Raman Spectra of DeuteroEthylenes

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All the different ethylenes, have been prepared, their Raman spectra in the liquid state measured and classified. A comparison between experimental data and theoretical predictions permits an estimate of the order of magnitude of the anharmonicity.

(1) Introduction

MANY authors have attempted to calculate accurately the potential function of polyatomic molecules in their normal state. Although, such calculations have been made successfully for diatomic molecules, the study of visible and ultraviolet absorption spectra has given little information concerning polyatomic molecules. Only infra-red and Raman spectra furnish the experimental data necessary for a determination of this function. Unfortunately, the amount of such data is small, and it is not possible to calculate all the constants involved and *a fortiori* to check the proposed function. For instance, in the case of ethylene, investigated by several authors,[1] the harmonic potential function with regard to the planar vibrations (involving all the coupling terms), contains fifteen parameters, and infra-red and Raman spectra give only nine experimental values. But the substitution of the hydrogen atoms by deuterium gives six new compounds, C_2H_3D, $C_2H_2D_2$ (*cis, trans,* asymmetrical) C_2HD_3, C_2D_4, corresponding to the same potential function. Since each of these compounds gives nine new frequencies, $9 \times 7 = 63$ experimental values are obtained by this process for the determination of fifteen coefficients.

(2) Brief Discussion of the Theory

The symmetrical coordinate method, introduced by Manneback[2] for the calculation of molecular vibration frequencies, shows that in the case of C_2H_4 and C_2D_4 it is possible to classify into four groups the frequencies corresponding to the planar motions of the molecule. The first group S_1[3] corresponds to the 3 symmetrical vibrations with respect to the two planes of symmetry, the second group S_2 corresponds to the two antisymmetrical vibrations with respect to the same planes, the third and the fourth group correspond to the two vibrations A_1 and A_2 symmetrical with respect to one of these planes and antisymmetrical with respect to the other. S_1 and S_2 are Raman active and inactive in the infra-red. A_1 and A_2 are Raman inactive and active in infra-red. In the case of $C_2H_2D_2$ (*trans*), a center of symmetry permits a separation of the frequencies into two groups, one symmetrical and the other antisymmetrical with respect to the center. $C_2H_2D_2$ (*cis* and asymm.) can also be divided into two groups π and σ, symmetrical and antisymmetrical with respect to their planes of symmetry. The asymmetrical compounds C_2H_3D and C_2D_3H have no symmetry at all, and no separation is possible.

(3) Preparation of Compounds

The ethylenes were prepared in two different ways. The first method employs the exchange of hydrogen atoms between ethylene and heavy water, by means of a catalyst.[4] One can, thus, by substituting new quantities of heavy water for that impoverished by the exchange, obtain a gradual enrichment of deuterium atoms in the ethylene. The monosubstituted ethylene appears first. It is gradually supplanted by the disubstituted forms, which themselves are finally transformed into the trisubstituted and tetrasubstituted ethylenes. We prepared two different samples by the method of exchange reaction. The

[1] G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. London **A148**, 250 (1935). J. M. Delfosse, Ann. Soc. Scient. **B55** (1935). L. G. Bonner, J. Am. Chem. Soc. **58**, 34 (1936). C. Manneback and Verleysen **B56**, 349 (1936). A. Verleysen and C. Manneback **B57**, 31 (1937).
[2] C. Manneback, *Calcul et identification des molécules* (Liège, 1935).

[3] The notation throughout this paper is the same as that employed by Manneback and Verleysen (reference 1).
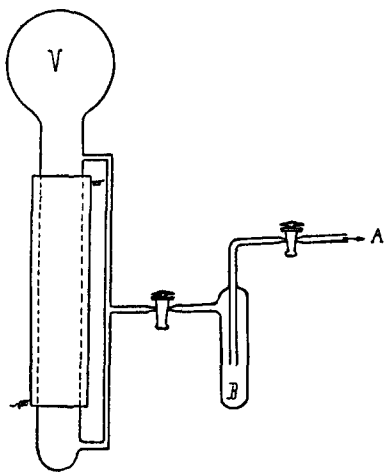[4] J. Horiuchi and Polanyi, Trans. Faraday Soc. **30**, 1164 (1934).

FIG. 1.

heavy water employed was 99.6 percent pure. The light ethylene used for the exchange process was prepared by the ordinary method of dehydrating alcohol by sulfuric acid. It was prepared separately for each of the exchanges and carefully distilled. For the first exchange, we made use of a catalyst prepared by the precipitation and calcination of nickel hydroxide by ammonia on pumice. The catalyst was then reduced in the apparatus employed for the reaction, at a temperature of 350 degrees, by a stream of hydrogen. The hydrogen was pumped out and a sample of heavy water, (5 g) introduced in trap A (Fig. 1), was carefully outgassed and then distilled into trap B. The ethylene was then introduced into the vessel V and the heavy water distilled into the same vessel. The apparatus was constructed in such a way that the constituents would be thoroughly mixed. The mixture was then heated at 100 degrees for several days, after which the ethylene was examined. Then it was reacted again with a new sample of heavy water. The first sample of ethylene was subjected to three exchanges. The results are represented by the microphotometer curves a, b, c. In the second case, 6 liters of ethylene at one atmosphere, were exchanged with 15 g of heavy water. The catalyst employed was an industrial one, generously furnished us by Professor H. S. Taylor. The mixture was heated at 150 degrees during several days. In addition, we have been able to prepare certain deutero-ethylenes in the pure state. The compounds thus obtained were:
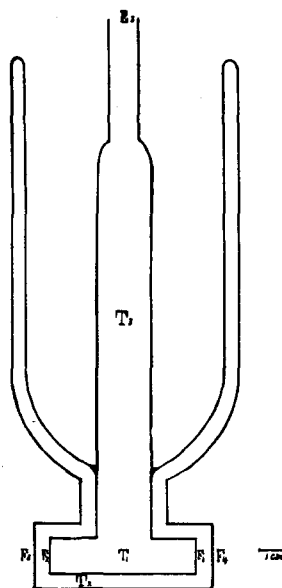
FIG. 2.

C_2H_3D, a mixture of $C_2H_2D_2$ (*cis* and *trans*), and C_2D_4. These compounds were prepared by reducing the corresponding ethylene dibromide with zinc in light water solution. In order to obtain the dibromide, we started with vinyl bromide and heavy hydrobromic acid in the first case, heavy acetylene and light hydrobromic acid in the second case, and finally, heavy acetylene and heavy hydrobromic acid.

$$\left.\begin{array}{ll} CH_2=CHBr+DBr & CH_2Br-CHDBr \\ CD\equiv CD+2HBr & CHDBr-CHDBr \\ CD\equiv CD+2DBr & CD_2Br-CD_2Br \end{array}\right\}+Zn$$

$$CH_2=CHD$$
$$CHD=CHD$$
$$CD_2=CD_2.$$
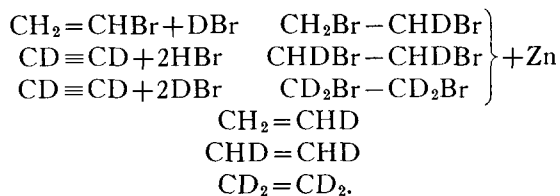
The vinyl bromide employed is a Fraenkel product. The hydrobromic acid was obtained by the action of water on phosphorous pentabromide distilled in vacuum. The acetylene was obtained by passing heavy water vapor over commercial calcium carbide at ordinary temperature. The carbide had previously been heated at 500 degrees for several hours in order to dry it. The synthesis of dibromide was slow in the first case. In the other two cases, it was necessary to accelerate the reaction by illuminating the product with ultraviolet light ($\lambda>3300A$). Since the ethylenes were obtained by two different

TABLE I. (cm^{-1}).

C_2H_3D	$C_2H_2D_2$(cis, trans)	C_2D_4
1599.5 (12)	1567.3 (20)	1514.7 (15)
3014.9 (7)	3046.7 (1)	2251.6 (15)
2266.2 (5)	3033.1 (1)	981.6 (1,5)
1395.7 (9)	2290.7 (8)	2306 (0,2)
1286.4 (8)	2276.0 (8)	2272.6 (1)
2964.2 (3)	1215.0 (7)	2215.4 (0,8)
3007.6 (1)	1282.2 (7)	995.8 (2)
1340.3 (6)	763.4 (0,2)	1215 (0,1)
1619.2 (2)	863.4 (0,2)	1283.4 (0,6)
	2216.7 (0,4)	1567.3 (4)
		1544.3 (4)
24276	22793	24835
22794	22276	23534
21511	22235	21893
21501	22460	21438
		21376

TABLE II. $C_2H_4+C_2H_2D_2$ (cm^{-1}).

FIRST EXCHANGE	SECOND EXCHANGE	THIRD EXCHANGE
		981.0 (0,1)
		994.4 (0,1)
		1215.1 (0,7)
		1282.7 (0,4)
1286.0 (1)	1286.3 (0,5)	
1341.0 (13)	1341.3 (1)	1340.9 (0,1)
		1379.1 (0,5)
1397.5 (5)	1397.7 (0,5)	1397.3 (0,1)
		1514.4 (0,3)
	1544.3 (0,4)	1544.7 (4)
1567.3 (1,5)	1567.4 (2)	1567.3 (3)
	1581.2 (0,3)	1581.6 (1)
1600.7 (10)	1600.2 (1)	1600.4 (2)
1620.8 (15)	1621.0 (0,7)	
		2213 (0,2)
		2221.0 (0,2)
		2252.0 (0,1)
2266.2 (2)	2266.6 (0,3)	2266.8 (0,1)
		2273 (0,3)
		2291.4 (0,1)
2965.8 (5)	2966.0 (0,8)	2965.0 (0,4)
3007.1 (7)	3007.0 (3)	3006.8 (0,05)
3015.6 (6)	3015.3 (1)	3015.7 (0,05)
21817		
21833		
21622		

methods, it was possible to classify the lines unambiguously and to eliminate the lines arising from impurities.

(4) RAMAN SPECTRA OF THE PRODUCTS

(a) Technique

Light from two mercury vapor lamps operating at 3.8 amp. and 120 volts was converged on a cylindrical tube containing the liquefied gas by means of two condensers (132 mm in diameter). The tube was arranged parallel to the lamps. The optical system employed a diaphragm placed close to the tube in order to use the maximum amount of scattered light and eliminate light reflected by the walls of the tube. The image of the diaphragm was focused without magnification on the slit of the spectrograph by means of a lens. A three-prism Cojan spectrograph of aperture $f:6$ was employed. The dispersion of the instrument in the region of 4100A is 7A per mm.

We used "Superguil" plates, with a sensitivity of 2100 HD. Exposure times of 40 hours were necessary to bring out the weak lines. In spite of these long exposure times, no lines corresponding to the non-planar vibrations were detected. The Raman flask consists of a cylinder T_1 closed by two polished quartz windows F_1 and F_2. Another tube T_3 is sealed to T_1. A tube T_2 concentric to T_1 is also closed by two quartz windows F_3 and F_4. Finally, a Dewar vessel is joined on as shown in Fig. 2. The gas introduced at E_3 is liquefied in tube T_3, runs into tube T_1 and is kept at a temperature sufficiently low so that it remains liquefied. The Raman lines were measured with a

TABLE III. (cm^{-1}).

	C_2H_4 exp.	C_2H_3D* theor.	C_2H_3D* exp.	$C_2H_2D_2$ (cis) theor.	$C_2H_2D_2$ (cis) exp.	$C_2H_2D_2$ (trans) theor.	$C_2H_2D_2$ (trans) exp.	$C_2H_2D_2$ (asymm.) theor.	$C_2H_2D_2$ (asymm.) exp.	C_2HD_3 exp.	C_2D_4 theor.	C_2D_4 exp.
ν_1	1620.1	1570.2	1600.2	1516.2	1567.3	1514.2	1567.3	1555.3	1581.4	1544.4	1428.0	1514.5
ν_2	3007.3	3030.5	3015.3	3065.0	3046.4	3049.2	3033.1			2272.6	2283.9	2251.8
ν_3	1340.7	2254.7	2266.4	2304.2	2290.1	2291.1	2275.9	2221.0	2221.0	2215.0	1008.9	981.3
ν_4		1380.3	1396.6	1247.2	1282.2	1240.2	1215.0	1357.8	1379.1	995.2		
ν_5		1261.8	1286.2	752.7	763.4	807.9	863.4					
ν_6		2986	2964.7								2308	2306
ν_7	944.0										758.3	780
	3072.0											

* The theoretical frequencies of C_2H_3D have been calculated by C. Lemaitre, Y. L. Tchang and C. Manneback. (C. Lemaitre, Y. L. Tchang and C. Manneback, Ann. Soc. Scient. **B121** (1937)). Recently Tchang, correcting the potential function for the anharmonicity, obtained theoretical frequencies which fit the experimental data with an error less than 0.5 percent. (In publication: Ann. Soc. Scient. Bruxelles.)

FIG. 3(a). First exchange.

FIG. 3(d). C₂H₃D.

FIG. 3(b). Second exchange.

FIG. 3(c). Third exchange.

comparator by using an iron spark spectrum for comparison.

The results are given in Tables I–III. Tables I and II give directly the frequencies between the measured Raman lines, while the numbers in parenthesis indicate their relative intensities. Each of them comes from at least two different lines, and the mean value has been taken. The parent lines are:

27388.0   27354.4   24705.4   22938.0   (cm⁻¹).

Table I gives the lines corresponding to the spectrum of C_2H_3D, $C_2H_2D_2$, C_2D_4 prepared in the pure state. At the bottom of the table are given several weak lines for which we have not yet found satisfactory explanation. Table II gives the lines corresponding to the three different exchanges. Table III gives the classification of all the frequencies of vibration and a comparison with the theoretical predictions.

(5) IDENTIFICATION OF FREQUENCIES

Because of the use of not absolutely pure heavy water, the C_2D_4 and the $C_2H_2D_2$ contain a few percent of C_2HD_3 and C_2H_3D, respectively. Some lines of C_2HD_3 appearing also in the spectrum of $C_2H_2D_2$ can be explained by the presence of some heavy water remaining in the

C_2D_2 and giving exchange with HBr. Thus, the classification of frequencies needs careful consideration. To this end we are helped by the variation in intensities of the lines obtained in the successive exchange processes. After the first exchange, Fig. 3(a), the lines of C_2H_3D are visible, as shown in the microphotometer curve (a). The other two exchanges, Figs. 3(b) and (c), show an increasing intensity of the lines of C_2H_3D and a decreasing intensity of the lines of C_2H_4. At the same time, the lines of $C_2H_2D_2$ appear (microphotometer curves b and c). Another exchange using a large excess of heavy water gives all the compounds. From the equal intensities of the corresponding C_2H_4 and C_2D_4 lines, as well as those arising from C_2H_3D and C_2D_3H, it is obvious that the proportion of $C_2H_2D_2$ has reached a maximum. Therefore, the spectrum will give most information about the $C_2H_2D_2$ compounds. Finally, we shall use the theoretical prediction about the numerical values of the frequencies, their intensities and their depolarization factors. For example, the A frequencies of $C_2H_2D_2$ (*trans*) are forbidden in Raman effect by the selection rules. With regard to $C_2H_2D_2$ (*cis* and asymm.), all the frequencies are allowed, but the π are more intense than the σ ones. Using the different criteria, it has been possible to classify all the observed lines.

C_2H_4

This compound has been investigated by many authors. Its lines are very well known and we obtain:

3007.3   3072.0   1620.1   1340.7   944.0.

C_2H_3D

This compound contains a small amount of the light ethylene, whose lines are well known (microphotometer curve d). The frequencies obtained for C_2H_3D are:

1600.2 3015.7 2964.7 1396.6 1286.2 2266.4 3104.

This assignment is confirmed by the presence of all these lines in the spectrum of the first exchange, the decrease of their intensities in the following exchange, and by comparing their numerical values with the theoretical ones given by Manneback and Verleysen.

C_2D_4 and C_2D_3H

The lines of C_2D_3H are visible but very weak in the spectrum of C_2D_4 prepared from ethylene -d_4 dibromide. On the other hand, they are found together with those of C_2D_4 in the spectrum of the third exchange, but in the latter case their relative intensities are reversed. This reversal is very useful in making the classification. For instance, the 1514.5 line, four times more intense than the 1544.4 one in the C_2D_4 spectrum, is ten times less intense in the spectrum of the third exchange. 1514.5 is therefore one C_2D_4 line and 1544.4 one C_2D_3H line. The same method has been used to classify the other lines. We obtain:

C_2D_4 : 1514.5   2251.2   981.2   780.0   2304
C_2D_3H : 2215.0   2272.6   1544.4   995.2.

$C_2H_2D_2$ (*cis* and *trans*)

In the spectrum of $C_2H_2D_2$ prepared from ethylene-d_2 dibromide, the strongest lines of C_2D_4, C_2D_3H, C_2H_3D and C_2H_4 appear very weakly, the other lines are found in the exchange spectrum with expected intensities, and we find:

2275.9   2290.0   3033.3   3046.4   763.4
863.4   1215.0   1282.2   1567.3.

The 1282.2 line cannot be mistaken for any C_2H_3D line, because the strongest line in C_2H_3D, 1600, does not appear. In the same way $\nu_3 = 2275.9$ is different from $\nu_2 = 2272.6$ found in C_2D_3H, because $\nu_1 = 1545.4$ four times more intense than 2272.6, should also appear but does not. The 1567.3 is extremely strong and its first harmonic is very intense. This frequency corresponds to a vibration of the CHD groups against one another, and it is plausible that this vibration should be the same for $C_2H_2D_2$ (*cis* and *trans*). With regard to the other frequencies, the discrepancy between our results and the prediction of Manneback and Verleysen is so great that no classification is possible. However, if we observe that the product of the *cis* frequencies divided by the product of those of the *trans*, has a theoretical value of $[0.900816]^{\frac{1}{2}}$ we can choose a combination of the ten frequencies in such a way that the ratio

$$\frac{\omega_1^2\omega_2^2\omega_3^2\omega_4^2\omega_5^2}{\omega_1'^2\omega_2'^2\omega_3'^3\omega_3'^4\omega_3'^5} = 0.900816 \qquad (1)$$

agrees best with the theoretical value. We find:

$$\left[\frac{1567 \times 3046 \times 2290 \times 1282 \times 763}{1567 \times 3033 \times 2276 \times 1215 \times 863}\right]^2 = 0.88974.$$

The relation (1) is rigorous only for harmonic motion, but it may be observed that the anharmonic correction shifts the *cis* and *trans* frequencies by the same amount. Therefore, the left member remains quite constant.

$C_2H_2D_2$ (asymmetrical)

This compound has not been obtained in the pure state, and it appears only in the exchange spectrum. The lines of the other compounds are well known. Hence we find:

$$1581.4 \quad 1379.1 \quad 2221.0.$$

(6) DISCUSSION OF RESULTS

Table III gives the comparison between the experimental values and those calculated by Manneback and Verleysen. The frequencies corresponding to the motion of the radicals against each other are a good illustration of the Rayleigh law concerning the increasing frequency of a vibrating system accompanying the decreasing mass of one part of the system. If we consider these frequencies, as coming from a diatomic molecule, the mass of each atom being the mass of the corresponding radical, it is to be observed that for $C_2H_2D_2$, C_2H_4, C_2D_4, they rigorously obey the following formula

$$\nu^2 = \kappa F/\mu,$$

where $F = 10.796$ dynes/cm; μ is the reduced mass and κ a constant.

These frequencies are: 1514.5 (C_2D_4), 1544.5 (C_2HD_3), 1567.3 ($C_2H_2D_2$ *cis trans*), 1581.4 ($C_2H_2D_2$), 1600.2 (C_2H_3D), 1620.1 (C_2H_4). Manneback and Verleysen observe that the value of the high frequencies ν_1 and ν_3 of the disubstituted isomers are each approximately equal to the arithmetic mean of two high frequencies which combine to give the mode of vibration under consideration. One of these pairs of high frequencies arises from C_2H_4 and the other from C_2D_4. For example, the motion corresponding to the frequency (*trans*) ν_2 in which the D atom does not move, can be thought of as the superposition of the ν_2 and ν_6 frequencies in C_2H_4. Therefore the motion is not much influenced by the substitution of H by D. In the same way, the vibration of $C_2H_2D_2$ (*trans*) ν_3 can be represented by the superposition of the ν_2 and ν_6 vibrations of C_2D_4. The frequencies must have the following values,

$$\tfrac{1}{2}(3007.3 + 3072) = 3039; \quad \tfrac{1}{2}(2251 + 2304) = 2277.$$

By a similar argument, we find for ν_2 (*cis*) and ν_3 (asymm.) the following formula:

$$\tfrac{1}{2}(3007 + 3107) = 3057; \quad \tfrac{1}{2}(2251 + 2193^5) = 2221$$

as compared with the experimental values: 3046 and 2221. We can also expect for the infra-red frequency of C_2D_4 the approximate value:

$$2329 = 2 \times 2290 - 2251.$$

The discrepancy between the experimental values seems to be due partly to the anharmonicity. It is easy to show how important this correction is. The ratio between the product of C_2H_4 and C_2D_4 frequencies belonging to the same symmetry group, supposing the vibration to be harmonic, is:

$$\omega_{1H}\omega_{2H}\omega_{3H}/\omega_{1D}\omega_{2D}\omega_{3D} = 1.998;$$
$$\omega_{6H}\omega_{7H}/\omega_{6D}\omega_{7D} = 1.666.$$

Substituting experimental values we find:

$$\frac{1621.1 \times 3007.3 \times 1340.7}{1514.5 \times 2251.2 \times 981.2} = 1954;$$

$$\frac{3072 \times 944}{2304 \times 780} = 1.623.$$

The anharmonicity correction is thus of the order of 2 percent for the S_1 group and 3 percent for the S_2 group.

In conclusion we wish to thank G. Maes for his constant assistance during the course of these experiments.

5 This value has been found by Sutherland. See G. B. B. Sutherland and G. K. T. Conn, Nature **140**, 644 (1937).