

the calculated values of  $C_p$ , probably because the value of  $C_p - C_v$ , and also the contribution due to angular oscillations, become appreciable. The observed heat capacities therefore show that, besides the lattice oscillations, another oscillation responsible for the origin of the new line takes place at low temperatures, the nature of the oscillation being such that its contribution to  $C_p$  is that of the corresponding Einstein function. It appears that this oscillation takes place in pairs of carbon dioxide molecules, the molecules in each pair being connected to each other by a weak electronic bond.

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<sup>1</sup> Sirkar, S. C., and Gupta, J., *Curr. Sci.*, 5, 214 (1937).

<sup>2</sup> "International Critical Tables", 5, 86.

<sup>3</sup> Pauling, L., *Phys. Rev.*, 36, 430 (1930).

### Structure of the Methane Molecule

AN explanation of the complex rotational fine structure of the 1306  $\text{cm}^{-1}$  fundamental vibrational band of methane<sup>1</sup> has been found which is based on a tetrahedrally symmetrical model for the molecule. The cause of the splitting of the rotational lines is a Coriolis coupling between the rotational levels of this threefold degenerate mode of vibration  $\nu_4$  and the rotational levels of the infra-red inactive twofold degenerate vibration  $\nu_2$  at 1536  $\text{cm}^{-1}$ , which lies 230  $\text{cm}^{-1}$  above it. The perturbation is appreciable in spite of the distance between the pairs of levels concerned, because the Coriolis coupling term in question is essentially a first-order term in the Hamiltonian. A general expression for this term in methane was given by one of us in a previous paper<sup>2</sup>. It involves the components of vibrational angular momentum obtained by combining the displacements of  $\nu_4$  with the momenta of  $\nu_2$  and *vice versa*<sup>3</sup>. It is to be noted that since the two vibrations belong to different symmetry types, the perturbation affects only the rotational levels and leaves the origin of the  $\nu_4$  band unaltered.

The perturbation, which produces a splitting as well as a displacement of the rotational levels, has been calculated up to the tenth rotational quantum number. From these perturbed levels a theoretical spectrum has been derived which agrees very well with the observed spectrum, even though we have not taken into account any change in the moment of inertia or any centrifugal expansion of the molecule. These latter effects are therefore probably small. It should be pointed out that theoretical intensities which take into account correctly the nuclear spin weights of the equivalent hydrogen nuclei have not been given before. We have made use of the recent work of Maue<sup>4</sup> to calculate these, and the theoretical intensities agree well with experiment (for example,  $R(1)$  and  $R(5)$  weak).

It is to be noted that when, as in the low-frequency fundamental of methane, the perturbation comes from above, the levels are all pushed down. This produces, since the perturbation increases

with the rotational quantum number, a converging  $R$  branch, a diverging  $P$  branch and a broad  $Q$  branch which extends well into the  $P$  branch, thus producing the effects of an apparent increase in the moment of inertia. A perturbation from below would, however, produce just the opposite effect, namely, a divergence in the  $R$  branch, a convergence in the  $P$  branch and a  $Q$  branch extending into the  $R$  branch. The fundamental  $\nu_4$  of germane ( $\text{GeH}_4$ ) does indeed appear to have this structure<sup>5</sup>, and we have here just the required conditions to produce this effect, for the perturbing vibration  $\nu_2$  lies below  $\nu_4$  (Steward and Nielsen<sup>5</sup> give  $\nu_4 = 934 \text{ cm}^{-1}$ ,  $\nu_2 = 820 \text{ cm}^{-1}$ ) (In silane ( $\text{SiH}_4$ ), on the other hand, the  $Q$  branch would appear to extend into the  $P$  branch<sup>6</sup> and this is in agreement with the assignment of the frequencies ( $\nu_4 = 910$ ,  $\nu_2 = 978$ ) given by Stitt and Yost<sup>7</sup> which makes the perturbation come from above. We would like to believe that the apparent additional  $Q$  branch found near 978  $\text{cm}^{-1}$  in the 910  $\text{cm}^{-1}$  band of silane comes from activity being imparted to  $\nu_2$  by the perturbation.)

Similar perturbations may be expected in the spectra of all polyatomic molecules possessing a threefold or higher axis of symmetry, for such molecules can have degenerate modes of vibration with a vibrational angular momentum, and if the conditions are fulfilled there may be a large Coriolis coupling between the rotational levels of different bands. Thus, for example, these new effects may be looked for in the perpendicular bands of the methyl halides and ammonia and possibly in the deformation bands of linear molecules.

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<sup>1</sup> Nielsen and Nielsen, *Phys. Rev.*, 48, 864 (1935).

<sup>2</sup> Jahn, H. A., *Ann. Phys.*, 23, 529 (1935).

<sup>3</sup> See also Teller, E., "Hand- und Jahrbuch d. Chem. Phys.", 9 II, 152.

<sup>4</sup> Maue, V.-W., *Ann. Phys.*, 30, 555 (1937).

<sup>5</sup> Steward and Nielsen, *Phys. Rev.*, 48, 861 (1935).

<sup>6</sup> Steward and Nielsen, *Phys. Rev.*, 47, 828 (1935).

<sup>7</sup> *J. Chem. Phys.*, 4, 82 (1936).

### Photographic Action of Artificial Radio-Elements

IN the literature concerning artificial radioactivity, we find no indication of attempts to show the photographic action of radio-elements. Accordingly we decided to carry out a few experiments, the results of which are given below.

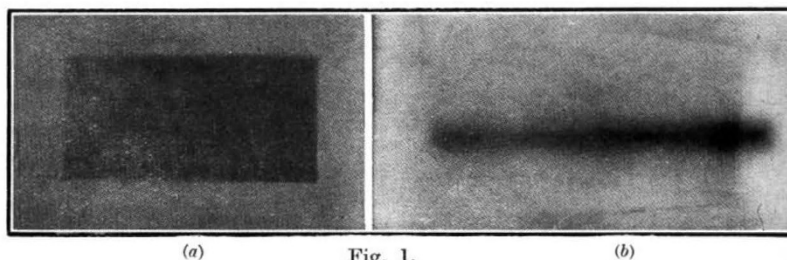


Fig. 1.

It is known that iridium irradiated with neutrons slowed down in paraffin shows a strong activity of period 19 hours. We placed an activated sheet of