

inactive and extremely weak in the Raman effect; this explains why the two lines of lowest frequency could not be observed. The mode 6 is an averaging of the four modes 6, 7, 8, 9 of C_2D_4 .

In the case of C_2H_3D , three more lines should appear in the Raman spectrum below 900 cm^{-1} ; they are due to motions out of the plane of the molecule. For the symmetrical molecule C_2H_4 , two of these modes are Raman inactive; the third one has not yet been observed.

A more extended account of the work is in course of publication in the *Annales de la Société Scientifique de Bruxelles*. The experimental work has been carried out in the laboratory of Prof. M. de Hempinne.

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*Manneback, C., and Verleysen, A. *NATURE*, **133**, 367 (1936).
id., *Annales Soc. Scient. Bruxelles*, B, **56**, 349 (1936); **57**, 31 (1937).

Force Constants and Molecular Structures

WE have examined the infra-red absorption spectrum of phosgene vapour. The following fundamental modes have been assigned: $A_1: \omega_1=1827$, $\omega_2=578$, $\omega_3=300$; $B_1: \omega_4=845$, $\omega_5=c.300$; $B_2: \omega_6=444$ cm^{-1} , the allocation being in agreement with the recent polarization measurement of Ananthakrishnan¹.

The persistence of molecular constants throughout various radicals has been remarked many times: Linnett and Thompson² have proposed using values of the force constants in C_2Cl_4 when compared with those of CCl_4 and C_2H_4 to determine the extent of contribution from resonating structures in the first molecule. The difficulty in obtaining even semi-quantitative measurements in such cases lies in the uncertainty as to what any particular force constant implies: thus for CCl_4 the values for the CCl force constant in the literature range from 1.74 to 3.85 ($\times 10^5$ dynes/cm.) according to the force field used, while Linnett and Thompson introduce another estimate of 4.38. One must hesitate in utilizing force constants derived from not necessarily comparable force fields, especially when the molecules have different symmetry.

The force constants for the ethylenic linkage in C_2H_4 and C_2Cl_4 given by these authors are respectively 9.0 and 5.8: if a correction is applied to the Badger relation so that it may hold for a carbon-carbon link, the first represents the true ethylenic distance of 1.37 A., while the second gives 1.45 A. or a 75 per cent single bond effect! Actually, even the refined methods of electron diffraction can scarcely distinguish between the supposed interatomic distances of 1.37 A. and 1.38 A.; consequently any great difference between the two force constants is illusory. The divergence may arise from the use of too artificial a force field, and also because the calculations employed are rigorously applicable only to infinitesimal amplitude frequencies.

We have met with rather more success in the treatment of the similar molecules phosgene, formaldehyde and urea. The carbonyl force constants are of the order of 12.3, 11.5 and 10.2 respectively: and

we may safely regard the carbonyl frequency, ω_1 , for HCHO (1,744 cm^{-1}) as the normal value. Hence the latter arises from a pure double bond; urea ($\omega_1=1,655$ cm^{-1}) has a considerable single bond contribution, but phosgene in accordance with the very high value $\omega_1=1,827$ cm^{-1} has a marked triple

Cl-

bond effect arising from such structures as $\begin{array}{c} C \equiv O^+ \\ \diagup \\ Cl \end{array}$,

rather than the single bond nature postulated by Pauling, Brockway, and Beach³ and deriving from

$\begin{array}{c} Cl^+ \\ \diagdown \\ C=O^- \\ \diagup \\ Cl \end{array}$. The interatomic distances obtained by

these authors for $COCl_2$ are $CO=normal (?)=1.28$, and $CCl=1.68 < normal=1.76$; the original results of Dornte⁴ ($CO=1.15 < normal$, $CCl=1.80 A. > normal$) are qualitatively more in agreement with the spectroscopic observations, while the chemical evidence is altogether in favour of the interpretation of phosgene as an acid chloride and not as a halogenated ethylene.

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¹ *Proc. Ind. Acad. Sci.*, **5**, 285 (1937).

² *NATURE*, **139**, 509 (1937).

³ *J. Amer. Chem. Soc.*, **57**, 2705 (1935).

⁴ *J. Amer. Chem. Soc.*, **55**, 4128 (1933).

Measurement of Pressures in the Upper Atmosphere

IN the course of a series of photographs of the spectrum of the auroral afterglow in pure nitrogen at pressures varying from about 1 mm. to 0.01 mm., it was observed that the ratio of the intensity of the first-negative system of bands to that of the second-positive system changed gradually as the pressure changed. The first negative bands, which are emitted by the molecule ion, increased in intensity until, at the lowest pressure at which it was possible to photograph the afterglow, the spectrum consisted almost entirely of bands due to the ionized molecule.

This result suggests the possibility of measuring accurately pressures in the upper atmosphere of the earth, by simultaneous observations of the ratio of these two band systems in an auroral display and of the height of the aurora. A comparison of these results with those obtained in the laboratory should then give the pressure. A series of careful experiments is now in progress to determine the effect of a small quantity of oxygen on the intensity ratio of these two band systems and also to study the effect of tube size on this ratio. In view of the present results, auroral observers may be led to make observations of the intensity ratio of these band systems as well as of the heights of the displays.

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