Absolute Signs of Dipole Moment Derivatives in Carbonyl Sulphide

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Summary By comparison of i.r. intensity measurements and microwave Stark effect information, it is established experimentally that the absolute signs of the dipole moment derivative for carbonyl stretching in OCS is negative; that is $\partial \mathbf{p}/\partial r_{CO} = -1\cdot5\,e\,\mathbf{e}_{CO}$ where e is the charge on the proton and $\mathbf{e}_{CO}$ is a unit vector from the carbon towards the oxygen atom, or, in more familiar, non-SI units the dipole moment gradient with respect to CO stretch is 7 D/Å with the oxygen becoming more negative

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IT is well known that the square of molecular dipole moment derivatives with respect to normal co-ordinates can be obtained from i.r. intensity measurements but that sign ambiguities arise in extracting the square roots. These can be removed for diatomic molecules by measuring individual rotational line strengths,[1] but the method looks unpromising for polyatomics.[2] Use of isotopic dipoles[3] measured by classical means[4] also appears to be unsuitable for polyatomic species, although isotopic moments from Stark effect measurements might be useful. The use of the change of the dipole moment with vibrational excitation appears more promising. The measurement of the dipole from the microwave Stark effect for molecules excited to one quantum in the bending mode[5] in OCS is the basis of the present sign determination, in conjunction with the determination of the absolute sign of the dipole[6] which is a

vector from O towards S *i.e.* the oxygen is negative. It is convenient to introduce a unit vector $\mathbf{e}_{AB}$ pointing from A to B so that $\mathbf{e}_{OC} = \mathbf{e}_{CS} = -\mathbf{e}_{CO} = -\mathbf{e}_{SC}$. The dipole moment[7] $\mathbf{p} = 14.9\,e\,\mathbf{e}_{OS}$ pm (0.715 D), where e is the proton charge,† for the zero point state and $\mathbf{p}_{(010)} - \mathbf{p}_{(000)} = -0.19\,e\,\mathbf{e}_{OS}$ pm (-0.009 D) where $\mathbf{p}_{(000)}$ refers to the zero point state and $\mathbf{p}_{(010)}$ to that with one quantum of bending excited.[5]

Three quantities, the first derivative of the dipole moment with respect to each of the stretching co-ordinates and the second derivative with respect to bending, contribute to four observations, namely the intensities of the two stretching fundamentals,[8-10] the gas phase intensity of the bending overtone at 1047 cm^{-1} measured in this work to give a cross section, $\Gamma = 230$ cm^2 mol^{-1}, and the dipole moment difference,[5] $\mathbf{p}_{(010)} - \mathbf{p}_{(000)}$. Preliminary measurements on the overtone and combination band intensities show that second derivatives with respect to stretching can only give small correction terms relevant to the discussion of these observations. Also required is the anharmonic force field for which the values of Morino and Nakagawa[11] were used and from which the anharmonic wave functions were derived by computer diagonalisation on a basis set of over 30 harmonic oscillator products in each of the Σ^+ and π symmetry classes. The problem is overdetermined and only one satisfactory solution could be obtained to satisfy the four equations in the three unknowns and this resolves the three sign ambiguities. The only acceptable set of dipole derivatives are shown in equations 1, 2, and 3.

$$\partial\mathbf{p}/\partial r_{CS} = -0.9\,e\,\mathbf{e}_{CS}; \quad (-4 \times 10^{-10}\,\text{cm}^{\frac{3}{2}}\,\text{g}^{\frac{1}{2}}\,\text{s}^{-1}) \quad (1)$$

$$\partial\mathbf{p}/\partial r_{CO} = -1.5\,e\,\mathbf{e}_{CO}; \quad (-7 \times 10^{-10}\,\text{cm}^{\frac{3}{2}}\,\text{g}^{\frac{1}{2}}\,\text{s}^{-1}) \quad (2)$$

$$\partial^2\mathbf{p}/\partial\alpha^2 = +40\,e\,\mathbf{e}_{OS}\,\text{pm}; \quad (+1.9\text{D}) \quad (3)$$

where α is the departure of the OCS angle from π.

It is very difficult to give errors to these preliminary results as they are sensitive to the force field as well as to the experimental observations, but as good a fit with reversed signs for the stretching derivatives would require a change by a factor of 4 in the observed overtone intensity or a factor of 2 in the cubic potential constants.

Braslawsky and Ben-Aryeh[12] discuss aspects of this problem but do not emphasize that the argument fixes the absolute signs of derivatives with respect to internal co-ordinates; the first derivatives with respect to normal co-ordinates, which they consider, are arbitrary as are the signs of the columns of the L matrix. Also the anharmonic force field used here[11] differs from the earlier form[13] which Braslawsky and Ben-Aryeh[12] used.

It is comforting that the signs determined experimentally in the present work confirm those suggested by Thorndike[14,8] on the chemical grounds that if the carbonyl bond is stretched, the resonance structure $O^--C\equiv S^+$ becomes more important.

† Unfortunately the Debye is not compatible with the SI units. One must consequently learn new numbers and for discussions in Chemistry a better intuitive feeling for the order of magnitude involved is obtained by quoting moments as a length times the proton charge rather than in m s A.

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