Recalculation of the Bond Moments and the Bond Derivatives of the Dichloromethane Molecule

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Straley[1] measured the absolute intensities of perpendicular bands of dichloromethane in vapor, expessed $\partial\mu/\partial Q_i$ (where μ is the dipole moment and Q_i is the normal coordinates of the molecule) in terms of the bond moments (μ_{CH}, μ_{CCl}) and the bond derivatives ($(\partial\mu/\partial r)_{\mathrm{CH}}$ and $(\partial\mu/\partial r)_{\mathrm{CCl}}$), and calculated the values of the bond moments and the bond derivatives. (The results are given in column I of Table I.) In this case, one half of the observed intensity of the doublet centered at 2995 cm^{-1}, was allotted to the intensity of ν_6 (the antisymmetrical stretching vibration).

Several recent studies[2-5] have shown, however, that it is reasonable to assign the doublet centered at 2995 cm^{-1} to the P and R branch maxima of ν_1 (the symmetrical stretching vibration) and that ν_6 is not observed because of its very weak intensity in vapor. The present authors have, therefore, recalculated the bond moments and the bond derivatives by using the new assignment; the method is described below, and the results are shown in Table I.

1) The values in column II are the result of the recalculation made by following the process of Ref. 1 except that A_6 is set at zero. These values agree with those in column I except that the absolute value of $(\partial\mu/\partial r)_{\mathrm{CH}}$ is smaller than that in column I.

2) When the above calculations (Ref. 1 and 1)) were made, it was assumed that the vector sum of the all bond moments obtained by infrared work was equal to the total dipole moment determined by dielectric measurements. However, this assumption is not valid, particularly if there are lone-pairs present, as Coulson indicated.[6] Therefore, the recalculation was made without using this assumption. The results are shown in column III.

3) Finally, the authors made more rigorous

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[1] J. W. Straley, *J. Chem. Phys.*, **23**, 2183 (1955).

[2] T. Shimanouchi and I. Suzuki, *J. Mol. Spectry.* **8**, 222 (1962).

[3] R. E. Kagarise, *Spectrochim. Acta*, **19**, 1371 (1963).

[4] M.-T. Forel, A. Lafaix, P. Saumagne and M.-L. Josien, *J. Chim. Phys.*, 875 (1963).

[5] U. Kanbayashi, This Bulletin, **36**, 1173 (1963).

[6] C. A. Coulson, *Spectrochim. Acta*, **14**, 161 (1959).

TABLE I. BOND MOMENTS AND BOND DERIVATIVES OF THE DICHLOROMETHANE MOLECULE CALCULATED FROM THE PERPENDICULAR BANDS

	I	II	III	IV
A_6 (c. p. s./cm. at NTP)	48.0×10^{10}	0	0	0
μ_{CH} (D)	+0.45	+0.45	+0.60	+0.58
μ_{CCl} (D)	−0.95	−0.95	−1.4 or −3.0	−1.4 or −3.0
$(\partial\mu/\partial r)_{CH}$ (D/A)	+0.3 or −0.2	+0.06	+0.09 or +0.24	+0.11 or +0.23
$(\partial\mu/\partial r)_{CCl}$ (D/A)	+3.7	+3.7	±3.8	±4.5

calculations of $\partial\mu/\partial Q_i$ by using the newest data on the normal vibrations of the dichlorometane molecule7) and so got the following relations:

$$\pm\frac{\partial\mu}{\partial Q_6} = 1.679x + 95.525x' + 7.444y \qquad (1)$$

$$(3081\ \mathrm{cm}^{-1})$$

$$\pm\frac{\partial\mu}{\partial Q_7} = 54.539x + 4.458x' + 14.625y \qquad (2)$$

$$(901\ \mathrm{cm}^{-1})$$

$$\pm\frac{\partial\mu}{\partial Q_8} = 108.708x + 2.085y + 0.496y' \qquad (3)$$

$$(1264\ \mathrm{cm}^{-1})$$

$$\pm\frac{\partial\mu}{\partial Q_9} = 18.602x + 6.518y + 28.182y' \qquad (4)$$

$$(747\ \mathrm{cm}^{-1})$$

$$\pm\frac{\partial\mu}{\partial Q_1} = 11.661x + 62.514\chi' + 3.504y + 2.637y'$$

$$(3019\ \mathrm{cm}^{-1}) \qquad (5)$$

where $x=\mu_{CH}$ (Debye), $x'=(\partial\mu/\partial r)_{CH}$ (Debye/Å), $y=\mu_{CCl}$ (Debye), and $y'=(\partial\mu/\partial r)_{CCl}$ (Debye/Å). (The numbers in parentheses reprsent the calculated frequencies.)

After Straley's observed values of $\partial\mu/\partial Q_7$ (±11.7), $\partial\mu/\partial Q_8$ (±63.1) and $\partial\mu/\partial Q_9$ (±123.0), and zero for $\partial\mu/\partial Q_6$ had been introduced into Eqs. 1—4, the bond moments and the bond derivatives for the perpendicular bands were calculated; they are given in column IV. It is interesting that the values of column IV based on the more accurate data agree approximately with those of column III.

The value of $\partial\mu/\partial Q_1$ calculated from Eq. 5 using the values in column IV was 20—25 (if $(\partial\mu/\partial r)_{CCl}=+4.5\ D/A$) or $\partial\mu/\partial Q_1=-3$— -2 (if $(\partial\mu/\partial r)_{CCl}=-4.5\ D/A$). Neither of these values coincides with the value determined from the intensity of the doublet centered at 2995 cm^{-1} observed by Straley1) (±32). In this case, the values of the bond moments and the bond derivatives calculated from the perpendicular bands are different from those calculated from the parallel bands, as has previously been pointed out.8–10)

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7) I. Suzuki and T. Shimanouchi, *J. Mol. Spectry.*, 6, 277 (1961).

8) D. F. Hornig and D. C. McKean, *J. Phys. Chem.*, 59, 1133 (1955).

9) G. M. Barrow and D. C. McKean, *Proc. Roy. Soc.*, 213A, 27 (1952).

10) H. W. Thompson, "Molecular Spectroscopy," The Petroleum Institute (1955), p. 94.