

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE NORMAL VIBRATIONS OF ACETYLENE

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RECEIVED AUGUST 11, 1931

PUBLISHED JANUARY 7, 1932

About a year ago Mecke¹ published an analysis of the normal vibrations of acetylene, and used the results to interpret the infra-red spectrum of acetylene which had previously been studied by Levin and Meyer.²

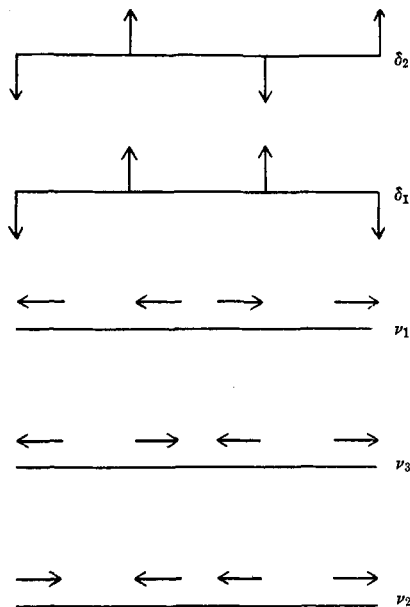


Fig. 1.

In this analysis Mecke assumed a linear model, and listed the five normal modes of vibration shown in Fig. 1. He observed that δ_1 was symmetrical and that δ_2 was anti-symmetrical with respect to reflection on the center of gravity, but nevertheless concluded that both were optically active. The ratio of $\delta_1:\delta_2$ which he derived was 1:1.88, and so on this basis he assigned the band at 730 cm.^{-1} to δ_1 and the band at 1326 cm.^{-1} to δ_2 .

It seems to the authors of this article that since δ_1 is symmetrical, it cannot be observed in the absorption spectrum except in combination bands, and that the ratio $\delta_1:\delta_2$ must be in error. We have therefore recalculated the frequency ratios for the normal vibrations by classical

mechanics. We assume a linear molecule and infinitely small vibrations. The forces are assumed to be such that we can write the potential energy in the first approximation in the form

$$\frac{1}{2} K_1 [(\Delta S_1)^2 + (\Delta S_2)^2] + \frac{1}{2} K_2 (\Delta S_2)^2 + \frac{1}{2} K_3 [(\Delta \alpha_1)^2 + (\Delta \alpha_2)^2]$$

where K_1 , K_2 and K_3 are coefficients of the restoring forces, S_1 , S_2 and S_3 are equilibrium distances, and α_1 and α_2 are angles as shown in Fig. 2.

In Fig. 3, which refers to the vibration δ_1 , d is the distance between carbon and hydrogen, and $2l$ is the distance between the carbons; α is the angle between the C-C bond and the C-H bond. In order that the molecule as a whole shall have no rotation it is necessary that $m_2 l \dot{x}_2 = (l + d) m_1 \dot{x}_1$ where m is the mass; the subscript 2 refers to the carbon and the subscript 1 to the hydrogen. For small angles we can set $\alpha = \sin \alpha$, and so

¹ R. Mecke, *Z. Physik*, **64**, 173 (1930).

² Aaron Levin and Charles F. Meyer, *J. Opt. Soc. Am.*, **16**, 137 (1928).

$\dot{\alpha}d = \dot{x}_1 + j\dot{x}_2$ where $j = (l + d)/l$. The kinetic energy $T = m_1 \dot{x}_1^2 + m_2 \dot{x}_2^2$. By solving for \dot{x}_1 and \dot{x}_2 in terms of $\dot{\alpha}$, d and m and substituting we get $T = \dot{\alpha}^2 d^2 m_1 m_2 / (m_2 + m_1 j^2)$.

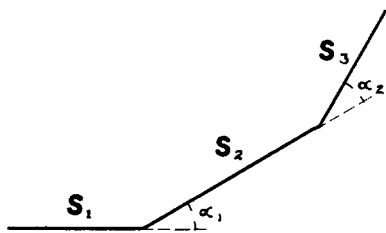


Fig. 2.

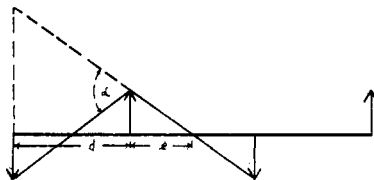


Fig. 3.

In Fig. 4 β replaces α as the angle between the two bond directions; otherwise the notation is the same as before. Here we must impose the condition for no translation of the molecule, and so $m_1 \dot{x}_1 = m_2 \dot{x}_2$.

$\beta d = \dot{x}_1 + \dot{x}_2$ and T is again equal to $m_1 \dot{x}_1^2 + m_2 \dot{x}_2^2$. On substitution we get $T = \beta^2 d^2 m_1 m_2 / (m_1 + m_2)$. Therefore $\delta_2/\delta_1 = (m_1 + m_2)^{1/2} / (m_1 j^2 + m_2)^{1/2}$.

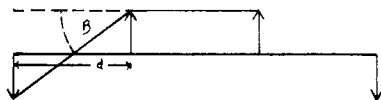


Fig. 4.

We can get a fair estimate of j from Birge's³ compilation of band spectra data. Setting $2l = 1.31 \text{ \AA.}$ and $d = 1.13 \text{ \AA.}$, we find $j^2 = 7.45$, and so $\delta_2/\delta_1 = 0.816$, compared to Mecke's value of 1.88.

With respect to ν_1 , ν_2 and ν_3 we can set up the expressions for the kinetic and potential energies immediately, and from them derive the relation which must hold between these frequencies. The kinetic energy T for all three vibrations will have the form $T = m_1 \dot{x}_1^2 + m_2 \dot{x}_2^2$ where x_1 is the displacement of the hydrogen atom, and x_2 is that of the carbon atom.

If K_1 is the coefficient of the restoring force between carbon and hydrogen along the bond and $K_2/2$ that between the carbons, then for the vibration ν_2 , the potential energy will be given by $V = K_1(x_1 + x_2)^2$ and from the condition for no translation we get $m_1 x_1 = m_2 x_2$.

For the vibrations ν_1 and ν_3 the potential energy takes the form

$$V = K_1 x_1^2 - 2K_1 x_1 x_2 + (K_1 + K_2) x_2^2$$

where x_1 and x_2 are independent. Solving the equation for the fundamental frequencies by the usual method for small vibrations, we obtain

$$\begin{aligned} \nu_1^2 : \nu_2^2 : \nu_3^2 &= \frac{13 K_1 + K_2 - (169 K_1^2 - 22 K_1 K_2 + K_2^2)^{1/2}}{24} : \frac{13 K_1}{12} \\ &: \frac{13 K_1 + K_2 + (169 K_1^2 - 22 K_1 K_2 + K_2^2)^{1/2}}{24} \end{aligned}$$

These values of ν_1 , ν_2 and ν_3 are not inconsistent with Mecke's interpretation

³ R. T. Birge, "International Critical Tables," McGraw-Hill Book Co., New York, Vol. V, p. 409.

of the spectrum, but if our values of δ_1 and δ_2 are correct some revision of Mecke's correlation with experiments must be made.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE TRANSFERENCE NUMBER OF LITHIUM CHLORIDE AS A FUNCTION OF THE CONCENTRATION

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RECEIVED AUGUST 13, 1931

PUBLISHED JANUARY 7, 1932

Introduction

According to the classical dissociation theory of Arrhenius the mobilities of the ions are expected to be independent of the concentration and hence transference numbers should be constants which do not vary with the concentration. On the other hand, according to the modern interionic attraction theory of Debye and Hückel, the mobilities of the ions vary with the concentration and this variation is not relatively the same for all ions but depends on the size of the ions and especially on the valence. Therefore it may be predicted from this theory that transference numbers will vary with the concentration. It has been shown by Jones and Dole¹ that the transference numbers of the barium ion in barium chloride can be expressed by an equation having the form, $t = [A/(1 + B\sqrt{c})] - 1$, (1) over the entire range from 0.001 to 1.0 molal. It was also shown that although erroneous values for the transference number of barium chloride were obtained by Lucasse² from data on the electromotive force of concentration cells with and without transference, the fault lay, not in the data themselves, but in their interpretation, and that a more rigid mathematical procedure gave results in essential agreement with the analytical method.

It seemed to be desirable to test the general validity of the equation, $t = [A/(1 + B\sqrt{c})] - 1$, for the variation of the transference number with the concentration. The experimental determination of transference numbers is tedious and difficult and the classical theory gave no incentive for studying the variation of transference numbers with the concentration. These considerations are probably responsible for the fact that sets of data on transference numbers for any salt of sufficient precision for our purpose and covering a wide range of concentration and obtained by the same method are extremely rare in the chemical literature. The most important exception to this general rule is the set of values for lithium chloride from 0.001 to 3.0 normal obtained by the electromotive force

¹ Grinnell Jones and Malcolm Dole, *THIS JOURNAL*, **51**, 1073 (1929); Malcolm Dole, *J. Phys. Chem.*, **35**, 3647 (1931).

² W. W. Lucasse, *ibid.*, **47**, 743 (1925).