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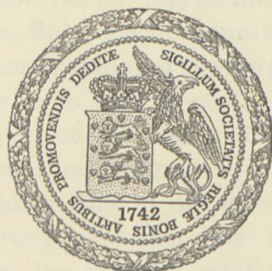
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# HINDERED ROTATION IV

## THE RAMAN SPECTRUM OF DEUTERATED ETHYL BROMIDES

BY

A. LANGSETH AND B. BAK



KØBENHAVN

I KOMMISSION HOS EJNAR MUNKSGAARD

1947

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## THE RAMAN SPECTRUM OF DIFFERENTIATED ETHYL BROMIDE

BY J. J. VAN DER LINDEN AND H. B. VAN DER LINDEN

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## INTRODUCTION

In classical stereochemistry complete freedom of rotation about single bonds is assumed because it has been impossible to isolate isomers corresponding to different orientations of groups connected by a single bond. Even the simple quantum mechanical conception of the carbon-carbon single bond implies free internal rotation about the bond axis as far as the wave function of the bond is assumed to have rotational symmetry. For the double bond, however,  $\pi$ -electrons have a node coplanar with the plane containing the two carbon atoms and the four adjacent atoms (or groups), thus producing a torsional restriction sufficiently large to make a separation of the contingent rotational isomers possible. It is known that in molecules containing two or more double bonds or aromatic rings the  $\pi$ -electrons may interact, tending to form molecular orbitals covering greater parts of the molecule, which results in a restriction of the internal rotation about bonds represented as single bonds in the classical formula. But even in saturated molecules a similar—though much weaker—rotational hindrance due to interactions between the electrons is to be expected. In ethane, for instance, the mutual perturbation of the two methyl groups will distort the potential curve for their azimuthal orientation. From symmetry reasons it follows that it must exhibit three potential barriers. In fact, strong evidence has in recent times been collected showing that the internal rotation in the ethane molecule is rather strongly restricted. On the basis of entropy measurements KEMP and PITZER<sup>1</sup> found it necessary, in order to obtain agreement between theory and experiment, to assume a

<sup>1</sup> Journ. Amer. Chem. Soc. 59, 276 (1937).

value of about 3000 cal/mol for the height of each barrier. This result was confirmed by KISTIAKOWSKY, LACKER and STITT<sup>1</sup> who from the heat capacity data of  $C_2H_6$  and  $C_2D_6$  found the value 2750 cal/mol. It must be emphasized, however, that the computed height of the barriers depends on the assumed form of the potential function.<sup>2</sup> On the other hand, there seems to be no other possibility of explaining the observed variation of the heat capacity of ethane with temperature than assuming torsional barriers of considerable heights (at least 1500 cal/mol).

The presence of rotational barriers in the ethane molecule involves the existence of certain stable configurations, which will naturally be indistinguishable because of the trigonal symmetry of the methyl groups. Under normal conditions torsional vibrations around the molecule axis will occur, only with occasional jumps over the potential barrier. The frequency of this vibration will be of the order of magnitude of  $300\text{ cm}^{-1}$  if the barriers have the computed heights of about 3000 cal/mol. No direct information, however, can be obtained either from the infra-red absorption or from the Raman spectrum, because the fundamental torsional frequency is inactive in both spectra. Theoretically it may, however, appear in combination with other active frequencies or—in the Raman spectrum—as even overtones. In the Raman spectrum of liquid ethane GLOCKLER and RENFREW<sup>3</sup> as well as CRAWFORD, AVERY and LINNETT<sup>4</sup> have reported a faint line at  $620\text{ cm}^{-1}$  which might be interpreted as the Raman-active overtone of the torsion frequency. On the basis of a sinusoidal potential function this corresponds to a height of the barrier of ca. 3400 cal/mol in good agreement with the entropy value. Although the molecular spectra of ethane (and hexadeuteroethane) have been very thoroughly investigated and discussed, it has not yet been possible to obtain an unambiguous confirmation of the torsion frequency. Furthermore no conclusive evidence has been gained from the spectroscopical material to permit a choice between the two possible configurations: the

<sup>1</sup> Journ. Chem. Phys. **7**, 289 (1939).

<sup>2</sup> Cf. A. CHARLESBY: Proc. Physic. Soc. **54**, 471 (1942).

<sup>3</sup> Journ. Chem. Phys. **6**, 295, 409 (1938).

<sup>4</sup> Journ. Chem. Phys. **6**, 682 (1938).

$D_{3d}$ -symmetrical ("staggered") or the  $D_{3h}$ -symmetrical ("opposed") model.

There is another way of tackling the problem. If substituents are introduced into the two methyl groups of ethane, the presence of a rotational restriction makes the existence of "rotational" isomers possible. Because of the low potential barriers these will be too labile to allow separation and isolation. The Raman spectrum, however, should reveal the coexistence of such isomers and in favorable cases produce a conclusive proof of the rotational restriction. K. W. F. KOHLRAUSCH<sup>1</sup> was the first who on the basis of the Raman spectra of several halogenated paraffins and other alifatic compounds postulated the existence of rotational isomers. Even if in this way—mainly by KOHLRAUSCH and coworkers—it has been possible to collect an extensive material supporting this assumption, still some uncertainty remains because of the great complexity of the spectra. The main difficulty arises from the fact that the various possible rotational isomers may have fairly different thermodynamical stabilities, and that *a priori* very little can be said about the proportion in which they occur in the equilibrium mixture. This difficulty is overcome by the investigation of the spectra of molecules in which the asymmetry responsible for the rotational isomerism is caused by the presence of isotopic atoms. From considerations of symmetry it is evident that for example 1,2-dideutero-ethane,  $\text{CH}_2\text{D}\cdot\text{CH}_2\text{D}$ , must be a mixture of 3 rotational isomers, two of which are mirror-images of one another and therefore will have Raman spectra which are identical, but different from the spectrum of the third. As the three isomers have the same statistical weight their thermodynamical stability must also be approximately the same.<sup>2</sup> The Raman spectrum of the equilibrium mixture should therefore be a superposition of two spectra with an intensity ratio of about 1:2 according to the abundance of the two spectroscopically different molecular species in the mixture.

<sup>1</sup> Zeitschr. phys. Chem. **B**, 18, 61. 217 (1932).—For a compilation of the work done along this line, cf. K. W. F. KOHLRAUSCH: Ramanspektren. Hand- und Jahrb. chem. Phys. Bd. 9, VI (1943).

<sup>2</sup> A slight difference due to small departures in zero-point energy and moments of inertia is neglected in this connection.

The chance of a successful analysis of the Raman spectrum along this line, however, depends entirely on the possibility of obtaining a spectrum of the best attainable quality and completeness. As there will be great technical difficulties in getting sufficiently good spectra of ethane and its deuterium derivatives, we decided instead to investigate mono-deutero-ethyl bromide,  $\text{CH}_2\text{D}-\text{CH}_2\text{Br}$ . If there is a restriction of the internal rotation this molecule must exhibit a similar rotational isomerism as  $\text{CH}_2\text{D}-\text{CH}_2\text{D}$ . From an experimental point of view ethyl bromide is far easier to handle. Its physical properties are convenient for the experimental procedure, it can be prepared in sufficient quantities in a chemically and optically pure state, and the molecule has a comparatively low number of vibrational frequencies to ensure a spectrum which is not too complex for an unambiguous demonstration of the expected effect. Furthermore, ethyl bromide fulfils the important requirement that the rotational problem is not obscured by the effect of interacting dipoles or by steric hindrance as is generally the case with the molecules investigated by KOHLRAUSCH and coworkers.

### Experimental Procedure and Results.

All the Raman spectra were taken with a spectrograph of high dispersion and with a Raman apparatus of very high light-gathering power. The positions of the lines were measured against an iron-arc comparison spectrum on photographic enlargements (1:15).

The purified substance under investigation was dried over  $\text{P}_2\text{O}_5$  and in high vacuum distilled into the Raman tube. The apparatus used is shown in fig. 1. The tube was sealed off at S. By repeated distillation (surface evaporation in the high vacuum) from B to R and pouring back to B by tilting the tube all dust particles were removed from the liquid in R and collected in B. In this way very strongly exposed Raman spectra could be obtained without the continuous background getting too predominant. The Hg-line  $4358 \text{ \AA}$  was used for excitation, the violet Hg-lines being cut off by a  $\text{NaNO}_2$ -filter.

The spectrum of  $\text{CH}_2\text{D}\cdot\text{CH}_2\text{Br}$  and for comparison those of  $\text{CH}_3\cdot\text{CH}_2\text{Br}$ ,  $\text{CH}_3\cdot\text{CHDBr}$ , and  $\text{CD}_3\cdot\text{CD}_2\text{Br}$  were measured. The

preparations of these substances are described in the appendix. The observed spectra are given in Tables I and II. The intensities have been estimated visually on an arbitrary scale of 10. Diffuse lines are marked "d", broad lines "b". As mentioned in the appendix we did not succeed in preparing a sample of  $\text{CH}_2\text{D}\cdot\text{CH}_2\text{Br}$  entirely free from contamination with other isotopic species. In order to identify the spectrum of the pure compound,

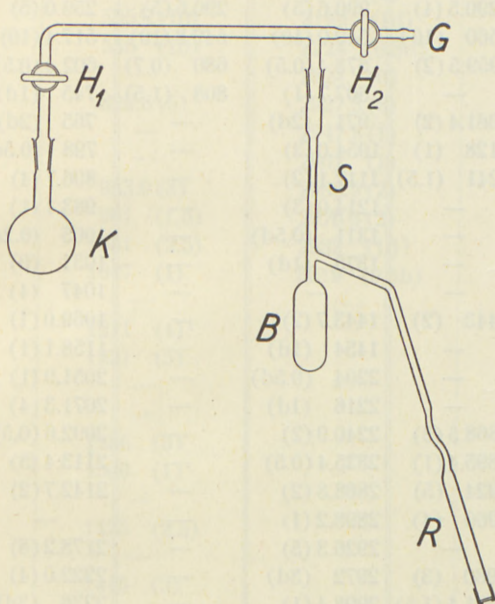


Fig. 1.

it was prepared in three different ways (I, II, III). Intermediate products were in most cases tested for isotopic purity by taking their Raman spectrum. As pointed out in the appendix Preparation I contained as impurities only higher deuterated species, Preparation II only lower deuterated species (i. e.  $\text{C}_2\text{H}_5\text{Br}$ ), and Preparation III both higher and lower deuterated species. By careful and critical comparison of the spectra all lines due to other isotopic molecules rather than  $\text{CH}_2\text{D}\cdot\text{CH}_2\text{Br}$  could be eliminated with certainty.

Owing to the improved technique the recorded spectra are more complete than those measured by previous authors.<sup>1</sup>

<sup>1</sup> Cf. K. W. F. KOHLRAUSCH, Smekal-Raman Effekt, *Ergänzungsband*, p. 206; J. WAGNER, *Zeitschr. phys. Chem. (B)* **40**, 439 (1938); **45**, 69, 341 (1939).

Table I.  
Observed Frequencies and Intensities.

| CH <sub>3</sub> ·CH <sub>2</sub> Br |              | CH <sub>3</sub> ·CHDBr |              | CD <sub>3</sub> ·CD <sub>2</sub> Br |              |
|-------------------------------------|--------------|------------------------|--------------|-------------------------------------|--------------|
| Present authors                     | De Hemptinne | Present authors        | De Hemptinne | Present authors                     | De Hemptinne |
| —                                   | 143.2 (0.5)  | —                      | —            | —                                   | —            |
| 290.4 (6)                           | 290.5 (4)    | 290.6 (5)              | 290.6 (5)    | 259.0 (5)                           | 259 (2)      |
| 560.4 (10)                          | 560 (10)     | 549.0 (10)             | 549.8 (10)   | 517.4 (10)                          | 518 (10)     |
| 959.3 (2d)                          | 959.5 (2)    | 678.4 (0.5)            | 680 (0.7)    | 602.4 (0.5)                         | —            |
| 1022 (0.5b)                         | —            | 807.7 (1)              | 808 (1.5)    | 745 (1d)                            | —            |
| 1062.0 (3)                          | 1061.4 (2)   | 971 (2d)               | —            | 765 (2d)                            | —            |
| —                                   | 1128 (1)     | 1054.0 (3)             | —            | 798 (0.5d)                          | —            |
| 1241.5 (2)                          | 1241 (1.5)   | 1117.1 (2)             | —            | 896.7 (4)                           | 897 (2)      |
| 1250 (0.5d)                         | —            | 1214.0 (3)             | —            | 983.1 (1)                           | —            |
| 1255 (1d)                           | —            | 1311 (0.5d)            | —            | 1005 (0.2d)                         | —            |
| 1348.5 (0.5)                        | —            | 1378 (1d)              | —            | 1031 (0)                            | —            |
| 1378.5 (1)                          | —            | —                      | —            | 1047 (4)                            | 1050 (1)     |
| 1443.3 (2)                          | 1443 (2)     | 1443.7 (2)             | —            | 1069.0 (1)                          | —            |
| 1453 (1d)                           | —            | 1454 (1d)              | —            | 1158.1 (1)                          | —            |
| 2736.9 (1)                          | —            | 2204 (0.5d)            | —            | 2051.9 (1)                          | 2051 (0.7)   |
| 2825.5 (0.5)                        | —            | 2216 (1d)              | —            | 2071.3 (4)                          | 2072 (3)     |
| 2867.8 (3)                          | 2868.5 (3)   | 2240.9 (2)             | —            | 2092.6 (0.5)                        | 2094 (0.7)   |
| 2893 (1d)                           | 2895.4 (1)   | 2825.4 (0.5)           | —            | 2113.4 (5)                          | 2115 (4)     |
| 2926.3 (7)                          | 2924 (5)     | 2868.8 (2)             | —            | 2142.7 (2)                          | 2144 (2)     |
| 2961.2 (5)                          | 2960 (4)     | 2898.2 (1)             | —            | —                                   | 2169 (1)     |
| 2970 (1d)                           | —            | 2926.3 (5)             | —            | 2178.2 (8)                          | 2181 (5)     |
| 2980.2 (3)                          | 2980 (3)     | 2972 (3d)              | —            | 2222.0 (4)                          | 2222 (2)     |
| 3022 (1d)                           | 3021.4 (1.5) | 2998.4 (1)             | —            | 2236 (3d)                           | 2235 (1)     |
|                                     |              |                        |              | 2275 (2d)                           | —            |
|                                     |              |                        |              | 2311.1 (2)                          | —            |

M. de HEMPTINNE and C. VELGHE<sup>1</sup> have investigated the Raman spectra of several deuterium derivatives of ethyl bromide prepared by a method similar to that used by us in Preparation I (cf. Appendix). They have not, however, succeeded in isolating pure samples of the different derivatives, and the measured spectra are incomplete. For comparison the recorded frequencies are included in Tables I and II. The agreement is generally excellent.

<sup>1</sup> Physica 5, 958 (1938).



Table II.  
 $\text{CH}_2\text{D}\cdot\text{CH}_2\text{Br}$   
 Observed Frequencies and Intensities.

| Present authors | De Hemptinne          | Present authors | De Hemptinne |
|-----------------|-----------------------|-----------------|--------------|
| 280.8 (5)       | 282 (5)               | 2110 (0.3)      | 2108 (0.7)   |
| 287.0 (3)       | —                     | 2167.7 (2)      | 2167 (5)     |
| 536.7 (5)       | 535.8 (10)            | 2192 (1d)       | 2188 (3)     |
| 557.5 (10)      | 556 (10)              | 2224 (0.5d)     | 2225 (2)     |
| 703.8 (0.5)     | —                     | 2824 (0)        | —            |
| 826.4 (2)       | 825.6 (5)             | 2927.3 (6)      | 2925 (8)     |
| 896.8 (0.5)     | —                     | 2947.8 (1)      | 2947 (4)     |
| 912.0 (0.3)     | —                     | 2961 (1)        | —            |
| 935.2 (2)       | 933.9 (3)             | 2966.5 (2)      | 2968 (8)     |
| 960.8 (1.5)     | 961 (1.5)             | 2976.6 (2)      | 2978 (8)     |
| 1031.0 (1.5)    | 1031 (2.5)            | 2982 (1d)       | —            |
| 1046.4 (1)      | 1047 (1)              | 3019 (0.5b)     | —            |
| 1181 (0.5d)     | —                     | —               | 3076 (2)     |
| 1189 (0.5d)     | 1211 (4) <sup>1</sup> |                 |              |
| 1231.2 (3)      | 1231 (5)              |                 |              |
| 1247 (0.5d)     | —                     |                 |              |
| 1260 (0.5d)     | —                     |                 |              |
| 1286.3 (2)      | 1286 (3)              |                 |              |
| 1309.9 (0.8)    | 1309 (1)              |                 |              |
| 1347 (0.2)      | —                     |                 |              |
| 1424.5 (1)      | 1425 (2.5)            |                 |              |
| 1437 (0.5d)     | —                     |                 |              |
| 1444.5 (2)      | 1445 (3)              |                 |              |
| 1453 (1d)       | —                     |                 |              |

<sup>1</sup> This strong line presumably belongs to some other isotopic molecule ( $\text{CH}_3\text{CHDBr}$ ?).

### Discussion of Observed Spectra.

As none of the molecules under consideration (viz.  $\text{CH}_3\cdot\text{CH}_2\text{Br}$ ,  $\text{CH}_3\cdot\text{CHDBr}$ ,  $\text{CH}_2\text{D}\cdot\text{CH}_2\text{Br}$ , and  $\text{CD}_3\cdot\text{CD}_2\text{Br}$ ) can have more than one plane of symmetry all vibrations will be Raman-active. Consequently, there is no need for discussing the symmetries of the molecules and their contingent rotational isomers; all the molecular species must exhibit  $(3n-6) = 18$  Raman lines. Five of these will correspond to hydrogen (or deuterium) stretching vibrations with frequencies  $\sim 3000\text{ cm}^{-1}$  (resp.  $\sim 2000\text{ cm}^{-1}$ ). Only 13 Raman lines are to be expected in the region below  $1600\text{ cm}^{-1}$ .

Table III.

| CH <sub>3</sub> ·CH <sub>2</sub> Br | CH <sub>3</sub> ·CHDBr | CH <sub>2</sub> D·CH <sub>2</sub> Br |             |
|-------------------------------------|------------------------|--------------------------------------|-------------|
|                                     |                        | A                                    | B           |
| 290.4 (6)                           | 290.6 (5)              | 280.8 (5)                            | 287.0 (3)   |
| 560.4 (10)                          | 549.0 (10)             | 557.5 (10)                           | 536.7 (7)   |
| 959.3 (2)                           | 678.4 (0.5)            | 826.4 (2)                            | 703.8 (0.5) |
| 1022 (0.5)                          | 807.7 (1)              | 896.8 (0.5)                          | 912.0 (0.5) |
| 1062.0 (3)                          | 971 (2)                | 935.2 (2)                            | 960.8 (1.5) |
| 1241.5 (2)                          | 1054 (3)               | 1031.0 (1.5)                         | 1046.4 (1)  |
| 1250 (0.5)                          | 1117.1 (2)             | 1181 (0.5)                           | 1189 (0.5)  |
| 1255 (1)                            | 1214.0 (3)             | 1231.2 (3)                           | 1247 (0.5)  |
| 1348.5 (0.5)                        | 1311 (0.5)             | 1286.3 (2)                           | 1260 (0.6)  |
| 1378.5 (1)                          | 1378 (1)               | 1309.9 (0.8)                         | 1347 (0.5)  |
| 1443.3 (2)                          | 1443.7 (2)             | 1444.5 (2)                           | 1424.5 (1)  |
| 1453 (1)                            | 1454 (1)               | 1453 (1)                             | 1437 (0.5)  |

Table I shows that 12 lines are observed in CH<sub>3</sub>·CH<sub>2</sub>Br and in CH<sub>3</sub>·CHDBr and 13 lines in CD<sub>3</sub>·CD<sub>2</sub>Br. As the 1031 cm<sup>-1</sup> line found in deuterioethyl bromide probably is an overtone (of the 517.4 frequency), this means that only one fundamental frequency in this region remains unobserved. Table II, however, shows that CH<sub>2</sub>D·CH<sub>2</sub>Br has a much more complicated spectrum with 24 measured lines. A closer examination of the frequencies reveals that this seems to be due to splitting into pairs of the lines corresponding to those found in the other compounds.

This is exactly the kind of spectrum to be expected if CH<sub>2</sub>D·CH<sub>2</sub>Br is a mixture of two closely related, but spectroscopically slightly different, molecular species. This difference is not caused simply by the presence of one deuterium atom in the molecule since CH<sub>3</sub>·CHDBr shows no trace of a similar effect. Evidently it is the destruction of the trigonal symmetry of the methyl group by the deuterium atom in CH<sub>2</sub>D·CH<sub>2</sub>Br that is responsible for the isomerism. The only reasonable explanation seems to be rotational isomerism.

As mentioned above, the equilibrium ratio between the two spectroscopically different rotational isomers should be approximately 1:2. Therefore the intensities of the component lines in each pair should be different. It will depend on the difference in the modes of vibration of the two rotational isomers how

close the observed intensity ratio will be to 1:2. For several of the frequencies there will presumably only be a slight difference. In these cases the intensity ratio should approximately be 1:2. It is seen from Table II that the observed intensity ratios for the two low-frequency pairs (280.8—207.0 and 536.7—557.5  $\text{cm}^{-1}$ ) are resp. 3:5 and 5:10 in good accordance with the expected ratio. As these lines have fairly isolated positions in the spectrum, we are confident of their assignment as pairs.

On the basis of different intensities an assignment of the spectra corresponding to the two rotational isomers in  $\text{CH}_2\text{D}\cdot\text{CH}_2\text{Br}$  is tentatively given in Table III. Because of the incompleteness of the spectra—only 12 instead of 13 frequencies being observed—it is impossible to obtain further support of this assignment by the use of TELLER's product rule.

## Appendix.

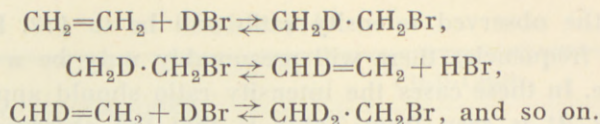
### Preparations.

1.  $\text{C}_2\text{H}_5\text{Br}$  was made in the usual way and finally purified by a careful fractional distillation through a 60 cm column over  $\text{P}_2\text{O}_5$ . Boiling interval:  $38^\circ.45$ — $38^\circ.55$  (760 mm).

2.  $\text{C}_2\text{D}_5\text{Br}$  was prepared from  $\text{C}_2\text{D}_5\text{OD}$  (supplied by "Norsk Hydro"),  $\text{H}_2\text{SO}_4$  and  $\text{HBr}$ . The Raman spectrum taken shows that no exchange takes place between the hydrogen in the acids and the deuterium atoms attached to carbon in the  $\text{C}_2\text{D}_5$ -group. The sample was carefully purified as above. Boiling point:  $37^\circ.35$ — $37^\circ.45$  (760 mm), that is,  $1^\circ.1$  lower than for  $\text{C}_2\text{H}_5\text{Br}$ .

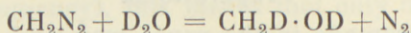
3.  $\text{CH}_2\text{D}\cdot\text{CH}_2\text{Br}$ . In spite of several attempts we have not succeeded in preparing a pure sample of this compound. Raman spectra were taken of the following three preparations:

*Preparation I.* A dry mixture of ethylene and deuterium bromide in equimolar portions was led through a tube containing a  $\text{BiBr}_3$ -catalyst at  $200^\circ$ . Yield: 15 per cent. The deuterated ethyl bromide formed was condensed and purified as above. Boiling point:  $38^\circ.30$ — $38^\circ.70$  (760 mm). It is to be expected that this sample must be a mixture of different isotopic molecules because the  $\text{BiBr}_3$  catalyses the exchange reactions

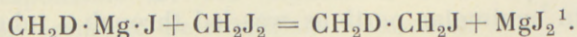


The Raman spectrum taken was fully consistent with this view. As the reaction velocity was rather low at the experimental conditions chosen (hence the low yield), it is seen that the formation of  $\text{CH}_3\cdot\text{CH}_2\text{Br}$  was less probable than the formation of higher deuterated compounds. Actually, no lines from  $\text{CH}_3\cdot\text{CH}_2\text{Br}$  were present in the Raman spectrum.

*Preparation II.* An ethereal solution of diazomethane (1 mole) (Organic Synt. 15) was dried for one hour over solid KOH (mechanical stirring). During the drying process a slight decomposition of the diazomethane took place, visible by the evolution of nitrogen, and resulting in the formation of a small quantity of methyl alcohol. Through a separatory funnel the ethereal solution of diazomethane was dropped to the reaction products of  $\text{D}_2\text{O}$  (25 g) and  $\text{P}_2\text{O}_5$  (15 g). The reaction



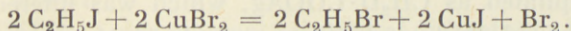
is catalysed by hydrogen ions. The evolution of nitrogen being reduced to a minimum, the ether was distilled off through a 100 cm column. By continuing the fractionation the mixture of  $\text{CH}_2\text{D}\cdot\text{OH}$  and  $\text{CH}_3\cdot\text{OH}$  contaminated with  $\text{CH}_2\text{D}\cdot\text{OD}$  and  $\text{CH}_3\cdot\text{OD}$  was isolated. Yield: 50 per cent. Boiling with constant boiling hydrogen iodide transformed the alcoholic mixture into a mixture of  $\text{CH}_2\text{DJ}$  and  $\text{CH}_3\text{J}$ . Yield: 0.3 mole. By a Grignard reaction  $\text{CH}_2\text{DMgJ} + \text{CH}_3\text{MgJ}$  was prepared, and the ethereal solution at once dropped to an ethereal solution of methylene iodide at  $10^\circ$ – $20^\circ$ . The evolution of heat during the reactions taking place was considerable.



The mixture of  $\text{CH}_2\text{D}\cdot\text{CH}_2\text{J}$  and  $\text{CH}_3\cdot\text{CH}_2\text{J}$  was isolated by fractionated distillation through a 60 cm column. Boiling point:  $71^\circ$ – $75^\circ$ . Yield: 25 per cent.

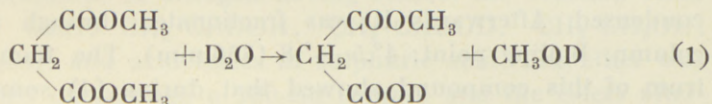
<sup>1</sup> A corresponding reaction with  $\text{CH}_2\text{Br}_2$  is not feasible.

Substitution of iodine by bromine was effected by a method mentioned in LASSAR-COHN: Arbeitsmethoden der org. Chem. (1907), p. 382, by which

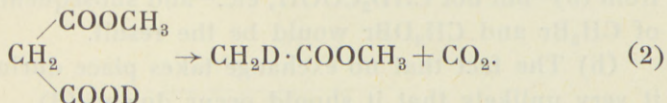


The reaction was carried through by boiling for 4 hours under reflux condenser. Yield: 90 per cent. Purification as usual. The sample obtained must be a mixture of  $\text{CH}_2\text{D}\cdot\text{CH}_2\text{Br}$  and a small amount of  $\text{CH}_3\cdot\text{CH}_2\text{Br}$ . There seems to be no possibility of the presence of higher deuterated compounds. These views were fully substantiated by the Raman spectrum.

*Preparation III.* To 2.5 moles of dimethyl malonate was added  $\frac{1}{2}$  cc conc. sulphuric acid and 50 cc  $\text{D}_2\text{O}$ . After standing for 15 hours at room temperature methyl alcohol formed by the reaction

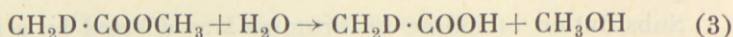


was slowly distilled off through a 60 cm column at  $63^\circ\text{--}65^\circ$  (760 mm). Preliminary experiments had shown that under the conditions chosen the saponification only extends to one of the ester groups. At the point at which an evolution of  $\text{CO}_2$  starts, the receiver is shifted, thus collecting a mixture of  $\text{CH}_3\text{OD}$  and  $\text{CH}_2\text{D}\cdot\text{COOCH}_3$  originating from the reaction



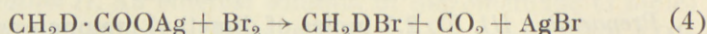
A preliminary experiment had shown that actually a rather pure sample of  $\text{CH}_2\text{D}\cdot\text{COOCH}_3$  is obtained in this way, not being contaminated with  $\text{CH}_3\cdot\text{COOCH}_3$ ,  $\text{CHD}_2\cdot\text{COOCH}_3$ , etc. This was clearly demonstrated by the lack of lines originating from these compounds in the Raman spectrum of the sample.

At the present experiment, however,  $\text{CH}_2\text{D}\cdot\text{COOCH}_3$  was not isolated, but the mixture of the compound and the accompanying  $\text{CH}_3\text{OD}$  was boiled for 18 hours with 5 n  $\text{H}_2\text{SO}_4$ . The reaction



having taken place,  $\text{CH}_2\text{D}\cdot\text{COOH}$  was distilled off, neutralized and precipitated as  $\text{CH}_2\text{D}\cdot\text{COOAg}$ , which was filtered, washed with water, alcohol, and ether, and dried to constant weight (227 g) in vacuum. The theoretical yield from 2.5 moles of dimethyl malonate is 420 g.

225 g  $\text{CH}_2\text{D}\cdot\text{COOAg}$  suspended in 500 cc dry  $\text{CCl}_4$  was gently boiled and a solution of 90 cc dry bromine in 150 cc  $\text{CCl}_4$  was added drop by drop. The two gases from the reaction

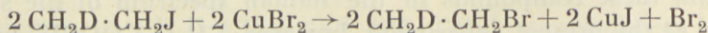
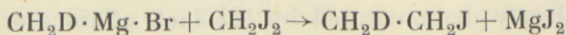
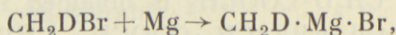


were led through 3 wash-bottles with 4 n NaOH, absorbing carbon dioxide. The deuterated methyl bromide was dried and condensed. Afterwards it was fractionated through a 60 cm column. Boiling point:  $4^\circ.5$ — $4^\circ.8$  (760 mm). The Raman spectrum of this compound showed that during (4) some sort of exchange reaction had taken place which had destroyed the isotopic purity of the sample: it was a mixture of  $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{D}\text{Br}$ ,  $\text{CHD}_2\text{Br}$  and a little  $\text{CD}_3\text{Br}$ . The possibility that the exchange should have occurred during (3)—and not during (4)—can be excluded by the following arguments:

(a) If exchange had taken place during (3) and not during (4), a mixture of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_2\text{DCOOH}$  would result from (3)—but not  $\text{CHD}_2\text{COOH}$ , etc.—and subsequently a mixture of  $\text{CH}_3\text{Br}$  and  $\text{CH}_2\text{D}\text{Br}$  would be the result.

(b) The fact that no exchange takes place during (1) makes it very unlikely that it should occur during (3).

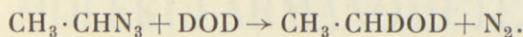
In spite of this derailment we carried through the reactions



and finally got a sample containing  $\text{CH}_2\text{D}\cdot\text{CH}_2\text{Br}$ ,  $\text{CH}_3\text{CH}_2\text{Br}$ ,  $\text{CHD}_2\cdot\text{CH}_2\text{Br}$ , and a little  $\text{CD}_3\cdot\text{CH}_2\text{Br}$ .

Consequently the Raman spectrum was the least valuable of the three taken. It shows all the lines ascribed to the  $\text{CH}_2\text{D}\cdot\text{CH}_2\text{Br}$  from the study of the spectra of the preparations number I and II.

4.  $\text{CH}_3\cdot\text{CHDBr}$ . A dry ethereal solution of diazoethane (0.5 mole) was prepared by a method quite analogous to the one used for obtaining diazomethane. Owing to the decomposition of the diazoethane during the drying process it is inevitable that this solution should contain a little  $\text{CH}_3\cdot\text{CH}_2\text{OH}$ . The ethereal solution was dropped to a mixture of 25 g  $\text{D}_2\text{O}$  and 5 cc conc.  $\text{H}_2\text{SO}_4$ :

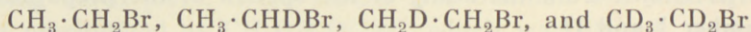


Owing to the use of  $\text{H}_2\text{SO}_4$  instead of  $\text{D}_2\text{SO}_4$  about 4 per cent. of the reaction product must be  $\text{CH}_3\cdot\text{CH}_2\text{OH}$ .

The evolution of nitrogen having ceased, the reaction flask contains: ether,  $\text{CH}_3\cdot\text{CHDOH}$ ,  $\text{CH}_3\cdot\text{CHDOD}$ ,  $\text{CH}_3\cdot\text{CH}_2\text{OH}$ ,  $\text{CH}_3\cdot\text{CH}_2\text{OD}$ , and acid esters of sulphuric acid. The ether was fractionated off through a 100 cm column and the esters afterwards saponified. The alcohols were distilled off and transformed into the mixture  $\text{CH}_3\cdot\text{CHDBr}$  and  $\text{CH}_3\text{CH}_2\text{Br}$  in the usual way. Theoretical yield from 0.5 mole diazoethane: 54 g ethyl bromide. We got 18 g of the pure product. Boiling point:  $38^\circ.40$ – $38^\circ.60$  (760 mm). The considerations concerning the composition of the sample was confirmed by the Raman spectrum.

### Summary.

1. The Raman spectra of



are measured and the frequencies recorded.

2.  $\text{CH}_2\text{D} \cdot \text{CH}_2\text{Br}$  is shown to be a mixture of two spectroscopically different rotational isomers.

3. The intensity ratio of corresponding lines due to the two rotational isomers strongly supports the assumption of a three-minimum potential curve for the internal rotation about the C-C bond.

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