THE MICROWAVE STARK EFFECT IN OXYGEN*

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The Stark effect of the 118 GHz oxygen transition has been observed. From measured frequency shifts in strong electric fields, the sign and magnitude of the electric polarizability anisotropy were found to be $\alpha_\parallel - \alpha_\perp = 1.12 \pm 0.07$ A^3.

The fine structure transition of molecular oxygen at 118 GHz has been observed to shift to a lower frequency by an amount proportional to the square of an applied electric field. The shift yields directly the electric polarizability anisotropy $\alpha_\parallel - \alpha_\perp$. This is believed to be the first observation of the Stark effect in a non-polar molecule by microwave spectroscopy.

Polarizability anisotropies have been previously measured with microwave spectroscopy for a few polar molecules. In these, comparison of precise Stark measurements on several transitions are required for separation of the small polarizability effect from the much larger permanent dipole moment contribution [1]. A direct measurement of $\alpha_\parallel - \alpha_\perp$ has recently been made for the non-polar hydrogen molecule by a molecular beam magnetic resonance method [2]. Polarizability anisotropies are important for the study of rotational Raman intensities, Rayleigh scattering and depolarization constants, van der Waals forces, and pressure and electric field induced spectra [3]. Values of $\alpha_\parallel - \alpha_\perp$ are also required for the derivation of magnetic anisotropies and molecular quadrupole moments from the results of several laser-optical experiments [4].

The Stark effect of the oxygen $^3\Sigma$ ground electronic state is strongly influenced by the two unpaired electron spins. The electron field perturbation Hamiltonian, with constant terms omitted, is [5]

$$\mathcal{H} = -\tfrac{1}{2}(\alpha_\parallel - \alpha_\perp)\,\mathcal{E}^2\Phi_{Zz}^2, \tag{1}$$

where Φ_{Zz} is the direction cosine between space-fixed and bond axes. The first order evaluation of $\mathcal{H}$, which is adequate for our purposes, requires the matrix elements of Φ_{Zz}^2 in the Hund's case (b) representation $|J\,M_J\,N\,S\rangle$. These elements are found by a transformation to $|N\,M_N\,S\,M_S\rangle$. The resulting energy expression is

$$E_{\mathcal{E}} = -(\alpha_\parallel - \alpha_\perp)\,\mathcal{E}^2\,\frac{2J+1}{3(2N-1)(2N+3)} \times \sum_{M_S=-1}^{1}\begin{pmatrix} 1 & N & J \\ M_S & M_J-M_S & -M_J\end{pmatrix}^2 [N(N+1)-3(M_J-M_S)^2] \tag{2}$$

where the first quantity in the summation is a squared 3-j symbol. This expression yields for the 118 GHz, $J = 0 \rightarrow 1, N = 1 \rightarrow 1$ transition of oxygen the field-induced frequency shifts,

$$(\Delta\nu)_{\Delta M_J=0} = \frac{1}{15h}(\alpha_\parallel - \alpha_\perp)\,\mathcal{E}^2,$$
$$(\Delta\nu)_{\Delta M_J=\pm 1} = -\frac{1}{30h}(\alpha_\parallel - \alpha_\perp)\,\mathcal{E}^2. \tag{3}$$

A Stark cell designed for high field strengths (up to 75 kV/cm) and low temperatures (77°K) was constructed for the measurements. Parallel field plates, 5 X 75 cm, were supported at a separation of 1 mm by adjustable glass rods outside the high field region. Liquid nitrogen was passed through cooling coils attached to the plates, and the assembly was enclosed in a cylindrical vacuum cell. The cell was magnetically shielded with concentric mu metal sheets and wound with a compensating solenoid to reduce the line broadening effect of the earth's magnetic field. Transitions were induced by the magnetic component of the microwave radiation perpendicular to $\mathcal{E}$ so that the $\Delta M_J = \pm 1$ transitions, both at the same frequency,

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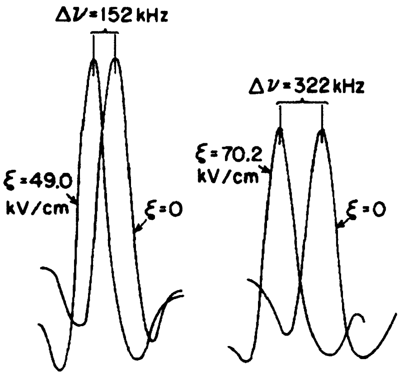

Fig. 1. The Stark shift of the 118 GHz line of oxygen ($\Delta M_J = \pm 1$).

were observed. The 118 GHz radiation was the fifth harmonic of a K-band klystron which was phase-locked to a high crystal oscillator harmonic and to low harmonics of two variable frequency oscillators. One of these oscillators was tuned mechanically in synchronization with a chart recorder, and the other was frequency modulated. A crystal detector and lock-in amplifier were used for observation of a second-derivative line shape (fig. 1).

The Stark effect frequency shift was measured for different electric fields and tuning conditions; the mean anisotropy value (and probable error) obtained from eq. (3) is $\alpha_\parallel - \alpha_\perp = 1.12 \pm 0.07\ \mathrm{A}^3$. This result may be compared with a less direct value calculated from laser depolarization scattering and bulk polarizability measurements [6,7]. This bulk value, which is a population weighted average over vibrational and rotational states, is obtained for optical frequency electric fields rather than static electric fields. After correction for the latter effect [3], the static field anisotropy valued obtained is $|1.09|\ \mathrm{A}^3$. This magnitude is in satisfactory agreement with the value obtained here. The sign of $\alpha_\parallel - \alpha_\perp$ cannot be obtained from bulk measurements; the sign determined here from the Stark effect agrees with the predictions of bond polarization models [6].

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