

LETTERS TO THE EDITORS

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Internal Rotation of Methyl Groups in Cadmium Dimethyl

IN view of current interest in the problem of free or restricted internal rotation in molecules, we may mention briefly some results which indicate free rotation of methyl groups about the Cd—C bond in cadmium dimethyl. We have already described¹ measurements on the rotational fine structure of some vibrational bands of zinc dimethyl and mercury dimethyl, which provided strong evidence for such free internal rotation in these molecules. The infra-red absorption spectrum of cadmium dimethyl has now been measured with greater resolving power than that previously used by Gutowsky², particularly in the region of 3μ .

Our results agree substantially with those of Gutowsky, although we have not observed some weak bands found by him, and the contour of some bands suggests a different frequency assignment. There is a parallel-type band at $2,925\text{ cm.}^{-1}$ with spacing of \bar{P} — \bar{R} branch maxima close to 17 cm.^{-1} , which agrees with that to be expected from the rough value of the moments of inertia. The most important feature is a perpendicular-type band centred around $2,980\text{ cm.}^{-1}$ with clearly separated Q branches, roughly 10 cm.^{-1} apart, each third line being stronger than its neighbours. As pointed out in the earlier paper, the separation of Q branches in the same species of band with ethane is about 5 cm.^{-1} , and the greater separation found here, which agrees with that reported for zinc dimethyl and mercury dimethyl, cannot be explained satisfactorily by Coriolis interaction. It falls into line exactly with the spacing expected if there is free internal rotation.

Full details of this band and the whole spectrum will be described later elsewhere.

D. R. J. BOYD
R. L. WILLIAMS
H. W. THOMPSON

St. John's College,
Oxford.
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¹ *Trans. Farad. Soc.*, Cambridge Discussion, 1950.

² *J. Amer. Chem. Soc.*, **71**, 3194 (1949).

Evaporation and Mobility of Naphthalene Molecules

IN a recent communication¹ under this title, V. J. Clancey has given a short account of a beautiful experiment on this subject. Among his very interesting results he gives a provisional value for the mean displacement x_s of adsorbed molecules of the order of a few millimetres. Having been connected with these problems, during the development of a theory of crystal growth from the vapour, in collaboration with W. K. Burton and F. C. Frank², his value seems to me too high for ordinary temperatures. The purpose of the present communication is to show that much smaller values of x_s can be deduced indirectly from Dr. Clancey's results.

The experimental arrangement is as follows. A spot of solid naphthalene was placed on a surface

(mica, glass, etc.) and covered by a thin glass hemisphere, leaving a small aperture between the two. Adsorbed molecules will then escape from the hemisphere and travel for an average distance x_s prior to evaporation into the vacuum. Two such assemblies were mounted, facing opposite directions, at the sides of an axis of suspension, to produce a torque when evaporation took place.

The concentration N of adsorbed molecules outside the hemisphere must satisfy the equation

$$x_s^2 \nabla^2 N = N, \quad (1)$$

where x_s , the mean displacement, is given by

$$x_s^2 = D_s \tau_s, \quad (2)$$

D_s being the diffusion coefficient and τ_s the mean life of the adsorbed molecules. The boundary conditions at the edge of the hemisphere become $N = N_0$ if the edge is open and $N = 0$ otherwise. We suppose the aperture to cover an angle 2θ on the side opposite to that facing the axis of suspension. The torque T produced by the corresponding distribution N is readily calculated, and the result is

$$T = T_0 \{ (K_1/K_0) \theta + (\rho/X) (K_2/K_1) \sin \theta \}, \quad (3)$$

$$T_0 = \alpha (2\pi mkT)^{1/2} \tau_s^{-1} N_0 x_s \rho X. \quad (4)$$

In these expressions K_1 are Bessel functions going exponentially to zero for $r \rightarrow \infty$; the argument is always ρ/x_s , where ρ is the radius of the hemisphere. X is the distance from the centre of the hemisphere to the axis of suspension. The factor α in (4) is a complicated one, depending on the actual law of interaction and the mechanism of energy transfer between the surface and the adsorbed molecules³; in simple cases it should not be very different from unity.

We think it a good approximation to suppose $\rho/x_s \gg 1$ (otherwise the calculations would have to be more complicated); then (3) becomes, neglecting $(x_s/\rho)^2$,

$$T = T_0 \left\{ \theta + (\rho/X) \sin \theta + \frac{1}{2} \frac{(x_s/\rho)}{[\theta + 3(\rho/X) \sin \theta]} \right\}. \quad (5)$$

It is therefore clear that a value of x_s could be deduced, at least in principle, from the variation of T/T_0 as a function of θ , as it was originally intended by Dr. Clancey. Unfortunately, x_s/ρ is so small, in our opinion, that the second term in (5) cannot be used for this purpose.

Nevertheless, it seems to me possible to deduce interesting information from the absolute value (4) of T_0 . Let us assume that the adsorption energy is small and the temperature not too low, so that the concentration N_0 of adsorbed molecules inside the hemisphere is small. Then this concentration, in equilibrium with the vapour pressure p of naphthalene, will be given by $N_0 = p\tau_s(2\pi mkT)^{-1/2}$, and (4) will become

$$T_0 = \alpha(\rho X)(px_s), \quad (6)$$

where all the factors are known except x_s (if we accept $\alpha \sim 1$).

When the surface can be considered as a more or less perfect crystal surface, we can write for x_s

$$x_s \sim a \exp \left\{ \frac{1}{2} (A - U)/kT \right\}, \quad (7)$$

where A is the adsorption energy and U the activation energy necessary for the displacement of an adsorbed molecule from an equilibrium position to the next, distant a from each other. Then the exponential factor in (6) will be $\exp(-E/kT)$ with