Raman Spectra of Benzene and Isotope Effect

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seems certain is that dimethylhydrazine in heptane solution at 25°C is predominately of structure I.

Little can be added at present concerning the Raman spectrum of dimethylhydrazine to the general description already given. Two lines of 1010 cm^{-1} and 1118 cm^{-1} seem to be comparable with the pair at 904 cm^{-1} and 1117 cm^{-1} of hydrazine in aqueous solution,[16] of which one or other, or both, are due essentially to the $N-N$ vibration, while the line at 473 cm^{-1} is probably due to the corresponding bending vibration. With respect to acetaldazine we wish at present only to emphasize the asymmetry in the structure indicated by the moment of 1.16 D and the identification of the strongest line in the Raman spectrum, corresponding to a frequency of 1627 cm^{-1} as the C : N vibration.

[16] K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Julius Springer, Berlin, 1931), p. 312.

SUMMARY

The Raman spectra and electric moments of azomethane, $N-N'$ dimethylhydrazine and acetaldazine, and the infrared absorption of azomethane from $1-15\mu$ are reported. The results indicate a *trans* configuration for azomethane, and an unsymmetrical structure for dimethylhydrazine, derived from Penney and Sutherland's structure for hydrazine. Some of the data are; electric moments, azomethane, O, $N-N'$ dimethylhydrazine, 1.35 D, acetaldazine, 1.10 D; $N=N$ vibration frequency in azomethane 1442 cm^{-1}, $C=N$ vibration frequency in acetaldazine, 1627 cm^{-1}, dielectric constant of acetaldazine at 25°, 4.435.

Raman Spectra of Benzene and Isotope Effect

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(Received November 8, 1937)

A faint line accompanying the strong line in the region of 990 cm^{-1} is observed in the Raman spectra of benzene, chlorobenzene, bromobenzene, toluene and cyclohexane. The relative intensities of the weak 984 cm^{-1} line and the strong 992 cm^{-1} line of benzene are measured to be in the ratio 6 : 100. This together with an approximate theoretical estimate support the suggestion that the weak line is due to molecules in which one of the carbon atoms is an isotope of mass 13. The exceedingly low intensity of the corresponding faint line in cyclohexane seems to point to a nonplanar structure. Similar study on the 944 cm^{-1} line in C_6D_6 is suggested.

INTRODUCTION

THE Raman and the infrared spectra of benzene have been the subject of many investigations and the normal vibrations of the benzene molecule are well known.[1] Of the many Raman lines, the strong and polarized lines at 992 cm^{-1} and 3060 cm^{-1} are known to be the frequencies of the symmetrical pulsating motions of the carbon and the hydrogen rings.[2] The line at 992 cm^{-1} is accompanied by a very faint

line at 984 cm^{-1}. It has been suggested by Gerlach[3] that this faint line may be due to a molecule in which one of the carbon atoms is replaced by a heavy isotope of mass 13. Attempt to settle this question by means of polarization measurement of the weak line by Grassmann and Weiler[4] has not been conclusive because of the difficulty in obtaining exact values for the degree of depolarization of an extremely weak line in close proximity with a very strong one.

[1] K. W. F. Kohlrausch, Physik. Zeits. **37**, 58 (1936).
[2] J. Weiler, Zeits. f. Physik **72**, 206 (1931).

[3] W. Gerlach, Münch. Ber. **39**, Nr. 1 (1932).
[4] P. Grassmann and J. Weiler, Zeits. f. Physik **86**, 329 (1933).

In this study, we attempt to verify the suggestion of Gerlach by (i) measuring the relative intensities of the 992 and 984 cm^{-1} lines, (ii) studying the corresponding lines in other derivatives of benzene, and (iii) making an approximate theoretical estimate of the isotope shift due to the replacement of one of the carbon atoms in the benzene ring by an isotope of mass 13.

EXPERIMENTAL

The Raman spectra were studied with the conventional set-up and a three-prism Steinheil glass spectrograph giving a dispersion of about 12A per mm at the position of the 992 cm^{-1} line of C_6H_6 when excited by the 4358A line of mercury. For intensity measurements, intensity marks were put on the plate by means of a step diaphragm and relative intensities determined according to the method of Thomson and Duffendack.[5] Exposures for the 992, 984 cm^{-1} lines varied from four to ten hours while the exposures for intensity marks were five minutes. Polarization measurements were made by means of a Hanle combination crystals as described elsewhere.[6]

Because of the closeness of the 992 and 984 cm^{-1} lines, they were also examined with a telesystem attached to the Steinheil spectrograph. The dispersion attained was about 3A per mm. The two lines were then clearly separated; but with the consequent decrease in intensity, exposures had to be prolonged to about 100 hours. With the polarization crystals, exposures of even 300 hours failed to register the depolarized component of the weak 984 cm^{-1} line although the polarized component was detectable. Because of the excessively long exposure and the difficulty in putting on intensity marks with the telesystem which brought only a very narrow spectral region into sharp focus, these plates were not used in the actual intensity measurements.

In Fig. 1 is reproduced a spectrogram of the Raman lines 992–984 cm^{-1} of benzene excited by the 4358A Hg line. A typical microphotometer tracing of the two lines is given in Fig. 2. In determining their relative intensities, an in-
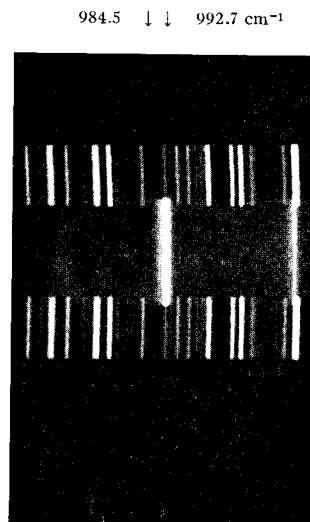
984.5 ↓↓ 992.7 cm^{-1}

FIG. 1. Raman lines 992, 984 cm^{-1} of benzene.

tensity curve for the contour of the two lines was plotted by means of the blackening-log intensity curve. Account is taken of the partial overlapping of the two lines and the presence of the continuous background in the spectrum. The relative intensities of the two lines as measured on four separate plates were 100 : 5, 100 : 6, 100 : 6, and 100 : 7. When allowance is made for the uncertainty introduced by the partial overlapping of a strong and a weak line, these values are as close as one can expect, and the average value of 100 : 6 cannot be very much in error.

The relative abundance of the carbon isotopes of mass 12 and 13 has been determined by a number of authors using spectroscopic, mass-
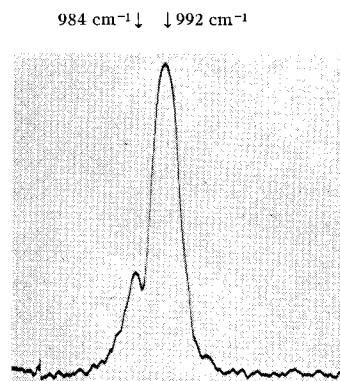
984 cm^{-1} ↓   ↓ 992 cm^{-1}

FIG. 2. Microphotometer curve of 992, 984 cm^{-1} Raman lines of benzene.

[5] K. B. Thomson and O. S. Duffendack, J. Opt. Soc. Am. 23, 101 (1933).
[6] Shen, Yao and Wu, Phys. Rev. 51, 235 (1937).

spectrograph and chemical methods.[7] The value arrived at by all is about 100 : 1. Considering the presence of six identical carbon atoms in the symmetrical benzene molecule, one would expect the relative abundance of the $C_6^{12}H_6$ and $C_5^{12}C_1^{13}H_6$ molecules to be in the ratio 100 : 6. The exact agreement between this value and the relative intensities of the 992 and 984 cm^{-1} lines of benzene seems to support strongly the suggestion that the weak line 984 cm^{-1} is due to an isotope effect of carbon in the benzene molecule.

It is hence desirable to examine the lines corresponding to the 992 cm^{-1} line of benzene in the Raman spectra of other derivatives. The results of the study on chlorobenzene, bromobenzene and toluene are tabulated in Table I.

TABLE I.

	ν_1(strong)	ν_1(weak)	$\Delta\nu$
Benzene	992 cm^{-1}	984 cm^{-1}	8 cm^{-1}
Chlorobenzene	1001	990	11
Bromobenzene	1000	993	7
Toluene	1004	993	11

Due to the weakness of one and the diffuseness of the two lines, these frequencies are probably accurate only to 1 cm^{-1}, and the difference between the two may be in error by 2 cm^{-1}. The significant point is that in each of these molecules, a much weaker line of lower frequency shift by about 8 cm^{-1} accompanies the strong line in the region of 990 cm^{-1}. Exact intensity measurement of the two lines in the derivatives could not be made on account of the rather strong background. But a rough estimate of their relative intensities and the order of magnitude of their frequency difference make it probable that the weak line has its origin in a molecule having one carbon isotope of mass 13.

An attempt to measure the degree of depolarization ρ of the 984 cm^{-1} line of benzene was made. Exposure of even 100 hours (without the use of telesystem) still failed to bring out the depolarized component while the polarized component was easily measurable. Thus although no numerical value has been obtained, we can with certainty place an upper limit for ρ at 0.40

and can safely say that it is probably lower. Hence it appears that the polarization characters of the 992 and the 984 cm^{-1} lines are the same.

Another molecule of considerable interest is cyclohexane C_6H_{12}. If the form of the molecule is one in which the six carbon atoms do not lie in one plane, then there will still be a faint line accompanying the 800 cm^{-1} line which polarization measurement[8] and theoretical calculation show to correspond to the symmetric vibrations of the carbon and hydrogen atoms, but the relative intensities would be lower than in the case of benzene, because of the lower symmetry. If the molecule is a plane, symmetric one, then one would expect the 800 cm^{-1} line to be accompanied by a weak line whose intensity is 6/100 of the 800 cm^{-1} line. Prolonged exposures of the Raman spectrum of cyclohexane show that while the microphotometer curve revealed a faint kick about 6 cm^{-1} to the low frequency displacement side of the 800 cm^{-1} line, their relative intensities are definitely much lower than the ratio 6:100 expected for a plane, symmetric model. The exceedingly low intensity of the weak line precludes any intensity or polarization measurement. All one can say is that from isotope shift consideration it seems that the plane, symmetric model is incompatible with the observed intensity ratio.

THEORETICAL CALCULATION

To examine further the possibility that the weak line 984 cm^{-1} in benzene may be due to the replacement of one of the six carbon atoms by an isotope of mass 13, we may make an approximate estimate of such an isotope shift by the "perturbation theory" method of Wilson.[9] The treatment of the normal vibrations of benzene by Wilson[10] shows that the frequencies of the two totally symmetric pulsating motions of the carbon and the hydrogen rings separate from the other frequencies in the determinantal equation. Following Wilson, let us denote the radial displacements of the carbon atoms, mass M, and the hydrogen atoms, mass m, by R and r,

[7] Baxter and Hale, J. Am. Chem. Soc. 59, 506 (1937).

[8] K. W. F. Kohlrausch and W. Stockmair, Zeits. f. physik Chemie B31, 382 (1936).
[9] E. B. Wilson, Phys. Rev. 45, 427 (1934).
[10] E. B. Wilson, Phys. Rev. 45, 706 (1934); 46, 146 (1934).

respectively. On introducing the generalized coordinates $Q_1 = (6M)^{\frac{1}{2}}R$, $Q_2 = (6m)^{\frac{1}{2}}r$, the kinetic energy becomes

$$T = 6/2[M\dot{R}^2 + m\dot{r}^2] = 1/2[\dot{Q}_1^2 + \dot{Q}_2^2]$$

and the potential energy

$$V = 6/2[KR^2 + q(R-r)^2]$$
$$= 1/2[(K+q)Q_1^2/M - 2qQ_1Q_2/(Mm)^{\frac{1}{2}} + qQ_2^2/m]$$

where K is the force constant between two neighboring carbon atoms and q the force constant between C$-$H atoms. Let the normal coordinates X, Y for the vibrations $\nu_1 = 992$, $\nu_2 = 3060$ cm^{-1} be defined through the transformation equations

$$Q_1 = a_{11}X + a_{12}Y, \qquad (1)$$
$$Q_2 = a_{21}X + a_{22}Y.$$

The determinantal equation is

$$\lambda^2 - [(K+q)/M + q/m]\lambda + qK/Mm = 0 \quad (2)$$

where $\nu = (\lambda)^{\frac{1}{2}}/2\pi$. Solution of this equation with $\nu_1 = 992$, $\nu_2 = 3060$ cm^{-1} gives $K = 7.50 \times 10^5$, $q = 5.05 \times 10^5$ dynes/cm. The transformation coefficients are readily obtained.

$$a_{11} = k_1(m\lambda_1 - q)/m, \quad a_{21} = k_2(m\lambda_2 - q)/m,$$
$$a_{12} = -k_1 q/(Mm)^{\frac{1}{2}}, \quad a_{22} = -k_2 q/(Mm)^{\frac{1}{2}}, \quad (3)$$

where
$$k_1 = [(\lambda_1 - q/m)^2 + q^2/mM]^{-\frac{1}{2}},$$
$$k_2 = [(\lambda_2 - q/m)^2 + q^2/mM]^{-\frac{1}{2}}.$$

When one of the particles of mass M is replaced by one of mass $M + \Delta M$, the change in the potential energy is

$$\Delta V = 1/12[-(K+q)\Delta M Q_1^2/M^2$$
$$+ q\Delta M Q_1 Q_2/M(Mm)^{\frac{1}{2}}]. \quad (4)$$

The isotope shifts $\Delta\nu = \Delta\lambda/8\pi^2\nu$ are given according to the perturbation method by

$$\Delta\lambda_1 = 1/6[-(K+q)\Delta M a_{11}^2/M^2$$
$$+ q\Delta M a_{11}a_{12}/M(Mm)^{\frac{1}{2}}],$$
$$\Delta\lambda_2 = 1/6[-(K+q)\Delta M a_{12}^2/M^2 \qquad (5)$$
$$+ q\Delta M a_{12}a_{22}/M(Mm)^{\frac{1}{2}}].$$

Substitution of $\Delta M = 1$ and the known values of the various quantities in these two expressions gives $\Delta\nu_1 \backsimeq -6.3$ cm^{-1} for the 992 cm^{-1} line, and $\nu_2 \backsimeq -1.2$ cm^{-1} for the 3060 cm^{-1} line.[11] This shows that the difference between the 992 and 984 cm^{-1} lines is just of the correct magnitude of the isotope shift. The calculated shift of 1.2 cm^{-1} for the 3060 line also explains why no weak line is observed accompanying it, for one strong and one weak line so close together would simply appear as a single line in the Raman spectrum.

Entirely similar calculations on hexadeuterobenzene C_6D_6 give for the 944 cm^{-1} line a shift $\Delta\nu \sim -5$ cm^{-1} and for the 2292 cm^{-1} line a shift $\Delta\nu \sim -1$ cm^{-1}. However, a weak line accompanying the 944 cm^{-1} line has not been reported in the work of Wood[12] and Angus and his collaborators.[13] Also on the assumption of a plane symmetrical model, similar calculations give for cyclopentane C_5H_{10} an isotope shift of about 6 cm^{-1} for the strong and polarized line 886 cm^{-1}. It would be interesting to reexamine these lines under greater dispersion; for their presence would lend further support to the isotope theory for the 884 cm^{-1} line of benzene.

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[11] From Eqs. (1) and (3), one can readily obtain the relative displacements of the carbon and the hydrogen atoms for the two normal vibrations; namely for $\nu_1 = 992$, $R/r \backsimeq 0.9$, and for $\nu_2 = 3060$, $R/r \backsimeq -0.09$. Thus roughly speaking in the vibration ν_1, the carbon and the hydrogen rings contract and expand in phase with each other, while in the vibration ν_2, the two rings vibrate against each other, about 9/10 of the relative displacement being traversed by the hydrogen atoms. Simple calculations from Eq. (2) show that while ν_2 depends strongly on the force constant q, ν_1 depends strongly on K, the force constant for two neighboring carbon atoms.

[12] R. W. Wood, J. Chem. Phys. 3, 444 (1935).
[13] Angus et al., Nature 135, 1033 (1935).