moments were determined in the present study. The dipole moment of DCOCl,[2] which had been determined with the weak field approximation, was re-determined in order to refine the value.

Generally speaking, the Stark components of asymmetric-top molecules shift proportionally to the square of the electric field strength. For a molecule with nuclear quadrupole coupling, the proportionality breaks down when the applied electric field is so strong that the Stark shift is comparable to or slightly larger than the splitting due to quadrupole coupling interaction.

The Stark effect of a molecule containing a single chlorine atom can be estimated by the method proposed by Mizushima, *i.e.*, the method of the intermediate field case.[4] The energy levels are characterized by the set of good quantum numbers J, I, M_J, M_I, and the pseudoquantum number τ. The shifts of an energy level due to the Stark effect are given as solutions of the following secular equation

$$|(J, \tau, I, M_J, M_I|H_Q|J, \tau, I, M_J', M_I') + (E_{J,\tau,I=0,M}-E)\delta_{M_J,M_{J'}}\delta_{M_I,M_{I'}}| = 0.$$

In the above equation, the first and the second terms represent the splitting due to nuclear quadrupole coupling and the Stark shift in case the nuclear quadrupole is absent, respectively. Kellogg *et al.* gave the matrix elements in the first term, which do not vanish only if $M_J+M_I=M_{J'}+M_{I'}$.[5] The secular equation is factorized into blocks for each value of $M(=M_J+M_I)$, which can be easily solved.

The dipole moment of DCOCl was determined from the measurements of the shifts for five Stark components of the $1_{11}\leftarrow0_{00}$ by a least squares fit. The result is given in Table 1, which shows a marked improvement of the accuracy compared to the values of $\mu_a=0.3(2)$ and $\mu_b=1.6(2)$ previously determined by using the weak field approximation.

The dipole moments of CD_2ClF, CHDClF, and CH_3CHClF were determined by observing $1_{11}\leftarrow0_{00}$ transitions with an electric field of 200—800 V/cm, and that of $CH_3CCl{=}CH_2$ was determined from the $1_{01}\leftarrow0_{00}$

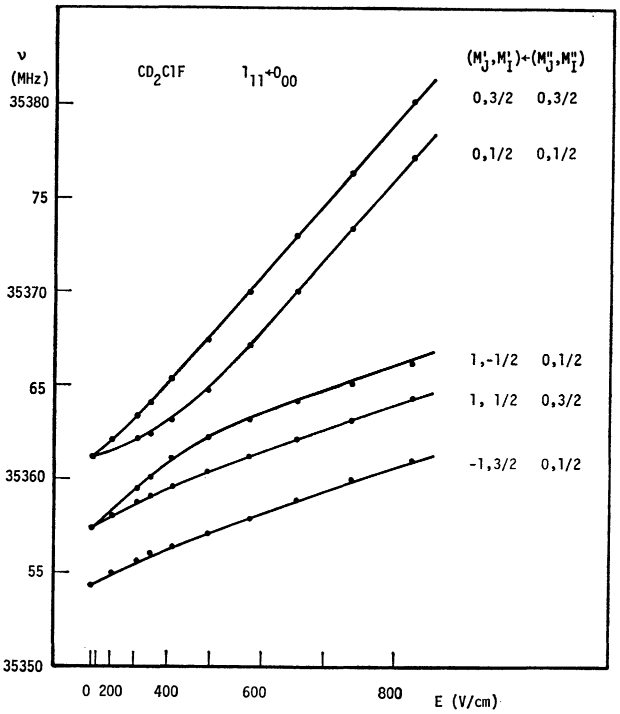

Fig. 1. The Stark shifts of CD_2ClF. The circles denote the measured displacements and the solid lines are theoretical ones.

TABLE 1. DIPOLE MOMENTS AND THEIR COMPONENTS (Debye)

Molecule	μ_a	μ_b	μ_c	μ_{total}
DCOCl	0.322(3)	1.780(15)	—	1.809(15)
CD_2ClF	0.302(3)	1.810(10)	—	1.834(10)
CHDClF	0.279(2)	1.787(10)	0.198(13)	1.819(10)
CH_3CHClF	0.953(8)	1.836(15)	0.013(24)	2.068(14)
$CH_3CCl=CH_2$	1.633(10)	0.211(14)	—	1.647(10)

transition with an applied field of 200—1000 V/cm. The Stark shifts of the $1_{11}\leftarrow 0_{00}$ transition for CD_2ClF are shown in Fig. 1 as a typical example. The dipole moments and their components determined by least squares fitting are given in Table 1. The limits of error were estimated by adding the errors due to the uncertainty of the applied electric fields to three times the standard deviations in the analysis.

The molecule which contains an atom with a nuclear quadrupole has the advantage that all the components of the dipole moment can be determined from the $J=1\leftarrow 0$ transition alone.[6] In addition, the analysis with the intermediate field approximation has been proved to give a sufficiently accurate dipole moment. In fact, the μ_c component of CHDClF could be determined, as shown in Table 1, although it has a rather large relative error because the energy levels which interact with the 0_{00} or 1_{11} level through the μ_c component are separated considerably. The dipole components of CHDClF obtained are consistent with the values calculated from those of CD_2ClF by rotation of the principal axes.

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