

## SHORT COMMUNICATIONS

### THE DIPOLE MOMENT OF SULPHUR DIOXIDE

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As a preliminary to a study of the dipole moments of a variety of compounds in the vapour phase, we used sulphur dioxide to test the operation of our microwave cavity apparatus. It was noticed that the literature values† were not entirely consistent, there being a small discrepancy between the bulk dielectric measurements<sup>2,3</sup> of the classical method and the molecular Stark effect measurements<sup>4</sup> of the microwave spectroscopic method. We therefore decided to redetermine the dipole moment of sulphur dioxide by both methods to attempt to resolve the matter, subsequently noting a more recent Stark-effect value by Morino *et al.*<sup>5</sup>

#### Experimental

All values are quoted in S.I. units using the conversions

$$1 \text{ debye} = 3.33563 \times 10^{-30} \text{ coulomb metre}$$

$$1 \text{ mmHg} = 133.32 \text{ newtons (metre)}^{-2}$$

#### (1) Stark Effect on Microwave Spectrum

The spectrometer was a 5-kHz Stark-modulated instrument with a Hewlett-Packard K03-8690A phase-locked backward-wave-oscillator source, frequency measurements being made with a Hewlett-Packard 5245L counter and 5252A prescaler. The counter was periodically checked with a Sulzer 2.5C laboratory frequency standard. Stark shifts were measured for three lines of  $^{32}\text{S}^{16}\text{O}_2$  in X-, K-, and R-bands, with fields in the range  $98.9 \times 10^3$ – $320.8 \times 10^3$  volt/metre. The shifts were found to be accurately quadratic in the field, and line frequencies could be measured to  $\pm 10$  kHz.

The Stark fields were calibrated by measuring shifts for the  $0 \rightarrow 1$ ,  $1 \rightarrow 2$ , and  $2 \rightarrow 3$  lines of  $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ , and assuming a dipole moment of  $2.3857 \times 10^{-30}$  C m ( $0.71521$  D) for the latter.<sup>6</sup>

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† In the valuable tabulation of dipole moments published by McLellan,<sup>1</sup> a value of  $\mu = 4.90 \times 10^{-30}$  C m ( $1.47$  D), attributed to  $\text{SO}_2$ , is in error. The measurements refer to  $\text{S}_2\text{O}$ .

<sup>1</sup> McLellan, A. L., "Tables of Experimental Dipole Moments." (Freeman: San Francisco 1963.)

<sup>2</sup> Zahn, C. T., *Phys. Rev.*, 1926, **27**, 455.

<sup>3</sup> Le Fèvre, R. J. W., Ross, I. G., and Smythe, B. M., *J. chem. Soc.*, 1950, 276.

<sup>4</sup> Crable, G. F., and Smith, W. V., *J. chem. Phys.*, 1951, **19**, 502.

<sup>5</sup> Morino, Y., Oka, T., Kikuchi, Y., Matsumma, C., and Saito, S., Proc. Int. Symp. of Molecular Structure and Spectroscopy, Tokyo, Dec. 1962, Pap. C312.

<sup>6</sup> Muenter, J. S., *J. chem. Phys.*, 1968, **48**, 4544.

## (2) Bulk Dielectric Measurements

The dielectric constant of the gas at various temperatures and pressures was measured by determining the resonant frequency of a microwave cavity filled with the gas, essentially as described by Magnusson.<sup>7</sup> The cavity used in this work had a resonant frequency of 9.3 GHz. The resonant frequency was measured by sweeping a phase-locked X-13 Klystron through a few MHz embracing the resonance, power being monitored by an SIM2 crystal detector and chart recorder while the frequency was monitored by measuring the beat frequency of a Hewlett-Packard 540B transfer oscillator, to which the Klystron was phase-locked, with a thermostatted 200-MHz crystal oscillator by means of a calibrated frequency meter. The resonant frequency could be determined in this manner to  $\pm 10$  kHz.

The cavity was mounted in an air thermostat and the temperature monitored with thermometers that had been calibrated *in situ* with a platinum resistance thermometer. Temperatures could be measured to  $\pm 0.01$  deg.

The gas pressure was measured by observing a quartz spiral gauge (manometer) inside the air thermostat which was approximately nulled with an external mercury manometer, the latter being observed with a cathetometer. Uncertainties in the pressure measurements were  $\pm 50$  N m<sup>-2</sup> ( $\pm 0.4$  mmHg).

## Calculation of Results and Analysis of Errors

(1) Sixty-two Stark shifts were measured for the nine transitions considered, yielding 62 measures of the dipole moment of SO<sub>2</sub>. The mean value was  $5.450 \times 10^{-30}$  Cm (1.634 D) with a standard deviation of  $0.003 \times 10^{-30}$  Cm (0.001 D). (This method has the advantage of preferentially weighting the measured frequency of the unperturbed line over that of the Stark lobes, the latter having a larger line-width and less symmetrical line-shape.) The rotational constants used were those reported by Kivelson<sup>8</sup> (Table 1).

TABLE 1

$A$  60.778790,  $B$  10.318100,  $C$  8.799960 GHz;  $\mu$   $5.450 \times 10^{-30}$   
 $\pm 0.003 \times 10^{-30}$  Cm (1.634  $\pm$  0.001 D)

Transition	$M$ Values	Frequency (GHz)	Previous Work
$1_{11} \leftarrow 2_{02}$	0,1	$12.25664 \pm 0.00001$	$12.25657^a$
$4_{04} \leftarrow 3_{13}$	0,1,2	$29.32115 \pm 0.00001$	$29.32122^3$
$5_{24} \leftarrow 6_{16}$	2,3,4,5	$23.41426 \pm 0.00001$	$23.41433^3$

<sup>a</sup> Lindfors, K. R., and Cornell, C. D., *J. chem. Phys.*, 1965, **42**, 149.

## (2) The Debye equation

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho} = \frac{4}{3} \pi N \left( \alpha + \frac{\mu^2}{3kT} \right)$$

in conjunction with

$$P(1 + AP)\bar{V} = RT$$

yields

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{RT}{P} = \frac{4}{3} \pi N \left( \alpha + \frac{\mu^2}{3kT} + \alpha AP + \frac{\mu^2 AP}{3kT} \right)$$

<sup>7</sup> Magnusson, D. W., *J. chem. Phys.*, 1952, **20**, 229.

<sup>8</sup> Kivelson, D., *J. chem. Phys.*, 1954, **22**, 904.

in which  $\epsilon$ , the dielectric constant, is determined from  $\epsilon = (\nu_0/\nu_P)^2$ , where  $\nu_0$  is the resonant frequency of the evacuated cavity and  $\nu_P$  is the resonant frequency of the cavity filled with gas at a pressure  $P$ . Also,  $\alpha$  is the polarizability,  $\mu$  the dipole moment,  $A$  a non-ideality parameter,  $M$  the molecular weight, and  $\rho$  the gas density. A least-squares fit of the right-hand side of this equation to the experimentally determined left-hand side yields the required values and standard deviations of  $\alpha$ ,  $\mu$ , and  $A$ .

The three temperatures, 344.12, 400.76, and 424.03°K, were used together with a total of 37 different pressures (12, 11, and 14 respectively) in the range 6.7–101 kN m<sup>-2</sup> (5–76 cmHg).

The results obtained were

$$\mu = (5.394 \pm 0.053) \times 10^{-30} \text{ C m } (1.617 \pm 0.016 \text{ D})$$

$$\alpha = (4.65 \pm 0.32) \times 10^{-30} \text{ m}^3$$

where the quoted error is the standard deviation. The standard deviation of  $A$  is too large for the values of  $A$  to be of any significance.

### Discussion

Crabbe and Smith<sup>4</sup> found  $\mu = 5.34 \times 10^{-30} \text{ C m } (1.60 \text{ D})^*$  on the basis of Stark-shift measurements on the  $1_{11} \leftarrow 0_{00}$  transition, while Morino *et al.*<sup>5</sup> more recently found  $\mu = 5.407 \times 10^{-30} \text{ C m } (1.62_1 \text{ D})^*$  from measurements on the  $2_{01} \leftarrow 1_{11}$  transition. Both of these values are low compared with the value found by use of the Stark effect in this work. This is probably due to the more sophisticated microwave equipment used here and also to the many measurements used to calculate the dipole moment.

The bulk dielectric dipole moment is in agreement with all three Stark-effect values, indicating that the method is indeed reliable but less accurate. This value is also in agreement with the value  $\mu = 5.44 \times 10^{-30} \text{ C m } (1.63 \text{ D})$  found by Boggs *et al.*<sup>9</sup> using a similar apparatus.

Le Fèvre *et al.*<sup>3</sup> found the value of the temperature-independent term in the equation representing the total polarization of SO<sub>2</sub>

$$P = a + b/T$$

to be given by  $a = (10.91 \pm 0.6) \times 10^{-6} \text{ m}^3$ . This yields a value for the polarizability of

$$\alpha = (4.32 \pm 0.24) \times 10^{-30} \text{ m}^3$$

which is in agreement with the resonant-cavity-apparatus value.

\* These were calculated from the originally published values using the most recent value for the dipole moment of <sup>16</sup>O<sup>12</sup>C<sup>32</sup>S.<sup>5</sup>

<sup>9</sup> Boggs, J. E., Crain, C. M., and Whiteford, J. E., *J. phys. Chem.*, 1957, **61**, 482.