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The Raman Spectra of the Deuteromethanes

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The four deuteromethanes were prepared. Their vibrational Raman spectra were photographed under high dispersion. A total of 20 lines were analyzed. A discussion, in the light of the general theory, is given of a sequence of observed overtones.

INTRODUCTION

THE structure and properties of the methane molecule are of particular interest because it is the simplest of the series of carbon hydrogen compounds. Its infrared and Raman spectra have been reported by a number of investigators and the theory of the structure of the molecule has also been extensively studied.¹ With the discovery of deuterium it became possible to prepare and study the deuteromethanes. These isotropic molecules are exceptionally well suited to the investigation of the isotopic effect on polyatomic molecules because of their simple structure. The infrared absorption spectrum of CH₃D has been investigated by Barker and Ginsberg,² and Dadiou and Engler³ have investigated the Raman spectrum of CD₄. There are, of course, five isotopic methanes depending upon the substitution of hydrogens by deuterium, and it is the purpose of this investigation to study the Raman spectra of all these compounds.

Rosenthal⁴ has developed a theory of the isotopic effect for such polyatomic molecules in terms of a general potential energy function involving five constants, the final expression for the normal vibrations being given in terms of the potential energy constants of normal methane and mass factors. Dennison and Johnston⁵ using the four frequencies of ordinary methane, as observed in the infrared and Raman spectra, and also making use of the rotation-vibration inter-

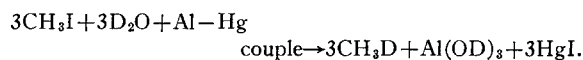
action of normal methane, have calculated the frequencies of the four deuteromethanes. It should be observed that several important inaccuracies enter into these calculations which preclude hope of any exact agreement between calculated and observed frequencies. Because of the lack of knowledge concerning the anharmonicity of the vibrations, the observed frequencies have been used in the theory to calculate force constants as if they were the normal vibrations with zero amplitudes. As a result the frequencies calculated by Dennison and Johnston for the deuteromethanes are not the normal vibrations. Also, the observed frequencies of these deuteromethanes differ from the normal vibrations by the anharmonicity corrections. In general, these anharmonicity corrections are of such magnitudes that agreement between calculated and observed frequencies for the deuteromethanes cannot be expected within about five percent.

The object of this investigation has been to determine carefully the Raman spectra of gaseous deuteromethanes.

EXPERIMENTAL

Preparation of compounds

Monodeuteromethane was prepared by the reaction of methyl iodide and deuterium oxide in the presence of an aluminum-mercury couple according to the following reaction,



Vacuum distilled methyl iodide and 99 percent pure deuterium oxide were used. The aluminum-mercury couple was prepared in the usual manner by the action of 0.5 percent HgCl₂ solution on clean aluminium clippings. The couple was washed with 95 percent alcohol and then vacuum dried to remove traces of hydrogen compounds,

¹ Angström, *Ofversigt af Kang Vetenskaps.—Akad. Forh.* **47**, 331 (1890); Coblentz, *Investigations of Infra-red Spectra*; J. P. Cooley, *Astrophys. J.* **62**, 73 (1925); D. M. Dennison, *Astrophys. J.* **62**, 84 (1925); V. Guilleman, *Ann. d. Physik* **81**, 173 (1926); Dickinson, Dillon and Rasetti, *Phys. Rev.* **34**, 582 (1929); S. Bhagavantam, *Ind. J. Phys.* **6**, 595 (1932); S. C. Beswas, *Phil. Mag.* **13**, 455 (1932).

² Barker and Ginsburg, *J. Chem. Phys.* **3**, 668 (1935).

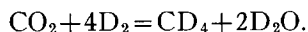
³ A. Dadiou and W. Engler, *Naturwiss.* **23**, 355 (1935).

⁴ J. Rosenthal, *Phys. Rev.* **45**, 538 (1934).

⁵ Dennison and Johnston, *Phys. Rev.* **47**, 93 (1935).

principally water. Methyl iodide and deuterium oxide were vacuum distilled onto the couple. The reaction proceeded as soon as the mixture reached room temperature. The gas formed was allowed to pass through a dry ice trap in order to catch the water vapor and other condensables and was stored finally in a glass bulb. A drawback of this method of preparation is that the couple reacts with the water, resulting in a deuterium impurity of about ten percent. This was ascertained by determining the pressure of the gas in a known volume at liquid-air temperature where the methane has a vapor pressure of 8 cm so that the excess pressure beyond this was due to deuterium, and at room temperature where the pressure is due to the methane and deuterium. The amount of impurity was determined approximately since it did not in any way interfere with the interpretation of the results, for the Raman frequencies of deuterium are known from the work of Teal and MacWood.⁶ Dideutero- and trideuteromethane were prepared in a similar fashion, using methylene iodide and bromoform, respectively.

Tetraduteromethane was prepared by a catalytic process in the gas phase.⁷ Deuterium and carbon dioxide were allowed to react in the presence of a supported Ni catalyst at a temperature of 310°C, according to the reaction,



The deuterium gas was prepared electrolytically from pure deuterium oxide. Commercial solid carbon dioxide was used as the source of carbon dioxide, the gas being purified by passage through 95 percent sulfuric acid. Deuterium and carbon dioxide were passed over the catalyst at 310°C in a four to one ratio. The rates were controlled by the electric current in the cell generating deuterium, and by a bubble-counter in the case of the carbon dioxide. The water formed was removed in a solid carbon dioxide trap and the methane collected as a liquid at liquid-air temperature. When enough liquid methane was collected, the reaction was stopped and the methane allowed to evaporate at -80°C (CO_2) into a large glass storage bulb. The only

impurity that can be expected in this case is a small amount of carbon dioxide. This impurity again causes no difficulty since its spectrum is well known from the work of Langseth and Nielson.⁸

Spectroscopic technique⁶

The Hilger E-1 quartz spectrograph which was used in this investigation was thermostated at $32 \pm 0.05^\circ\text{C}$ and barostated at 740 ± 0.1 mm. Imperial eclipse plates were used and found to be exceptionally fast. It should be mentioned, however, that for intensity measurements they would be of little value due to their high contrast. A Raman tube of the Wood type, 60 cm long and 2.5 cm in diameter was used. A platinum diaphragm plated with platinum black at the front end of the tube served to eliminate scattered light. The exciting light was obtained from three low pressure "Hanovia" 2537 mercury arcs, 133 cm long and 1 cm in diameter, bent into the shape of closed S's. These arcs give, according to the manufacturers, about 85 percent of their radiation in the $\lambda 2537$ resonance line, making them ideal sources for Raman work. The arcs were firmly held against the Raman tube by a polished aluminum reflector bound around them. A difficulty attending these arcs is the rapid production of ozone, due, no doubt, to considerable radiation in the $\lambda 1849$ region. This ozone between the reflector and the Raman tube, unless eliminated from the region, will reduce the intensity of the exciting light considerably. A moderate stream of nitrogen, flowing through this space, was found to decrease this effect. In order to prevent fogging of the plate by the Rayleigh scattered radiation, it was partially absorbed by the vapor of a small amount of mercury placed in the spectrograph.

For the Raman spectra of CH_3D , CH_2D_2 , and CHD_3 the pressure of the gas under investigation was about two atmospheres, because of the limited amounts of gas available. For CD_4 , a pressure of 5 atmospheres was used. The exposure times in all cases ranged between 150 and 200 hours.

As a reference spectrum, the iron arc was used, photographed immediately below and above the

⁶ G. Teal and G. MacWood, *J. Chem. Phys.* **3**, 760 (1935).

⁷ B. Neumann and K. Jacob, *Zeits. f. Elektrochemie* **30**, 557 (1924).

⁸ A. Langseth and J. Nielson, *Nature* **130**, 92 (1932).

TABLE I. *A comparison of previously observed Raman frequencies with those observed in this work.*

MOLECULE	PREVIOUSLY OBSERVED	THIS PAPER	
N ₂	2328.3 ⁹	2328.4	-0.1
	2331.0 ¹⁰	2328.3	0.0
		2328.9	-0.6
CO ₂	1388.9 ⁸	1388.4	0.5
		1389.2	-0.3
	1285.6	1388.7	0.2
		1285.8	-0.2
CH ₄	2914.8 ¹¹	2914.2	0.6
CHD ₃	2141.0 ⁸	2141.1	-0.1
CD ₄	2108.0 ⁸	2108.1	-0.1

Raman spectrum with the aid of a Hartman diaphragm at the end of the exposure. The error in the measurement of the Raman lines was about ± 0.5 cm⁻¹. This is substantiated by the results presented in Table I where a comparison of the frequencies of known molecules observed in this investigation with their accepted values is given.

RESULTS

Since the methane molecules have tetrahedral structure, each will have nine normal vibrations, but for reasons of symmetry some of these are identical. CH₄ and CD₄ have tetrahedral symmetry and they will have a non-degenerate symmetrical vibration of frequency, ν_1 , a doubly degenerate symmetrical vibration of frequency, ν_2 , and two triple degenerate antisymmetrical vibrations of frequencies ν_3 and ν_4 .¹² CH₃D and CHD₃ have only a threefold symmetry axis, and therefore there will be three non-degenerate parallel vibrations of frequencies ν_1 , ν_{3c} , ν_{4c} , and three doubly degenerate perpendicular vibrations of frequencies ν_2 , ν_{3ab} , ν_{4ab} . The molecule CH₂D₂ has only a twofold axis of symmetry and, hence, all the nine normal vibrations are non-degenerate and we designate the frequencies ν_1 , ν_{2a} , ν_{2b} , ν_{3a} , ν_{3b} , ν_{3c} , ν_{4a} , ν_{4b} , ν_{4c} .

In Table II are given the observed frequencies of the five methanes compared with those calculated by Dennison and Johnston.⁵ The calculated values are enclosed in parentheses.

⁹ Unpublished work of MacWood and Teal, see also reference 6, p. 763.

¹⁰ F. Rasetti, Proc. Nat. Acad. Sci. **15**, 234, 515 (1929).

¹¹ Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929).

¹² J. Rosenthal, Phys. Rev. **46**, 730 (1934).

TABLE II. *Vibrational frequencies of the isotopic methanes.*

CH ₄	CH ₃ D	CH ₂ D ₂	CHD ₃	CD ₄
ν_1 (2914.2)	ν_1 unobs. (2944)	ν_1 2139.0 (2141)	ν_1 2141.1 (2101)	ν_1 2084.7 (2061)
ν_2 (unobs.)	ν_2 unobs. (1460)	ν_{2a} 1332.9 (1317)	ν_2 1299.2 (1286)	ν_2 unobs. (1075)
		ν_{2b} unobs. (1424)		
$2\nu_2$ (3071.5)	$2\nu_2$ 2921.7	$2\nu_{2b}$ 2916.4	$2\nu_2$ 2512.4	$2\nu_2$ 2108.1
		ν_{3c} unobs. (2227)		
	ν_{3c} 2199.5 (2183)	ν_{3a} 2974.2 (2969)	ν_{2c} unobs. (2992)	
ν_3 (3022.1)	ν_{3ab} unobs. (3013)	ν_{3b} unobs. (3013)	ν_{3ab} 2268.6 (2222)	ν_3 2258.0 (2227)
	ν_{4ab} 1330.1 (1300)	ν_{4a} 1285.6 (1228)	ν_{4ab} unobs. (994)	
	$2\nu_{4ab}$ unobs.	ν_{4b} 1033.1 (1019)	$2\nu_{4ab}$ 1963.4	
ν_4 (unobs.)	ν_{4c} unobs. (1151)	ν_{4c} unobs. (1082)	ν_{4c} unobs. (1020)	ν_4 unobs. (987)
	$2\nu_{4c}$ 2314.8	$2\nu_{4c}$ 2179.6	$2\nu_{4c}$ 2092.8	

Rotational structure of CD₄ was observed associated with ν_3 . It was, however, too weak for measurement.

DISCUSSION

There are several interesting points which require investigation and which will have a bearing on the theory of the Raman effect. The following overtones are observed though the fundamentals are not observed with one exception,

CH ₄	- $2\nu_2$.
CH ₃ D	- ν_2 , $2\nu_{4c}$.
CH ₂ D ₂	- $2\nu_{2b}$, $2\nu_{4c}$.
CHD ₃	- ν_2 , $2\nu_{4c}$, (ν_2 observed but very weak).
CD ₄	- $2\nu_2$.

There is the further problem of the nonoccurrence of the following fundamental frequencies,

CH ₄	- ν_2 , ν_4 .
CH ₃ D	- ν_1 , ν_2 , ν_{2b} , ν_{4c} .
CH ₂ D ₂	- ν_{2b} , ν_{3b} , ν_{3c} , ν_{4c} .
CHD ₃	- ν_{3c} , ν_{4ab} , ν_{4c} , (ν_2 , weak).
CD ₄	- ν_2 , ν_4 .

The occurrence of the lines corresponding to the various normal vibrations is determined by the activity which depends entirely on symmetry

considerations. Placzek, Tisza and others¹³ have shown that for molecules having T_d , C_{3v} and C_{2v} symmetry, corresponding to CX_4 , CX_3Z and CX_2Z_2 , all the vibrations are active in the Raman effect. Then, since all the vibrations are active, the observability of the lines corresponding to the various normal vibrations will be determined by the intensity of the Raman wave-lengths.

In order to calculate the intensity of the various vibrational lines, we require a knowledge of the vibrational wave functions and the dependence of the polarizability on the normal coordinates.¹³ The latter relationship is in general unknown and the wave functions are taken to a first approximation as the product of the wave functions of harmonic oscillators.

The polarizability may be developed in terms of the normal coordinates, about the equilibrium position, giving

$$\alpha(q) = \alpha^0 + \sum_j \alpha_j^0 q_j + \frac{1}{2} \sum_{j,k} \alpha_{jk}^0 q_j q_k + \dots,$$

where $\alpha_j^0 = (\partial\alpha/\partial q_j)_0$, $\alpha_{jk}^0 = (\partial^2\alpha/\partial q_j \partial q_k)_0$, etc.

and the q 's are the normal coordinates.

If we form the matrix elements of α , we obtain for the vibrational transitions,

$$(\alpha)^{v_j, v_j+1} = (v_j+1)^{\frac{1}{2}} [\alpha_j^0 C_j + \frac{1}{6}(v_j+1)\alpha_{jjj}^0 C_j^3 + \dots],$$

$$(\alpha)^{v_j, v_j+2} = \frac{1}{2}((v_j+1)(v_j+2))^{\frac{1}{2}} \alpha_{jjj}^0 C_j^2 + \dots,$$

where $C_j = (h/8\pi^2\nu_j)^{\frac{1}{2}}$.

Now since the square of the matrix elements of the polarizability determines the intensity and since these are functions of C_j which are small quantities, it may be concluded that the overtones, $n\nu_j$, and combination tones, $n\nu_j + m\nu_k$, depending on C_j^n and $C_j^n C_k^m$, will in general be considerably weaker than the fundamentals. In special cases, where the quantity α_j vanishes or is very small, this rule may be changed, that is, the fundamental will not be observed and the first overtone may or may not be observed, depending upon the magnitude of α_{jj} . In connection with the magnitude of α_j it seems reasonable to assume that for vibrations along valence bonds the

change in the polarizability will be a maximum, as for ν_1 of CH_4 and CD_4 , since as the hydrogen atoms move in toward the carbon nucleus the polarizability will decrease approaching that of neon as a limit for the united atoms. For vibrations such as ν_2 or ν_4 of CH_4 and CD_4 in which the hydrogen atoms are moving on the surface of a sphere or an ellipsoid the change will be small as the carbon-hydrogen distance will change but little. The ν_2 and ν_4 vibrations for the other methanes, only overtones of which are observed, will be described by a motion similar to ν_2 or ν_4 of CH_4 and CD_4 and so would be expected to satisfy the above criterion.

Another phenomenon of interest in connection with the occurrence of overtones is quantum-mechanical resonance between certain of the energy states of the molecule due to accidental degeneracy or approximate coincidence of the levels corresponding to the various vibrations.¹⁴ The extent of resonance and the distribution of intensity in the lines corresponding to resonating levels have been found to be functions of the separation of the levels, of the frequency and of the anharmonicity of the vibrations.¹⁵ It should be observed that resonance will not in any way account for the nonappearance of the fundamental of the overtone taking part in the phenomenon.

The appearance of the overtones mentioned in the preceding paragraph may be aided by resonance and in particular the appearance of $2\nu_{4ab}$ of CHD_3 can be attributed to resonance with ν_1 . However, it hardly seems probable that all of these overtones are due to resonance since close coincidence with other fundamentals does not seem to occur in all cases and such a regularity as the appearance of these overtones is probably due to the same effect in all cases. We therefore are inclined to the view that they are due to the α_{jj} 's being large and the nonappearance of the fundamentals to the α_j 's being small.

The anharmonicity is another effect that must be considered. The effect of anharmonicity is to increase or decrease the intensity of overtones

¹³ G. Placzek, *Leipziger Vorträge*, p. 71 (1931); *Zeits. f. Physik* 70, 83 (1931); Placzek and Teller, *Zeits. f. Physik* 81, 209 (1933); L. Tisza, *Zeits. f. Physik* 83, 48 (1933); E. B. Wilson Jr., *J. Chem. Phys.* 2, 482 (1934); *Phys. Rev.* 45, 706 (1934).

¹⁴ E. Fermi, *Zeits. f. Physik* 71, 250 (1931); D. Dennison, *Phys. Rev.* 41, 304 (1932).

¹⁵ G. Placzek, *Handbuch der Radiologie*, VI, Vol. 2 (1934), pp. 316-323.

and combination tones depending upon the type of perturbation. As this is unknown, all that can be said is that the maximum effect will be of the order of the nonlinear terms in the development of the polarizability. The effect will therefore be small in general.

In conclusion, it may be said that the appearance of Raman lines is governed by the following factors: symmetry of the molecule, the effect of the motion of the hydrogens relative to carbon on

the magnitude of α_j , and α_{jj} , resonance interaction of nearly commensurable frequencies, anharmonicity of the vibrations involved. In the case of the isotopic methanes, the non-appearance of fundamentals may be attributed to the circumstance that α_j is very small. The appearance of overtones may be due either to the fact that α_{jj} is large, or to resonance, or their combined influence. The effect of anharmonicity should be small, but cannot be predicted.

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An Analytic Method of Interpretation of Electron Diffraction Photographs of Gases*

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An analytic procedure to be used in the interpretation of electron diffraction photographs for gases is developed. The experimentally determined positions of the maxima and minima are employed to solve directly for the interatomic distances through successive approximations. The method is then generalized so as to be applicable to molecules in which rotations or large oscillations about a bond are

permitted. As a test, three sets of data which have already been published are recalculated yielding somewhat altered values for the molecular parameters. New diffraction photographs of propane are analyzed. It is pointed out that the number of theoretical intensity curves which must be computed to obtain the correct structure is thereby greatly reduced.

I

IN the analysis of electron or x-ray diffraction photographs of gases, it has been customary to plot I versus x , of the function

$$I = k \sum_{ij} \psi_i \psi_j \frac{\sin l_{ij} x}{l_{ij} x}, \quad (1)$$

where

$\psi_i \text{ x-rays} = f_i(x)$ the structure factor for atom i

$\psi_i \text{ electrons} = 4\pi(Z_i - f_i(x))/x^2$

$x = 4\pi \sin(\theta/2)/\lambda$.

l_{ij} = distance between the i th and j th atoms,

for various values of the parameters l_{ij} , and to choose those values for which the corresponding curve shows the best fit with the experimentally determined intensity distribution both in general shape and in the positions of the maxima and

minima. Those investigators¹ working with electron beams found it advantageous to use various simpler functions for the form of ψ_i than the one given above.² Justification for these has been adequately discussed in the literature. It is evident that even with the simplest form of ψ_i ($\approx Z_i$), the labor involved in calculating the numerous curves for molecules having only three doubtful shape parameters becomes very great. Were it desirable to investigate three different values for each l_{ij} in such a case, it would be necessary to plot 3^3 curves for each conceivable model to take care of all possible combinations. Then, to obtain the best fit, it might be essential to interpolate between the curves. For more complicated molecules the necessary number of computations rises very rapidly. In practice, therefore, one must make frequent use of the assumption of the constancy of interatomic distances and angles for the same group of atoms in different molecules and can investigate only "reasonable" models.

* Contributions from Gates Chemical Laboratory, California Institute of Technology, No. 540.

¹ L. Pauling and L. O. Brockway, *J. Chem. Phys.* **2**, 867 (1934); L. R. Maxwell, S. B. Hendricks and Y. M. Mosley, *ibid.* **3**, 699 (1935).

² N. F. Mott, *Proc. Roy. Soc. A* **127**, 658 (1930).