Vibrational Assignments in Ethane

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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.

Vibrational Assignments in Ethane

In a recent number of this Journal, Crawford, Avery and Linnett[1] reported certain Raman and infra-red observations on ethane, and gave an excellent resumé of the available data and their interpretation. As this molecule has four different fundamental vibrations with frequencies approximating 1400 cm^{-1}, a unique correlation with observed bands is perhaps not yet possible. Some qualitative arguments may be presented, however, in favor of an interpretation slightly different from the one referred to.

Two nondegenerate parallel vibrations due to hydrogen bond deformations are found in ethylene at 1444 cm^{-1} and 1623 cm^{-1}, the former observed in the infra-red and the latter in Raman scattering. The motions differ primarily in phase, the lower frequency involving an oscillation of the two carbon atoms moving together, while at the higher frequency they move in opposite directions. Of the two corresponding vibrations in ethane, the antisymmetric one appears in the infra-red at 1380 cm^{-1}, and the symmetric oscillation has been assigned the frequency 1375 cm^{-1}. There are several reasons why this does not seem plausible: (1) a consideration of the motion and a comparison with the ethylene frequencies indicates that it should certainly be greater than 1380 cm^{-1}, (2) no Raman line has been observed at 1375 cm^{-1} although the harmonic of this frequency appears, and (3) a comparison[2] with methyl halide frequencies (ν_3) suggests that it is too small by at least 100 cm^{-1}.

There is a fairly strong Raman line due to ethane near 1460 cm^{-1}, but polarization measurements[1] indicate that it must be due to a degenerate vibration, in spite of the fact that usually such bands are very weak. The infra-red measurements of Levin and Meyer[3] place this band center at 1461 cm^{-1}, one half-space below the position of the strongest line. (The maximum of smaller intensity at 1492 cm^{-1} may be due to the difference band 2955 − 1461 = 1494.) However, an examination of the microphotometer curve on the 1460 cm^{-1} Raman line seems to indicate a weak polarized component on the high frequency side and not distinctly separated from the broad depolarized band. Its position may be estimated as approximately 1480 cm^{-1}. Why the Raman line due to the degenerate motion should be strong, and that due to the nondegenerate one weak, is not easy to explain, but it would be still more difficult to understand a vanishingly small Raman intensity supposing the frequency to be 1375 cm^{-1}. On the other hand,

there is one of the motions for which the fundamental is inactive both in Raman and in infra-red, with which the latter frequency may be associated.

The assignment here proposed for the frequencies of the hydrogen bond deformations, as compared with those in Table II of reference 1, using the symmetry symbols for the point group D_{3h}, is

$$A_1': 1480 \text{ instead of } 1375,$$
$$A_2'': 1380 \text{ unchanged},$$
$$E': 1460 \text{ instead of } 1480,$$
$$E'': 1375 \text{ instead of } 1460.$$

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University of Michigan,
Ann Arbor, Michigan,
February 23, 1939.

[1] B. L. Crawford, W. H. Avery and J. W. Linnett, J. Chem. Phys. 6, 682 (1938).
[2] A. Adel and E. F. Barker, J. Chem. Phys. 2, 627 (1934).
[3] A. Levin and C. F. Meyer, J. Opt. Soc. Am. 16, 137 (1928).

The Coupling of Vibrations with Electronic Levels in Rare Earth Compounds*

Many of the features of the absorption spectra of rare earth compounds have been accounted for by attributing the lines to transitions between $(4f)^n$ electronic configurations of the cation.[1] These levels are split by the electric fields within the solid into multiplets[2] giving rise to a number of possible transitions. However, it is necessary to assume coupling of vibrations with the electronic levels to account for the large number of lines actually observed. However, in no case in the knowledge of the authors has a definite absorption frequency difference been identified as a vibration frequency. It is the purpose of the present preliminary account of an investigation of the absorption spectra of the acetylacetonates of praseodymium and neodymium to present evidence for a vibration frequency of approximately 82 cm^{-1} and 103 cm^{-1}, respectively, for the two compounds.

The acetylacetonate compounds were chosen for investigation for the following reasons: (1) The fact that this type of compound possesses a molecular lattice should simplify the modes of vibration which couple with electronic levels; (2) the field perturbing the central ion should be approximately of octahedral symmetry since the work of Astbury[3] indicates that the tervalent acetylacetonate molecule probably consists of a cation surrounded by six oxygens at the corners of a regular octahedron with the

chain of three carbons of the β-diketone molecule spanning between a pair of oxygens.

The absorption spectra of solid anhydrous and hydrated praseodymium and neodymium acetylacetonate were observed in the near infra-red and visible at temperatures of 78°K, 120°K, 193°K and 298°K. The spectrum of the anhydrous neodymium compound was similar to that of $NdCl_3 6H_2O$,[4] although it possessed fewer strong lines as was expected. That of the praseodymium compound was markedly simpler than the spectrum of $Pr_2(SO_4)_3 \cdot 8H_2O$.[5]

Plates taken at 120°K using appropriate absorption thicknesses and optimum exposure times showed progressions of very diffuse weak bands extending from strong absorption multiplets to shorter wave-lengths. These bands were separated by fairly constant intervals which averaged 82 cm^{-1} in the case of $Pr(C_5H_7O_2)_3$ and 103 cm^{-1} in the case of $Nd(C_5H_7O_2)_3$. It seems reasonable to interpret these separations as vibrational frequencies because of their appearance and the fact that a qualitative application of the Franck-Condon principle explains their intensity. It is interesting to note that the praseodymium compound is the less stable of the two, a fact which might correlate with its lower vibration frequency. One or two similar intervals could be found on the long wave side of nearly every multiplet. The accuracy of the measurements is approximately ± 2 cm^{-1}.

If a term scheme which is a combination of those proposed by Ellis[1] and Mukherji[1] is used, the Stark levels produced by splitting due to an octahedral field plus the vibration levels are adequate to account for the lines in each multiplet of the neodymium compound. A similar scheme applies partially in the case of $Pr(C_5H_7O_2)_3$. However, many assignments are not unique, hence it seems advisable to calculate the theoretical splitting of all the excited states using a field which produces the splitting observed for the ground state of the ion before putting forth a scheme of analysis.

A more detailed description of the experimental work and discussion of results will be presented later.

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* From work done by W. S. Herbert in partial fulfillment of the requirements for the Ph.D. degree at the Ohio State University.
[1] H. A. Bethe and F. H. Spedding, Phys. Rev. 52, 454 (1937). Cf. references cited. H. Gobrecht, Ann. d. Physik 28, 673 (1937); J. H. Van Vleck, J. Phys. Chem. 41, 67 (1937); C. B. Ellis, Phys. Rev. 49, 875 (1936); P. C. Mukherji, Ind. J. Phys. 11, 123 (1937).
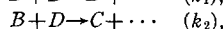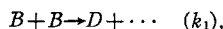[2] H. A. Bethe, Ann. d. Physik 3, 133 (1929).
[3] Astbury, Proc. Roy. Soc. A112, 448 (1926).
[4] F. H. Spedding and H. F. Hamlin, J. Chem. Phys. 5, 429 (1937).
[5] Spedding, Howe and Keller, J. Chem. Phys. 5, 416 (1937).

A Solution of an Equation Occurring in the Theory of Consecutive Reactions

The reactions

$$B+B \rightarrow D+\cdots \quad (k_1),$$
$$B+D \rightarrow C+\cdots \quad (k_2),$$

where k_1 and k_2 are the rate constants of the respective bimolecular reactions, lead to equations for the variations with time of $[B]$ and $[D]$ whose solution is not easy. The primary differential equations are:

$$\dot{B} = -2k_1B^2 - k_2BD,$$
$$\dot{D} = k_1B^2 - k_2BD,$$

where B and D represent the concentrations of the respective substances. Differentiating the first and substituting in the result the value of $\dot{D}$ from the second and D from the first, these reduce to

$$B\ddot{B} + B^2\dot{B}(2k_1+k_2) - \dot{B}^2 + 3k_1k_2B^4 = 0.$$

Let $2k_1+k_2 = l$, $3k_1k_2 = m^2$, $e^\beta = B$:

$$\ddot{\beta} + le^\beta\dot{\beta} + m^2e^{2\beta} = 0.$$

Expressing β as a power series in t, expanding $e^\beta\dot{\beta}$ and $e^{2\beta}$, and equating coefficients of like powers of t, one obtains:

$$\beta = \ln a + a_1t - \tfrac{1}{2}a(la_1 + m^2a)t^2 + \text{terms in higher powers.}$$

The constants of integration are a and a_1; the former is equal to the initial value of $B(B_0)$, and the latter equals $-2k_1B_0$. The error caused by neglecting powers of t higher than the square is equal to the quadratic term times atk_1 or atk_2 according as $k_1/k_2 \gtrless 1$. This gives for B:

$$B = B_0 \exp\left(-2k_1B_0t - \tfrac{1}{2}k_1B_0^2(k_2-4k_1)t^2\right)$$

which is seen to be the normal exponential decrease minus a quadratic correction due to the second reaction. The error in this value of B due to neglect of higher powers of t is, for values of t ordinarily met with in reaction rate measurements, smaller than 1 part in 10^4. In any case it may readily be calculated.

Substituting B in the original equations gives $D = f(t)$. But often k_2 is all that is desired and k_1 is known. For example, a rate of dimerization being known, a rate of trimerization is wanted, assuming a mechanism of successive reactions. For this it is necessary to know the values of B and D at $t = t_1$; call them B_1 and D_1. Then simplification of the expression for D gives

$$k_2 = 2k_1 \frac{B_0 - B_1 - 2k_1B_0^2t_1}{D_1 - k_1B_0^2t_1}.$$

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Raman Effect of Fluorotrichloromethane

Six Raman lines have been observed for fluorotrichloromethane using our usual equipment.[1] The sample was distilled into a Raman tube in the low temperature apparatus already described.[2] It was held at a temperature of about 0°C during the exposures. Illumination was by means of eight concentric neon-mercury lamps. No filters were used. Results are shown in Table I.

Eastman Spectroscopic Plates Type I-J and Type I-G were employed. Best results were obtained with the former. There was no noticeable photochemical action during a 46-hour exposure.

The material was furnished by the E. I. duPont de Nemours & Company and was a plant product considered 99 percent pure or better. We wish to thank Dr. A. F.