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Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Fluorescence of Naphthacene in Anthracene

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June 4, 1945

IN a recent communication to this Journal,[1] Dr. Ganguly has questioned the need to assume an "exciton" process in the fluorescence of solid solutions of anthracene and naphthacene. His experiments show that the dissolved naphthacene fluoresces when excited by blue light which it absorbs. This is clearly a case of direct excitation of the naphthacene molecules. When an exciting wave-length of 3650A is used, however, the phenomena are not so simple. Pure anthracene fluoresces in this light a violet color (bands 4030—4450A). A solid solution with as little as 1 mole naphthacene to 10^4 moles anthracene however fluoresces with the characteristic green color due to the naphthacene, and at a mole ratio of 5×10^4 the green is very strong and the anthracene emission largely suppressed. There are only three possibilities for this behavior:

(1) The naphthacene absorbs more light than the anthracene at 3650A. This is ruled out by the fact that the extinction coefficient of anthracene is several times larger than that of naphthacene at this wave-length, so that the ratio of absorptions is about 10^4:1 in favor of anthracene for the above solid solutions.

(2) The anthracene absorbs the light and emits its violet fluorescence which is taken up by the naphthacene and re-emitted as green fluorescence. This is likely to occur only when the absorption of the anthracene fluorescence by the naphthacene is at least as great as the absorption of 3650A by the anthracene crystal. Using extinction coefficient data obtained for liquid solutions of these hydrocarbons, a maximum value for the anthracene-naphthacene ratio satisfying the above condition is about 10, or one thousandth of the actual ratio.

(3) The anthracene absorbs the light and hands the quanta of excitation energy on from molecule to molecule through the crystal by a process of resonance until either an anthracene molecule loses it again by fluorescence or until it is trapped by a naphthacene molecule which is thereby caused to fluoresce.

The latter process explains why crystalline anthracene has a half-life for fluorescence of about 10^{-5} sec. while a liquid solution has a half-life of 10^{-8} sec. These figures indicate that the distance the excitation energy (exciton) travels between absorption and emission for pure anthracene is of the order of 1000 molecules. At naphthacene contents of 10^{-4} there would be one molecule of naphthacene for every 30 of anthracene in any linear direction in the crystal so that even at this low concentration there is a high chance of the energy reaching a naphthacene molecule.

Solution of these crystals in a liquid destroys the "exciton" effect, which is of course dependent on proper orientation of the molecules. A strongly green-fluorescing solid solution, when dissolved in benzene, shows only the blue fluorescence of pure anthracene. The fluorescence of solid organic compounds are liable to be much more sensitive to traces of impurities embedded in the crystal than the corresponding solutions in liquids. The hydrocarbon coronene, for example, fluoresces blue in solution, but even highly purified crystals extracted from tar fluoresce green; whence it is probable that these crystals still contain a minute quantity of impurity not detectable by ordinary organic chemical means.

The brilliance of the green fluorescence of anthracene containing a few parts in a thousand of naphthacene renders the substance very suitable for preparing fluorescent screens for focusing U.V. spectrographs. A hot acetone solution of the hydrocarbons is added to about three times its volume of warm dilute gelatine solution in water and the mixture allowed to dry in not too thin a layer on a glass plate. Such plates are translucent and permit sharp focusing. They are also useful for rapid visual observations with a U.V. spectrograph.

[1] S. C. Ganguly, J. Chem. Phys. **13**, 128 (1945).

The Ratio Rule

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May 17, 1945

NOETHER[1] has recently found that the results of his studies on the isotopic methyl halides could be expressed very well by the following empirical "ratio rule:"

$$\nu_n CD_3Cl = \nu_n CH_3Cl \frac{\nu_n CD_3X}{\nu_n CH_3X}, \quad (1)$$

where X is a halogen atom and ν_n refers to the corresponding frequency in each molecule. Moreover, he has shown that this rule could be successfully extended to other pairs of isotopic molecules as long as they were of similar symmetry. No theoretical derivation of this rule was known, although the results suggest that here is a phenomenon of considerable importance to the estimation of the effect of isotope substitution on molecular vibrations. It is the purpose of this note to indicate briefly the theoretical background of the ratio rule and to propose,

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in addition, a more useful but generally less accurate form of it.

The matrix expression for the frequencies of vibration of a molecular system is given by[2]

$$\lambda = L^{-1}GFL, \tag{2}$$

with λ a diagonal matrix whose elements are $\lambda_{ii}=4\pi^2\nu_i^2$; L is the transformation matrix from symmetry coordinates to normal coordinates, and G and F are respectively the kinetic and potential energy matrices. This equation may be regarded as a set of relationships between each λ_{ii} and the various L_{ki}. If the equation involving λ_{ii} is differentiated partially with respect to L_{ki}, one obtains after some manipulation

$$\partial\lambda_{ii}/\partial L_{ki}=0. \tag{3}$$

This is Rayleigh's principle and shows that λ_{ii} is stationary for small variations in the normal coordinates.[3] Thus when a somewhat approximate normal coordinate is available, Eq. (2), or its equivalent, yields a rather accurate value for the corresponding frequency of vibration.

These results may be applied directly to the isotope effect by taking each normal coordinate of the non-isotopic molecule as a first approximation to the corresponding normal coordinate of the isotopic molecule. Using L_0, λ^0 etc., and λ, G etc., to refer to non-isotopic and isotopic matrices respectively, one obtains from (2)

$$\begin{aligned}\lambda &\doteq (L_0^{-1}G\tilde{L}_0^{-1})(\tilde{L}_0FL_0)\\ &\doteq (L_0^{-1}G\tilde{L}_0^{-1})\lambda^0.\end{aligned} \tag{4}$$

Equating corresponding diagonal elements yields

$$\lambda_{ii}/\lambda_{ii}^0 \doteq \Sigma_{kj}\,\kappa_{ik}\kappa_{ij}G_{kj}/\Sigma_{mn}\,\kappa_{im}\kappa_{in}G_{mn}^0, \tag{5}$$

κ_{ik} being most simply thought of as the unnormalized coefficient $(L_0^{-1})_{ik}$. A more formal perturbation treatment (similar to that once proposed by Wilson[4]) shows that this equation is correct to the first order.

When symmetry coordinates are formed from internal coordinates (bond stretches, angle deformations, etc.), they can be made to correspond rather closely to normal coordinates. If the symmetry coordinates of the non-isotopic molecule have been so chosen, the principal terms in Eq. (5) involve κ_{ii}^2; and one may write that

$$\begin{aligned}\lambda_{ii}/\lambda_{ii}^0 &\approx \kappa_{ii}^2G_{ii}/\kappa_{ii}^2G_{ii}^0\\ &\approx G_{ii}/G_{ii}^0.\end{aligned} \tag{6}$$

Equation (5) is the fundamentally basic equation of the ratio rule (correct to the first order). Equation (6) is undoubtedly the most useful form of the rule, its field of application being limited only by the assumptions used in deriving it. Thus it is equally valid in calculating the frequency shifts resulting from the change CCl_4^{35} to $CCl_3^{35}Cl^{37}$ as for CH_4 to CD_4 both of which fall outside the scope of Eq. (1).

On the other hand Eq. (1) is the form of Eq. (5) which is valid whenever *two pairs* of molecules have essentially the same normal coordinates. Unfortunately this requirement restricts the use of Eq. (1). However, when these conditions are met, as with the two pairs CH_3Cl, CD_3Cl and CH_3Br, CD_3Br, Eq. (1) yields more accurate results than Eq. (6). This, of course, is the consequence of the fact that symmetry coordinates are not quite normal coordinates, a fact more fully corrected for in Eq. (1) than (6).

The kind of accuracy that may be expected from Eq. (6) under favorable conditions is indicated by Table VIII of the Noether paper, in which he notes the agreement between the frequency ratio and the square root of the G ratio for the methyl halides. However, calculations show that Eq. (6) does not give good results when a D-H substitution is accompanied by a symmetry change (i.e., CH_4-CH_3D). This is the result of near degeneracy in the A_1 and E symmetry classes; an approximate perturbation treatment appropriate thereto gives excellent results. It should also be pointed out that whenever a symmetry change is involved special symmetry coordinates should be used in setting up the G matrix. This whole topic will be discussed in greater detail in a forthcoming paper on this subject.

Since the ratio rule deals with individual frequencies of vibration, it may be expected that it will be even more useful than the well known Teller-Redlich product rule.[5]

[1] H. F. Noether, J. Chem. Phys. **11**, 97 (1943).
[2] E. B. Wilson, Jr., J. Chem. Phys. **9**, 76 (1941).
[3] See R. A. Frazier, W. J. Duncan, A. R. Collar, *Elementary Matrices* (Cambridge University Press, New York, 1938), p. 299, for a closely related discussion involving "modal columns."
[4] E. B. Wilson, Jr., Phys. Rev. **45**, 427 (1934).
[5] Teller, cf. C. K. Ingold *et al.*, J. Chem. Soc., London, 971 (1936); O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935); E. B. Wilson, Jr., reference 2.

Collisional Deactivation of Excited Ethylene Molecules

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May 28, 1945

IN the reaction of $Hg(^3P_1)$ atoms with ethylene it has been shown[1,2] that acetylene and hydrogen formation can be explained on the basis of the reactions

$$Hg(^3P_1)+C_2H_4=C_2H_4{}^*+Hg(^1S_0), \tag{1}$$

$$C_2H_4{}^*+C_2H_4=2C_2H_4, \tag{2}$$

$$C_2H_4{}^*=C_2H_2+H_2, \tag{3}$$

where $C_2H_4{}^*$ represents an excited ethylene molecule. This mechanism was based on the following experimental facts:

(a) Acetylene and hydrogen formation is not inhibited by nitric oxide.
(b) making allowance for the change in collision frequency with temperature for the bimolecular reaction (2), the rate of formation is independent of temperature, and
(c) the rate decreases with increasing ethylene pressure.

At 25°C almost all of the ethylene used up in the early stages of the reaction is accounted for by the acetylene and hydrogen formed. This makes it relatively easy to investigate the deactivation process, (2), at that temperature. If this reaction occurs then qualitatively at least, it is immaterial whether the deactivator is an ethylene molecule or not. Carbon dioxide was chosen as a deactivator because of its small quenching cross section relative to

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