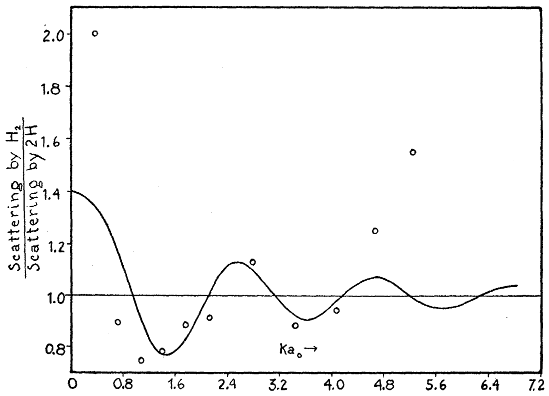

FIG. 4. Illustrating the diffraction pattern in hydrogen. *Ordinates*, Ratio of the scattering by H_2 to the scattering by 2H; *solid line*, Theoretical; *circles*, Observed values.

with which the experimental curve decreases with angle, its actual observation in H_2 is difficult. If, however, we calculate the ratio of the scattering by H_2 (experimental) to the theoretical scattering by two hydrogen atoms and plot the result as a function of Ka_0, we should get a curve which oscillates about the value unity. This has been done for 912 volts, and the result is shown in Fig. 4. The solid line is the theoretical ratio, the circles the experimental points. We note that the agreement is about as good as could be expected. At large values of Ka_0 the experimental points lie far above the value unity. The reason for this is that in the angular distribution curve the experimental values fall above the theoretical curve.

CONCLUSION

The writer takes this opportunity to express his appreciation to Professor A. L. Hughes who proposed this problem and whose suggestions were invaluable aids throughout the investigation.

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Isotope Effect in Acetylene

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The normal frequencies of the linear acetylene molecule have been computed for infinitesimal vibrations with the generalization that the masses of the two hydrogen atoms are different. Constants of the potential energy have been determined by using the well-known frequencies of normal acetylene. Numerical calculations have then been carried through for the molecules C_2HD and C_2D_2 and the results compared with observed frequencies.

RECENT measurements in the infrared of the absorption bands of acetylene in which one or both of the hydrogen atoms has been replaced by deuterium makes it desirable to calculate at least in first approximation the normal frequencies for this molecular model. It is well known that the four atoms of acetylene lie in one line and the consequent symmetry makes the problem of infinitesimal vibrations comparatively simple. If one takes as provisional coordinates, displacements of the atoms in their own line and perpendicular to it, a general expression for the energy containing only quadratic terms will contain squares of these coordinates and likewise products with the exception of those which involve the perpendicular displacements linearly. This is obvious from the symmetry of the model. The energy expression, therefore, separates into two parts each of which contains only one type of displacement and one may solve for the frequencies in two distinct calculations. The longitudinal displacements involve three normal coordinates and the transverse involves four coordinates which are degenerate in two pairs.

We shall first consider the longitudinal displacements choosing as coordinates the relative displacements of the particles $H-x_1-C-x_2-C-x_3-H$. The potential energy may then be written

$$2V=K_1(x_1^2+x_3^2)+K_2x_2^2+2K_3(x_1x_2+x_2x_3)+2K_4x_1x_3.$$

Only four constants are involved since the displacements x_1 and x_3 are symmetrical. Both K_3 and K_4 may be considered small since they record the interaction of nonadjacent atoms. K_4 is doubtless too small to influence these calculations appreciably.

Calling the change of coordinates of the four atoms taken in the same order, y_1, y_2, y_3, y_4,

$$2T=m_1\dot{y}_1^2+M\dot{y}_2^2+M\dot{y}_3^2+m_2\dot{y}_4^2.$$

Where m_1 and m_2 are the masses of the two hydrogens and M that of the carbon atom.

Four equations may be written of which three interrelate the x's and y's and the fourth states the condition for stationary centroid. With the help of these the kinetic energy may be written as follows:

$$\begin{aligned}2\Sigma T=m_1(m_2+2M)\dot{x}_1^2+(M+m_1)(M+m_2)\dot{x}_2^2\\+m_2(m_1+2M)\dot{x}_3^2+2m_1(m_1+M)\dot{x}_1\dot{x}_2\\+2m_1m_2\dot{x}_1\dot{x}_3+2m_2(m_1+M)\dot{x}_2\dot{x}_3,\end{aligned}$$

where $\Sigma=m_1+m_2+2M$, the total mass of the molecule.

Setting up the determinant in $\lambda(=(2\pi\nu)^2)$ one obtains a cubic equation which for the case $m_1=m_2=m$ may be factored into the two equations

$$\begin{aligned}\lambda^2-\lambda\left[\frac{\Sigma}{M(m+M)}K_2+\frac{\Sigma}{2mM}(K_1+K_4)\right.\\\left.-\frac{2\Sigma}{M(m+M)}K_3\right]+\frac{\Sigma^2}{Mm(m+M)^2}\\\times\left[\frac{K_2(K_1+K_4)}{2}-K_3^2\right]=0,\end{aligned}$$

$$\lambda-\frac{K_1-K_4}{2mM}\Sigma=0.$$

The linear equation does not contain K_3 and is therefore to be identified with a vibration which involves no relative motion of the two carbons. This frequency has been called ν_3 by Dennison. It will be seen that for this vibration the dependence of the frequency on m is given by the factor $(\Sigma/m)^{\frac{1}{2}}$, independent of the force constants.

This gives a ratio of $(13/7)^{\frac{1}{2}}$ for the frequencies ν_3 for C_2H_2 and C_2D_2.

For the remaining longitudinal frequencies which Dennison has called ν_1 and ν_2 the situation is not so simple and it is necessary to solve for the constants K. This may be done in close approximation by using the three known parallel frequencies of normal acetylene which are given by Sutherland[1] as

$$\nu_1=1974,\quad \nu_2=3372,\quad \nu_3=3288.$$

The equations contain four constants and with only three frequencies it will be necessary to set $K_4=0$. We thus obtain

$$K_1=5.850\times10^5 \qquad \text{dynes/cm}$$

$$\left.\begin{aligned}K_2&=15.587\\K_3&=0.0279\end{aligned}\right\}\text{ or }\left\{\begin{aligned}&27.432\times10^5\\&5.896\times10^5.\end{aligned}\right.$$

The double values of K_2 and K_3 arise from the quadratic equations in which they appear and for this calculation it is immaterial which pair is used since the results will be the same. It may be noted that the first pair in which K_3 is much smaller than K_1 is the more plausible.

Setting these constants into the quadratic equation for λ, one obtains, together with ν_3 the following frequencies for C_2D_2:

$$\nu_1=1750,\quad \nu_2=2690,\quad \nu_3=2414.$$

For the molecule C_2HD it is necessary to return to the cubic in λ in which have been substituted $m_1=1$, $m_2=2$, $M=12$ and the above values of K. This yields

$$\nu_1=1840,\quad \nu_2=3335,\quad \nu_3=2560.$$

To set up the potential energy expression for transverse displacements it is most convenient to choose as coordinates the angles made between the line connecting the two carbons and the lines connecting each hydrogen with its adjacent carbon. Calling these angles α_1 and α_2,

$$V=\tfrac{1}{2}K_1(\alpha_1^2+\alpha_2^2)+K_2\alpha_1\alpha_2.$$

For the kinetic energy

$$T=\tfrac{1}{2}(m_1\dot{x}_1^2+M\dot{x}_2^2+M\dot{x}_3^2+m_2\dot{x}_4^2).$$

Where x indicates the displacement of an atom normal to the axis of the molecule. These coordinates are related through the equations

$$\alpha_1=(x_2-x_1)/a+(x_2-x_3)/b,$$
$$\alpha_2=(x_3-x_4)/a+(x_3-x_2)/b.$$

Where a is the normal distance from H to C and b from C to C.

Translation and rotation may be removed with the equations

$$m_1x_1+Mx_2+Mx_3+m_2x_4=0,$$
$$aMx_2+(a+b)Mx_3+(2a+b)m_2x_4=0.$$

The determinant in λ is now of second order and yields the following equation:

$$\lambda^2a^4+\lambda^2a^2\left[-\frac{K_1}{M}\left(2+4c^2+4c+\frac{M}{m_1}+\frac{M}{m_2}\right)+\frac{K_2}{M}(4c^2+4c)\right]$$
$$+\frac{K_1^2-K_2^2}{M^2}\left[\frac{M^2}{m_1m_2}+\left(\frac{M}{m_1}+\frac{M}{m_2}\right)(1+2c+2c^2)+1+4c+4c^2\right]=0,$$

where $c=a/b$. It contains besides the two force constants K_1 and K_2, the two lengths a and b. For $m_1=m_2=m$, it may be factored into

$$\lambda_5a^2=(1+4c+4c^2+M/m)/M(K_1-K_2),$$
$$\lambda_4a^2=[(M+m)/Mm](K_1+K_2).$$

That frequency in which K_1 and K_2 enter symmetrically has been identified with ν_4 in which the two carbon atoms move in the same direction. Since one may write

$$\lambda_4a^2=A_1(1+M/m),$$

the dependence on m is very simple and one has the ratio of frequencies ν_4 for C_2H_2 and C_2D_2 equal to $(13/7)^{\frac{1}{2}}$.

Even in the case of ν_5 which may be written

$$\lambda_5a^2=A_2(1+4c+4c^2+M/m),$$

the ratio of frequencies is independent of K and may be evaluated by assuming a value for $c=a/b$.

By using the values given by Mecke $a=1.08\times10^{-8}$ and $b=1.19\times10^{-8}$, the ratio of the frequencies ν_5 for C_2H_2 and C_2D_2 is $(19.92/13.92)^{\frac{1}{2}}$.

For the molecule C_2HD it is necessary to evaluate the force constants with the help of the frequencies ν_4 and ν_5 for normal acetylene which are given by Sutherland[1] as $\nu_4=730$, $\nu_5=605$. By using Mecke's values for a and b

$$\left.\begin{aligned}K_1&=2.442\times10^{-12},\\K_2&=0.922\times10^{-12}\end{aligned}\right\}\text{ dyne cm/rad.}$$

Returning to the second order determinant with $m_1=1$ and $m_2=2$ we get $\nu_4=669$, $\nu_5=523$. The frequencies are thus as presented in Table I. Observations of absorption bands of C_2HD and C_2D_2 have been made in the infrared by Randall and Barker.[2] These bands are fundamentals and low order combinations and are therefore best suited for identification by this calculation which has not considered higher powers than the second in the potential energy. There is some difficulty in placing the center of the observed bands because of these perturbations but the agreement with calculation leaves little doubt as to the classification. Table II shows the data now available. It will be seen that the agreement between observation and calculation is good. The differences are of the magnitude 10 cm^{-1} which may easily be due to the anharmonic terms in the potential energy which have not been included in this calculation. In order to determine how these terms should transform, a much more detailed analysis would be necessary.

TABLE I. *Frequencies of acetylene molecule.*

	C_2H_2	C_2HD	C_2D_2
ν_1	1974	1840	1750
ν_2	3372	3335	2690
ν_3	3288	2560	2414
ν_4	730	669	535
ν_5	605	523	505

TABLE II. *Data on vibrational frequencies of acetylene molecule.*

Molecule	Assignment	Character	Freq. obs.	Freq. calc.
C_2D_2	ν_4	$\perp$	539.2	535
C_2D_2	$\nu_4+\nu_5$	$\parallel$	1043	1040
C_2DH	ν_4	$\perp$	679	669
C_2DH	ν_5	$\perp$	518.9	523
C_2DH	$\nu_4+\nu_5$	$\parallel$	1202	1192
C_2DH	ν_3	$\parallel$	2585	2560

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[1] Sutherland, Phys. Rev. **43**, 883 (1933).

[2] Randall and Barker, Phys. Rev. **45**, 124 (1934).