## Raman Spectrum of Trideuter-Acetic Deuteracid

AN account of the preparation of trideuteracetic deuteracid ($CD_3CO_2D$) by one of us (C. L. W.) will appear shortly in the *Journal of the Chemical Society*. Its Raman spectrum has been examined and gives preliminary results of great interest. The spectrum was obtained from 1·5 c.c. of the substance exposed for 23½ hours to excitation from a mercury arc filtered to transmit only the 4358 A. line.

| Displacement | *a* | *b* | *c* | *d* | *e* | *f* | *g* | *h* |
|---|---|---|---|---|---|---|---|---|
| $CH_3CO_2H$ | 447 | 621 | 895 | 1360 | 1430 | 1666 | 2942 | 3022 |
| $CD_3CO_2D$ | 411 | 580 | 800 | 1025 | 1093 | 1657 | 2150 | 2218 |

In the accompanying table, the Raman displacements observed are compared with definitely established displacements for acetic acid. All the displacements of $CH_3CO_2H$, except *f*, are modified to lower wave number values, but since this frequency is attributable to an inner vibration of the $CO_2H$ group, no change in its value is to be expected. The displacements *g* and *h* most probably have their origin in the C–H link, and preliminary calculations of the expected modification give results in good agreement with the observed values. It is possible that one of these displacements arises from an O–H link, but definite proof of this will be obtained, we hope, by an examination of the spectrum of acetic deuteracid ($CH_3CO_2D$). The examination of $CH_3CO_2D$ will also give valuable information regarding the other displacements. At present, the origin of these is a little uncertain. Most probably *a* and *b* are associated with bending frequencies of a C–C or C–O link; from intensity considerations, *c* almost certainly belongs to the C–C link; whilst *d* and *e* may arise from the $CH_3$ or $CO_2H$ groups, and it is hoped this will be decided by the proposed investigation of $CH_3CO_2D$.

Work is proceeding on $CH_3CO_2H$ prepared by the same method and measured by the same technique, partly to obtain comparable experimental data and partly to clear up certain points on which there is not complete concordance in the results of previous investigators.

The complete results for the three acids and a discussion of the origin of the frequencies will be published elsewhere as soon as the investigation is finished.

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## Infra-Red Absorption Spectrum of Crystalline Sodium Nitrite

THERE are very few data available in the infra-red absorption spectra of solids which enable an application of the modern ideas of point group symmetry to the classification of 'proper' vibrations. We have recently examined the absorption spectrum of sodium nitrite in the solid state. The substance has already been shown to be orthorhombic, and thus biaxial, with considerable separation between the indices of refraction. There are two molecules in the unit cell, and there will be eight particles in the basic group: accordingly we shall expect $3(8 - 1) = 21$ 'proper' vibrations, of which six will be 'inner' vibrations, and fifteen 'external' or lattice vibrations. Generally, some of the inner vibrations will coincide in pairs, but if the nitrite group is angular, its symmetry will be $C_{2v}$, which is the same as that of the crystal group[1], and we may expect considerable separation between the pairs. These conditions do not occur in the free ion, and A. Langseth and E. Walles[2] have obtained a clear and satisfying Raman spectrum for the aqueous solution with $\nu_1 = 1331$, $\nu_3 = 1240$, $\nu_2 = 813$ cm.$^{-1}$. In our case all the fundamental frequencies and overtones are doubled, bands occurring at $\nu_2 = 707$ and 834 (10); $\nu_3 = 1127$, 1220 (14); $\nu_1 = 1330$ and 1392 (10); $2\nu_2 = 1378$, 1626 (4); $2\nu_3 = 2252$, 2439 (2); $2\nu_1 = 2646$, 2762 (3). The numbers in brackets give an approximate measure of the relative intensities. The bands at 707 cm.$^{-1}$ and 834 cm.$^{-1}$ have faint wings on each side, which may perhaps be explained by the trichroism of the substance.

Dr. W. R. Angus and Mr. A. H. Leckie of this Department have kindly examined the Raman spectrum of the solid. They find a broad band in the region of 1350 cm.$^{-1}$ with a strong sharp maximum at 1314 cm.$^{-1}$, a weak indication at 1352 cm.$^{-1}$, and a weak but sharp peak at 1400 cm.$^{-1}$. We are continuing the infra-red analysis with polarised light.

Ziegler suggested a vertical angle of some 132°, but our results are in agreement with those of Langseth and Walles, since the frequencies satisfy a central force system with an angle of 96°. There seems to be a single bond between the nitrogen and each oxygen atom, whereas the binding in the nitro-group is of the same type as in $SO_2$, corresponding to a vertical angle of some 120°.

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[1] G. E. Ziegler, *Phys. Rev.*, **38**, 1040; 1931.

[2] *Z. phys. Chem.*, B, **27**, 209; 1934.

## A New Emission Spectrum in Selenium Vapour

IN the course of a systematic study of the excitation of selenium vapour in a high-frequency discharge, we have observed, on the short wave side of the main $^1\Sigma-^1\Sigma$ system[1], a new system of about forty weak and diffuse bands degraded to the red which may be approximately represented by the following formula:

$$\nu = 29{,}890 + 285\,n' - 3\,n'^2 - 390\,n''.$$

These bands appear at low temperatures, before the main system becomes visible; but when the temperature is raised, the main system becomes incomparably more intensified than the new one.

The similarity of the vibrational structure of the new system to the main one[2],

$$\nu = 25{,}905 + 281{\cdot}3\,n' - 2{\cdot}42\,n'^2 - 387{\cdot}2\;\;n'' + 0{\cdot}63\;\;n''^2,$$

together with the conditions of the excitation and their appearance (large structureless bands) make it plausible that the new system is to be attributed to the excitation of the $Se_2$ group in a polyatomic molecule of selenium. This seems to be confirmed by the fact that a set of absorption