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The Dipole Moment of Benzaldehyde

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Synopsis. The dipole moment and its components along the principal axes were determined by measuring the Stark effects of the rotational transitions. The most probable direction of the moment was discussed.

The microwave spectra of benzaldehyde in the ground and in the excited torsional states have been studied in detail by Kakar *et al.*,[1] especially with regard to the barrier to internal rotation of the aldehyde group. However, its electric dipole moment has not yet been determined by using the spectrum. By the dielectric constant measurements, various values of the moment, ranging from 2.72[2] to 3.03 D,[3] have been obtained in various nonpolar solvents. Therefore, it seemed that it would be interesting to determine the value by means of the Stark effect of the spectrum and to ascertain the orientations of the components of the moment.

Experimental

The microwave spectrum and its Stark effect were measured by using a conventional 100-kHz square-wave Stark modulation spectrometer. The measurements were made at room temperature by using a 3-m absorption cell.

The sample of benzaldehyde, obtained from a commercial source, was purified by distillation *in vacuo* (bp 66—67 °C/12 mmHg).

Results and Discussion

Kakar *et al.*[1] have reported the frequencies of the high J R- and Q-branch transitions, from which they determined the rotational constants. Since lower J transitions are adequate for determining the value of the dipole moment, we searched for the rotational lines of the transitions of $J=4\leftarrow3$. As are shown in Table 1, the transition frequencies for the ground vibrational state could be observed at almost the same values as these calculated from the known rotational constants.[1] These assignments were ascertained by means of their Stark displacements. It is certain that the rotational constants are not affected by the centrifugal distortion.

TABLE 1. OBSERVED AND CALCULATED FREQUENCIES OF THE $J=4\leftarrow3$ TRANSITIONS IN THE GROUND VIBRATIONAL STATE[a]

Transition	ν_{obsd}(MHz)	ν_{calcd}(MHz)
$4_{04}\leftarrow3_{03}$	10831.41	10831.42
$4_{13}\leftarrow3_{12}$	11741.06	11741.11
$4_{13}\leftarrow3_{13}$	10309.46	10309.54

a) Maximum uncertainty of the observed values is ±0.10 MHz.

TABLE 2. STARK EFFECT AND DIPOLE MOMENT OF BENZALDEHYDE[a]

Transition		Shift MHz (kV/cm)$^{-2}$ Obsd	Calcd
$4_{04}\leftarrow3_{03}$	$M=1$	−4.37±0.11	−4.32
	$M=2$	9.96±0.10	10.28
$4_{13}\leftarrow3_{12}$	$M=1$	3.02±0.08	2.83
$4_{14}\leftarrow3_{13}$	$M=0$	−6.14±0.11	−6.17
	$M=2$	28.26±0.47	28.17

$\mu_a=2.96_6\pm0.02_7$ D; $\mu_b=1.23_9\pm0.02_8$ D

$\mu_{total}=3.21_4\pm0.03_7$ D

$\theta=\tan^{-1}(\mu_b/\mu_a)=22.67\pm0.72°$

a) Electric-field calibration was made with OCS for which $\mu=0.7152$ D.

By using the transitions shown above, the components of the dipole moment for the ground vibrational state were determined from the second-order Stark effect. The values thus obtained are shown in Table 2, together with the observed and calculated Stark coefficients. The symbols used have their usual meanings. The obtained value of the total dipole moment is higher than those obtained by dielectric constant measurements in various solutions. Of the various values obtained in solutions, the value of 3.03 D in cyclohexane and that of 3.02 D in benzene obtained by Jones *et al.*[3] may be considered to be most plausible.

The principal axes, the a- and b-axes, for this planar molecule, as determined from the molecular parameters reported,[1] are shown in Fig. 1. It is reasonable to consider that the negative end of the C=O bond moment points toward the oxygen atom and that the total dipole moment is mainly due to the C=O bond moment.

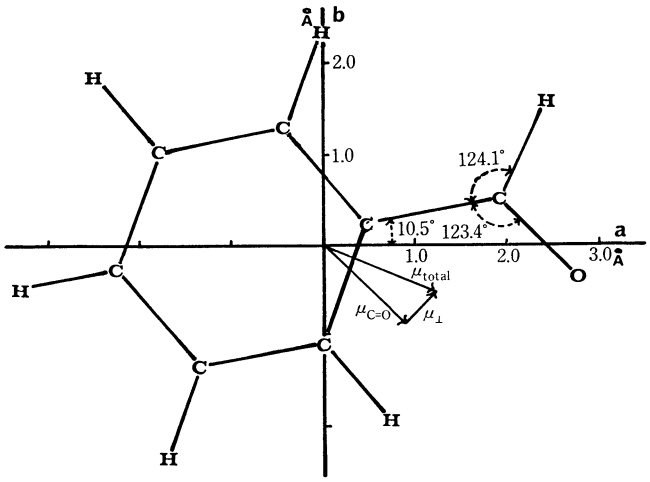

Fig. 1. The principal axes and the direction of the dipole moment of benzaldehyde.

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Therefore, of the four possible directions of the total dipole moment, the direction of μ_{total} indicated in Fig. 1 by an arrow is the most probable, for this direction makes the smallest angle of 23.4° with the direction of the C=O bond moment. The direction of μ_{total} makes an angle of 33.2° with the bond joining the carbon atom of the aldehyde group with the carbon atom of the benzene ring. This value is very close to that of 34.6° estimated for the same angle from the value of the dipole moment of the dichloro-derivative.[3] Therefore, the $\mu_{C=O}$ component of the dipole moment parallel to the C=O bond is calculated to be 2.95 D and the $\mu_{\perp}$ component of the dipole moment perpendicular to $\mu_{C=O}$ is 1.28 D. The value of $\mu_{\perp}$ may be due to the inductive effect of the moment of $\mu_{C=O}$ and to the partial migration of the π-electrons of the benzene ring to the C=O bond.

References

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