63. Raman Effect in Tetradeuterio-1, 2-Dibromoethane.

By San-ichiro MIZUSHIMA, Yonezo MORINO,
and Syunya SUGIURA.

Chemical Institute, Faculty of Science, Tokyo Imperial University.

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In our previous communications^{1) 2)} on Raman spectra and dipole moments we showed that the molecule of 1, 2-dibromoethane $\text{BrH}_2\text{C}-\text{CH}_2\text{Br}$ changes its configuration considerably by the internal rotation around the C-C bond as axis. The most stable position corresponds to the trans form having the symmetry of C_{2h} and practically all the molecules assume this form in the solid state, while in the liquid state or in solutions the mean internal state shows considerable deviation from this stable position. Our calculation^{2) 3)} proved that all the Raman lines observed in the solid state actually correspond to the normal vibrations symmetric to the center of symmetry of the trans form. To obtain another evidence for our conclusion we studied the isotopic effect on the totally symmetric frequencies of this configuration.

Using 99.6% D_2O , we prepared tetradeuterio-1, 2-dibromoethane $\text{BrD}_2\text{C}-\text{CD}_2\text{Br}$ according to the three following reactions:

The third reaction was effected by passing the reactants over mercuric bromide on asbestos maintained at 120°C .⁴⁾ The sample thus obtained was purified by redistillation. We prepared $\text{C}_2\text{H}_4\text{Br}_2$ also in the same

Raman lines 1, 2- $\text{C}_2\text{H}_4\text{Br}_2$ and 1, 2- $\text{C}_2\text{D}_4\text{Br}_2$ corresponding to the totally symmetric vibrations of the trans configurations.

$\text{C}_2\text{H}_4\text{Br}_2$		$\text{C}_2\text{D}_4\text{Br}_2$	
Frequency (cm^{-1})	Intensity*	Frequency (cm^{-1})	Intensity*
190	9	188	6
660	10	606	10
1053	4	906	2
1255	6	990	7
1440	2b	1153	3b
2972	5	2182	4

* Obtained by visual estimation.

1) Mizushima, Morino, and co-workers: *Physik. Z.* **35** (1934), 905; **38** (1937), 459; *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **25** (1934), 159; **29** (1936), 188.

2) Mizushima, Morino, and co-workers: *Sci. Pap. Phys. Chem. Res. Tokyo*, **26** (1934), 1; **29** (1936), 63.

3) Morino: *Bull. Chem. Soc. Japan*, **13** (1938), 189.

4) Wibaut: *Rec. trav. chim.*, **50** (1931), 313.

way to prove by the observation of Raman spectrum that the reaction product consists almost entirely of 1, 2-dibromoethane contaminated with a small amount of 1, 1-dibromoethane. Thus we can safely treat the isotopic shifts of the strong lines corresponding to the totally symmetric vibrations of the trans configuration. The accompanying table shows the Raman frequencies of this symmetry class for $C_2H_4Br_2$ and $C_2D_4Br_2$, the assignment of lines being made from our calculation¹⁾ of normal motions as well as from the spectral features.

According to Teller²⁾ and Redlich³⁾ the ratio of the frequency products of two isotopically related molecules for the vibrations of the same symmetry class can be calculated with no knowledge of the force system, nor indeed of any factor except the geometry of the molecule and the masses involved. Their equation applied to the present case becomes

$$\frac{\Pi \nu_H}{\Pi \nu_D} = \sqrt{\left(\frac{M_D}{M_H}\right)^3 \frac{I_H}{I_D}},$$

where M_H and M_D denote, respectively, the atomic masses of hydrogen and deuterium and I_H and I_D the moments of inertia of $C_2H_4Br_2$ and $C_2D_4Br_2$ molecules about the symmetry axis C_{2h} . The evaluation of the left-hand side with the experimental values in the table gives 2.76 and that of the right-hand side with the molecular constants, C-H=C-D=1.08 Å, C-Br=1.93 Å, C-C=1.55 Å, and valency angle=109°28', gives 2.82. The agreement between these two values is satisfactory, which not only justifies the above assignment, but also affords another confirmation of our previous conclusions in regard to the molecular structure of dihalogenoethane.

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1) Morino: Bull. Chem. Soc. Japan, **13** (1938), 189.

2) Quoted by Ingold and co-workers: Nature **135** (1935), 1033.

3) Redlich: Z. phys. Chem. **B**, **28** (1935), 371.