fluorine now disintegrates more and more into a neutron and fluorine 17, which then emits a positive electron. The final product in either case is oxygen 16.

W. D. HARKINS

Cornell University,
Ithaca, New York,
December 7, 1936.

[1] W. D. Harkins, Chem. Rev. **5**, 374 (1928).
[2] W. D. Harkins, D. M. Gans and H. Newson, Phys. Rev. **44**, 530, 533, 534, 537 (1933).
[3] W. D. Harkins and D. M. Gans, Phys. Rev. **46**, 397 (1934); Nature **133**, 794 (May, 1934).
[4] W. D. Harkins, Nat. Acad. Sci. **19**, pp. 307–318, March (1933).
[5] W. D. Harkins, Science **83**, 533 (1936). Address presented before Section C of the American Association for the Advancement of Science, and the St. Louis Section of the American Chemical Society, St. Louis, January 1, 1936.

## The Rotation-Vibration Spectrum of $C_2H_6$ and the Question of Internal Rotation

The problem of the order of magnitude of the potential restricting the relative rotation of the $CH_3$ groups about the symmetry axis in $C_2H_6$, once considered settled, has been revived by the statistical-mechanical calculations of several authors, the most recent being those of Kemp and Pitzer.[1] The latter authors find that by assuming a potential of about 3000 cal. restricting the internal rotation, it is possible to reconcile the equilibrium and calorimetric measurements of the $H_2 + C_2H_4 = C_2H_6$ reaction and to reproduce the experimentally determined entropy and specific heat of $C_2H_6$. The theoretical value of the restricting potential calculated by Eyring[2] is, on the other hand, only 350 cal.

We have made a dynamical study of a model of $C_2H_6$ in which vibration, over-all rotation and internal rotation subject to an arbitrary restricting potential may occur simultaneously, and have investigated how the rotation-vibration spectrum of $C_2H_6$ in the fundamental region will change in the transition from free to completely restricted internal rotation. In a comparison of theory and experiment the sole source of positive evidence concerning the extent of the freedom of the internal rotation is the rotational structure of certain perpendicular-type infrared bands in the fundamental region. From the observed structure of the bands a lower limit of 2000 cal. (700 cm$^{-1}$) is estimated for the potential restricting internal rotation. This result is in agreement with the conclusion of Kemp and Pitzer.[1]

It is found that there are two types of degenerate normal vibrations in $C_2H_6$, one of which is active, and one inactive in the infrared, regardless of the magnitude of the potential restricting internal rotation. The point group $D_3$, which assigned by Teller and Topley[3] to $C_2H_6$ and according to which they concluded that all degenerate vibrations would be active in the infrared, does not sufficiently describe the symmetry of the normal vibrations. The full symmetry properties of the vibrations are obtained by using the group $D_{3h}$ since the potential energy is invariant under a reflection in a plane perpendicular to the threefold symmetry axis regardless of the relative orientation of the $CH_3$ groups about the axis. (The transformation corresponding to this operation involves the internal angle.)

Barring *accidental* degeneracy of degenerate normal

TABLE I. *Rotational spacing in* $cm^{-1}$ *of perpendicular-type infrared bands of* $C_2H_6$.

| $\nu$ | $\Delta\nu$ obs. | $\Delta\nu$ calc. |
|---|---|---|
| 827 | 2.6 | 2.63 |
| 1480 | 4.9 | 5.60 |
| 3000 | 3.3 | 2.98 |

TABLE II. *Observed and calculated fundamental frequencies in* $cm^{-1}$.

| | Obs. | Calc. | | Obs. | Calc. |
|---|---|---|---|---|---|
| $\nu_1$ | 993 ⎫ | (993) | $\nu_6$ | 827 ⎫ | 840 |
| $\nu_2$ | 1460 ⎬ R | 1570 | $\nu_7$ | 1480 ⎬ I. R. | 1480 |
| $\nu_3$ | (liq.) ⎭ | 2910 | $\nu_8$ | 3000 ⎭ | 3020 |
| | 2927* | | | | |
| $\nu_4$ | 1380 ⎫ I. R. | (1380) | $\nu_9$ | — | 1005 |
| $\nu_5$ | 2926** ⎭ | (2900) | $\nu_{10}$ | — | 1515 |
| | | | $\nu_{11}$ | — | 3025 |

* $\nu_3 = 2927$ cm$^{-1}$ is the mean of the two Raman frequencies 2899 cm$^{-1}$ and 2955 cm$^{-1}$.
** $\nu_5 = 2926$ cm$^{-1}$ is the mean of the two infrared frequencies 2896 cm$^{-1}$ and 2955 cm$^{-1}$.

vibrations of different types (active and inactive), the same rotational structure of the infrared bands is predicted for all magnitudes of the potential restricting internal rotation. Consequently, the theory of the rotational spacings of the perpendicular-type infrared bands, inclusive of the effect of rotation-vibration coupling, is similar to the theory applied by Johnston and Dennison[4] to symmetrical top molecules without internal rotation. Table I gives the observed values of the line spacings of the perpendicular-type bands and the values we have calculated. However, as a result of the approximate accidental degeneracy between degenerate vibrations of different types with frequencies in the 1480 and 3000 cm$^{-1}$ regions, the internal rotation if it were free would be quasi-active and the simple rotational structure with the spacings calculated in Table I would not be observed. A perturbation calculation gives 2000 cal. as a limit to the potential restricting the internal rotation below which the rotational structure of the bands would be quite different from that observed.

A three-constant valence-force type of potential function was chosen with which to calculate a set of frequencies and normal coordinates to be used in the perturbation calculation above. Table II gives the observed and calculated fundamental frequencies, which on the whole agree well considering the simplicity of the potential function used. The estimate of the lower limit to the restricting potential is not very dependent upon the accuracy of the normal coordinate treatment.

J. B. HOWARD

Mallinckrodt Chemical Laboratory,
Harvard University,
Cambridge, Massachusetts,
December 9, 1936.

[1] Kemp and Pitzer, J. Chem. Phys. **4**, 749 (1936).
[2] Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).
[3] Teller and Topley, J. Chem. Soc. p. 885, July (1935).
[4] Johnston and Dennison, Phys. Rev. **48**, 868 (1935).