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Note on Electric Moments and Infrared Spectra, and the Structure of CO

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The desirability of measurements of infrared intensities in order to determine electric moments as functions of interatomic distances is illustrated by a discussion of available data on HCl, HI, CO and H₂O. Some new information on the structure of CO is obtained.

LITTLE attention seems usually to be paid to the limitations imposed by the fact that the ordinary data on electric moments, and the relations and conclusions therefrom, refer exclusively to molecules in their equilibrium configurations. The electric moment μ for each molecule or bond is known just for one particular value of the distance r between the atoms concerned. A deeper understanding of electric moments should result if we knew μ as a function of r over a range of r values for a number of different important bonds. Experimental data helping us to construct such curves can be obtained from measurements of the total-intensities of infrared vibration bands; theoretical relations between $\mu(r)$ curves and intensity data have been developed especially by Dunham.^{1, 2, 3} Unfortunately such data are at present very scanty.^{3a}

The few available data indicate interesting situations. We may consider first the hydrogen halides. In the case of HCl, which has been carefully discussed by Dunham,¹ infrared intensity measurements give information as to the variation of μ with r .² The result,¹ for r near r_e , is probably

$$\mu_{\text{HCl}} \times 10^{18} = 1.03 \pm (1.06\xi + 0.07\xi^2), \quad (1)$$

where $\xi = (r - r_e)/r_e$, with $r_e = 1.276 \times 10^{-8}$ cm.

¹ J. L. Dunham, *Phys. Rev.* **35**, 1347 (1930).

² D. C. Bourgin, *Phys. Rev.* **29**, 794 (1927); J. L. Dunham, *Phys. Rev.* **34**, 438 (1929).

³ L. Matheson, *Phys. Rev.* **40**, 813 (1932).

^{3a} In the writer's opinion, the serious discrepancies noted by Van Vleck (*Theory of Electric and Magnetic Susceptibilities*, Oxford, 1932, pp. 45-70) between "atomic polarization" data and infrared vibration-rotation band intensities may probably be attributed to gross inaccuracy in the early infrared intensity measurements and to experimental errors in other data (cf. Van Vleck, pp. 52, 68). A very serious discrepancy between observed intensities of pure rotation bands of HCl and those predicted from $\mu(r_e)$ remains.

The intensity data cannot show whether the coefficients of ξ and ξ^2 are positive or negative, but the signs may be capable of determination by systematic considerations. The coefficient of ξ^2 , it should also be noted, is obtained by solving a quadratic equation which gives 4.56 as a possible alternative to 0.07 in Eq. (1), but other considerations make this solution improbable. The experimental error in determining the coefficient of ξ^2 is really greater than 0.07, so we may say that this coefficient is zero (unless it should be 4.56) within experimental error.

Taking Eq. (1) as correct, and knowing that $\mu = 0$ for $r = 0$ and $r = \infty$, we can roughly sketch μ as a function of r (cf. Figs. 1a, 1b). The behavior of the curves near $r = 0$ is not certain; the forms assumed in Figs. 1a, 1b correspond to the existence of a maximum value, at some finite $r > 0$, for the effective charge q , where $\mu = qr$. [It may be, however, that q actually (for some molecules at any rate) rises asymptotically to a maximum at $r = 0$. In this case the $\mu(r)$ curves should be given a finite slope at $r = 0$.] With the foregoing and the very probable assumption that the $\mu(r)$ curve for HCl has only one maximum, its form is fairly well determined for each sign in Eq. (1). [It the coefficient of ξ^2 should be 4.56, the curve would go up with increasing steepness for $r > r_e$ in Fig. 1a, to a high maximum; in Fig.

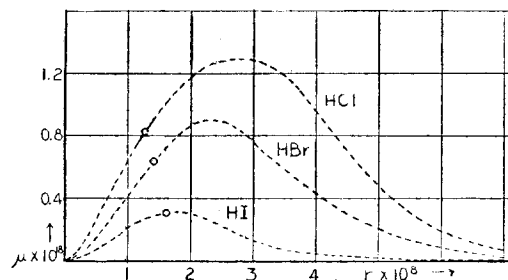


FIG. 1a. More probable forms of $U(r)$ curves (positive sign in Eq. (1)).

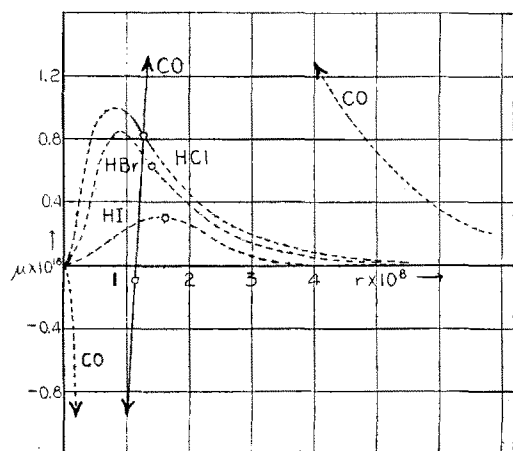


FIG. 1b. Negative sign in Eqs. (1), (3): less probable $U(r)$ curves for HCl, HBr, HI, most probable curve for CO.

1b it would descend with increasing steepness for $r > r_e$.]

No quantitative measurements on HBr or HI are available, but the extreme weakness⁴ of the fundamental vibration band of HI ($v=0 \rightarrow 1$) shows that the coefficient of ξ must be very small, hence that μ must have a maximum near $r=r_e$. This, together with the result $\mu = 0.38 \times 10^{-18}$ for $r=r_e = 1.617 \times 10^{-8}$ cm, allows us to sketch the curve shown in Fig. 1. For HBr the $0 \rightarrow 1$ band is known to be much stronger than that for HI, although nothing quantitative is known. Knowing $\mu = 0.79 \times 10^{-18}$ for $r=r_e = 1.411 \times 10^{-8}$ cm for HBr, we may plausibly interpolate between HCl and HI to get the curve shown in Fig. 1a or Fig. 1b.

Fig. 1a corresponds to a maximum of q at r slightly less than r_e in the case of HI, at r slightly greater than r_e in the case of HCl. For Fig. 1b, the maximum of q for HCl comes at r considerably less than r_e ; the HI curve is unchanged. It is not obvious which of these possibilities is correct.⁵ Two other possible curves, based on 4.56 as the coefficient of ξ^2 in Eq. (1), are less probable, but cannot be absolutely ruled out without further evidence. Even with these ambiguities, the curves show interesting changes in the series HCl, HBr, HI.

⁴ M. Czerny, *Zeits. f. Physik* **44**, 254-5 (1927). The pure rotation band of HI, whose intensity should depend on $\mu(r_e)$, is not much weaker than that of HBr, in agreement with theory.

⁵ The $U(r)$ curves given by L. Pauling, *J. Am. Chem. Soc.* **54**, 998 (1932), are of interest in this connection.

For CO, infrared intensity measurements⁸ combined with the values of $\mu(r_e)$ yield, for r near r_e ($r_e = 1.15 \times 10^{-8}$):

$$\mu_{CO} \times 10^{18} = 0.118 \pm (9.1\xi + 3.7\xi^2 \text{ or } -3.4\xi^2) \quad (2)$$

In this case it is clear that, whether we use $+9.1\xi$ or -9.1ξ in Eq. (10), μ must reverse its sign very close to $r=r_e$. This can be understood if we assume an electronic structure for CO similar to that suggested by Pauling⁵ (wave function ψ a mixture of $C^- \equiv O^+$ and $C=O$), but with the addition of a component $C^+ - O^-$ to ψ . [It may be noted that the structure given in terms of molecular orbitals by Hund and the writer is also equivalent to a linear combination of $C-O^+$, CO, C^+O^- etc.] For small r , polarity $C-O^+$ may reasonably be expected, since $C^- \equiv O^+$ should there be at its strongest.⁵ For large r , polarity C^+O^- is expected, since $C^+ + O^-$ then has considerably lower energy than $C^- + O^+$. Actually, it seems, $C-O^+$ and C^+O^- must appear with about equal weight in ψ for $r=r_e$, and the struggle between them must be very keen there. The $\mu(r)$ curve shows that one of the two forms, in all probability $C-O^+$, predominates decisively for small r , beginning with r not much less than r_e , and the other for r not much greater.⁶ Assuming $C-O^+$ dominant for small r , and calling μ negative for $C-O^+$, the signs in Eq. (2) must be chosen as follows:

$$\mu_{CO} \times 10^{18} = \mp 0.118 + 9.1\xi + 3.7\xi^2. \quad (3)$$

The alternative $-3.4\xi^2$ appears improbable. The only ambiguity remaining is then in the two possibilities ∓ 0.118 , which is so small that it does not matter much. The -0.118 choice is shown in Fig. 1b.

The foregoing examples indicate the desirability of further quantitative measurements of in-

⁶ Evidently the $U(r)$ curve for $C^+ + O^-$ comes about equally as low as that for $C^- + O^+$ for r near r_e . Pauling (reference 5, Fig. 7) considers only the $C-O^+$ curve. Probably the electron affinity of carbon is less than Pauling's estimate, so that the $C-O^+$ curve is not as low as he supposed, and the C^+O^- curve therefore relatively lower. It is here supposed, contrary to Pauling, that the neutral $C=O$ component of ψ does not make an important contribution to μ (a small contribution, of polarity C^+O^- , may, however, be present in spite of the homopolar character of the bond, because of the unequal size of the two atoms).

frared intensities. Attention may be called to the possibility of interesting results with polyatomic as well as diatomic molecules. For example, although H_2O is known to have a large permanent electric moment, available data on its infrared absorption bands⁷ indicate that terms analogous to the coefficient of ξ in Eq. (1) are relatively small. That is, μ_z , the component of the electric moment in the direction of the symmetry axis, is apparently near a maximum just as in HI, as regards symmetrical vibrations of the molecule: only a few weak bands are observed which correspond to an electric moment varying in the z direction ($\Delta v_3 = \text{even}$). For those infrared bands ($\Delta v_3 = \text{odd}$, where v_3 is the quantum number asso-

ciated with the normal coordinate corresponding to asymmetrical vibrations) whose intensity depends on a moment (μ_y) perpendicular to the symmetry axis, the intensities are high, indicating that for μ_y the coefficient analogous to that of ξ in Eq. (1) is high.⁸ For a non-vibrating molecule, $\mu_y = 0$, of course. The available data are unfortunately too qualitative in character to permit of a satisfactory interpretation in relation to the electronic structure of H_2O ; such a correlation, it may be pointed out, should involve relations between the coefficients of the expansion for μ_y as a function of the normal coordinates, and those of the similar μ_z expansion.

⁷ R. Mecke and collaborators: *Zeits. f. Physik* **81**, 313, 445, 465 (1933); *Phys. Zeits.* **33**, 833 (1932).

⁸ The fact that bands with $\Delta v_3 = \text{odd}$ depend on μ_y , those with $\Delta v_3 = \text{even}$ on μ_z , is easily deduced by group theory methods (procedure of L. Tisza, *Zeits. f. Physik* **82**, 48 (1933)). Cf. also W. Weizel, *Zeits. f. Physik* **88**, 214 (1934).

Raman Spectrum of Carbon Disulphide

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The Raman spectrum of liquid carbon disulphide has been investigated with high dispersion. In addition to the lines already known, five very faint lines have been observed. The intensities of the stronger lines were measured and, with a spectrograph of low dispersion, the degrees of depolarization of the two principal bands were determined. The results are in accord with the assumption made by Fermi, Dennison and Placzek that large perturbations of some of the energy levels occur on account of the approximate coincidence of ν_1 with $2\nu_2$. The values $\Delta = -120 \text{ cm}^{-1}$ and $|P| = 17.8 \text{ cm}^{-1}$ are obtained for the difference $\Delta = \nu_1 - 2\nu_2$ and for the coupling constant $P = \beta h^{\frac{1}{2}} / 4\pi^2 \mu_1^{\frac{1}{2}} \mu_2 (\nu_1 + 2\nu_2)^{\frac{1}{2}}$.

THE Raman spectrum of carbon disulphide has been studied by a number of investigators. The earlier workers^{1, 2, 3, 4} found a strong band near 656 cm^{-1} and a less intense band around 800 cm^{-1} . Krishnamurti⁵ observed

that the stronger of these two principal bands has a weak companion at 647 cm^{-1} . This was confirmed by Bhagavantam,⁶ Matossi and Aderhold,⁷ and Mesnage.⁸ The latter, employing a spectrograph of high dispersion, resolved the 800 cm^{-1} band into a band at 796.3 cm^{-1} and a weaker companion at 810.9 cm^{-1} . Pienkowski⁹

¹ C. V. Raman and K. S. Krishnan, *Nature* **122**, 882 (1928).

² A. Petriakaln and J. Hochberg, *Zeits. f. physik. Chemie* **B3**, 217, 405 (1929).

³ A. S. Ganesan and S. Ventekateswaran, *Nature* **124**, 57 (1929); *Ind. J. Phys.* **4**, 196 (1929).

⁴ Cl. Schaefer, F. Matossi and H. Aderhold, *Phys. Zeits.* **30**, 581 (1929).

⁵ P. Krishnamurti, *Ind. J. Phys.* **5**, 105 (1930).

⁶ S. Bhagavantam, *Ind. J. Phys.* **5**, 35, 59 (1930); *Nature* **126**, 995 (1930); *Phys. Rev.* **39**, 1029 (1932).

⁷ F. Matossi and H. Aderhold, *Zeits. f. Physik* **68**, 683 (1931).

⁸ P. L. Mesnage, *J. de Phys. et le Rad.* **2**, 403 (1931).

⁹ S. Pienkowski, *Acta. Phys. Pol.* **1**, 87 (1932).