

Raman Effect of Acetylenes II. Diiodoacetylene, Liquid Acetylene and Deuteroacetylenes

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numerous vibrational levels of the normal molecule are consistent with the Franck-Condon rule than is the case in absorption by the nonvibrating molecule. Even allowing this, one does not see why sharp band heads typical of absorption should not be visible in fluorescence.

The fluorescence of chlorobenzene and ethyl benzene was too faint to be followed into the region of low pressures.

In conclusion, it is a pleasant duty to thank Dr. E. B. Wilson for many valuable suggestions and criticisms.

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Raman Effect of Acetylenes

II. Diiodoacetylene, Liquid Acetylene and Deuteroacetylenes¹

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An apparatus consisting of eight discharge tubes for Raman work has been designed which is more convenient than the usual helical design of these light sources. It is possible to arrange these eight tubes concentrically around a Raman tube of any diameter. Cylindrical filters of any dimensions can be interposed with great convenience. The vibration Raman spectra of C_2I_2 : 191.3, 310.2, 627.0 688.2 and 2109.4; liquid C_2H_2 : 381.6, 618, 631, 1762, 1959 and 3338; gaseous C_2H_2 : 1973.8 and 3373.7; gaseous C_2HD : 1851.2 and 3334.8; gaseous C_2D_2 : 1762.4 and 2700.5 cm^{-1} have been observed and are interpreted in the usual manner on the basis of symmetry considerations. Striking

differences in the spectra of liquid and gaseous acetylene (C_2H_2) indicate a serious distortion of the molecules in the liquid state. The extent of this disturbance seems to change completely the symmetry of the molecules of the liquid which are no longer linear as in the gaseous state. Certain Raman lines are accompanied by faint satellites which fit a rotation formula and may be due to rotation effects. The free energies of C_2HD and C_2D_2 were calculated and the free energy change of the reaction $C_2H_2 + C_2D_2 \rightleftharpoons 2C_2HD$ has been evaluated and the equilibrium constant determined for a series of temperatures.

I. INTRODUCTION

OUR study of acetylenes has been continued with still further improvements in technique. The compounds used are C_2I_2 in alcohol and acetone solution; gaseous and liquefied C_2H_2 (at $-80^\circ C$); gaseous deuteroacetylenes: C_2D_2 and C_2HD .³

II. EXPERIMENTAL PROCEDURE

A new set of Ne-Hg discharge tubes

The helical tubes used as light sources in our

former researches⁴ were inconvenient in respect to the possibility of inserting into the helix, Raman tubes of various diameters. Obviously the internal diameter of the helix determines the maximum thickness of the Raman tubes and the various filters needed at times. The new arrangement shown in Fig. 1 admits any size Raman tube and any number or thickness of cylindrical filters. The greater number of discharge tubes adds to the intensity of illumination. Two such tubes are fed by a 200/7000-volt 3-kva transformer. The whole set-up is sufficiently flexible to have motion in all directions. A cylindrical reflector is used.

¹ Part of this work was reported at the Cleveland meeting of the A. C. S., September 1934.

² This article is based upon a thesis presented to the faculty of the Graduate School of the University of Minnesota by Charles E. Morrell in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

³ We are greatly indebted to Professor H. S. Taylor for a generous supply of C_2D_2 prepared under his direction at Princeton University by Dr. J. C. Jungers, C. R. B. fellow from Louvain. The liquid acetylene was prepared from a sample of very pure calcium carbide obtained through the

courtesy of Mr. E. C. MacQuigg from the Union Carbide and Carbon Chemicals Corp. to whom we express our thanks. The gas C_2HD was loaned us kindly by Professor L. H. Reyerson of the School of Chemistry of the University of Minnesota.

⁴ Glockler and Davis, *J. Chem. Phys.* **2**, 881 (1934) and *Phys. Rev.* **46**, 535 (1934); Glockler and Morrell, *Phys. Rev.* **46**, 233 (1934) and **47**, 569 (1935).

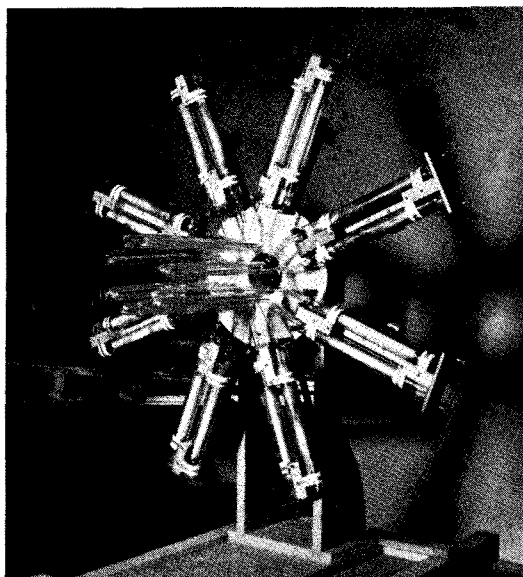


FIG. 1. Neon-mercury discharge tubes.

Preparation and source of compounds C_2I_2

This substance was prepared both according to the method of Biltz⁵ and according to Dehn.⁶ The latter method was found to give a purer and more stable product and was used in the preparation of samples which gave satisfactory Raman spectra. The product, recrystallized twice from petroleum ether, was pure white in color but slowly developed a yellow color when allowed to stand in a desiccator in the presence of air. The solid was used in solution in acetone and absolute alcohol. The former solvent was carefully purified by the sodium iodide method of Shipsey and Werner.⁷ The solutions in acetone, although thoroughly pumped with an oil pump to rid them of dissolved air and sealed into the Raman tubes in vacuum, became yellow in color after a few hours exposure. This objectionable change in color was probably due not only to photochemical decomposition but also to the action of residual oxygen on the diiodoacetylene, producing carbon monoxide and free iodine. The latter may unite with the diiodoacetylene producing lemon yellow tetraiodoethylene. The yellow color which developed during exposure was undesirable because it produced a strong

⁵ Biltz, Ber. 37, 4415 (1904).

⁶ Dehn, J. Am. Chem. Soc. 33, 1598 (1911).

⁷ Shipsey and Werner, J. Chem. Soc. 103, 1255 (1913).

background between $\lambda=4358\text{\AA}$ and $\lambda=4916\text{\AA}$ and also greatly weakened the intensity of scattered radiation by absorption within the solution. It was noted that samples not washed entirely free of alkali during preparation showed less tendency to become discolored. For such alkaline solutions, absolute alcohol prepared by the distillation of sodium ethylate, was chosen as solvent. They were prepared by dissolving 8.5–11.0 grams of C_2I_2 in 20–21 cc of the alcohol and adding 8–10 drops of a solution of 3.2 grams of carbonate-free potassium hydroxide solution in 50 cc of the alcohol. These solutions were placed in flat-end Raman tubes of about 20 cc capacity, pumped with alternate freezing and thawing and sealed under vacuum. One such solution was exposed 48 hours with satisfactory results. The Raman frequency of potassium hydroxide $\Delta\nu=3600\text{ cm}^{-1}$ was not found on any of the plates and it is extremely doubtful that any of the observed Raman lines are due to the comparatively small amounts of potassium hydroxide.

Acetylene, C_2H_2

This gas was prepared by the usual method from previously outgassed calcium carbide and purified by passing through alkaline sodium plumbite, chromic acid, concentrated sodium hydroxide, solid calcium chloride, and phosphorus pentoxide in the order named. It was solidified at liquid-air temperature and outgassed until no pressure could be read on a McLeod gauge. It was kept liquid in the Raman tube at -82°C at a pressure of about 895 mm in a specially constructed unsilvered Dewar flask shown in Fig. 2.

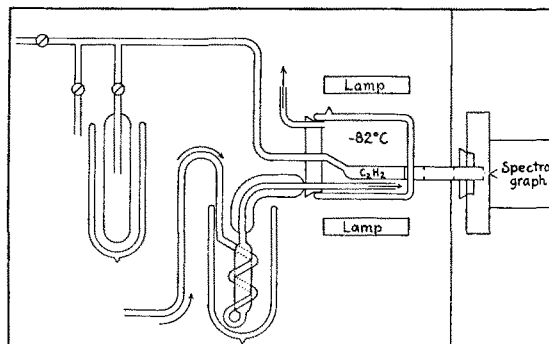


FIG. 2. Experimental arrangements for liquid acetylene.

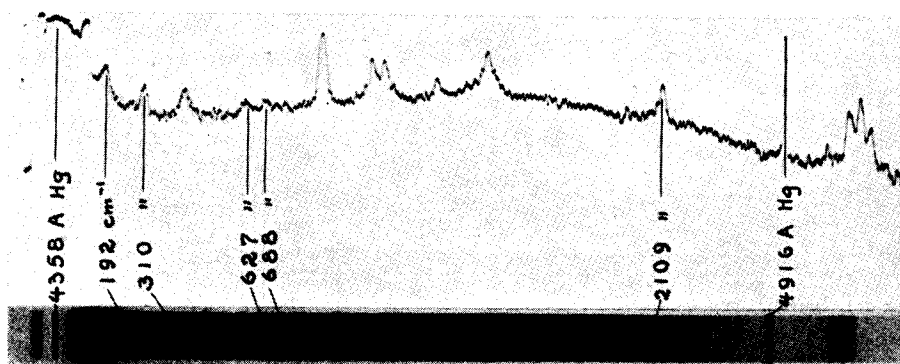


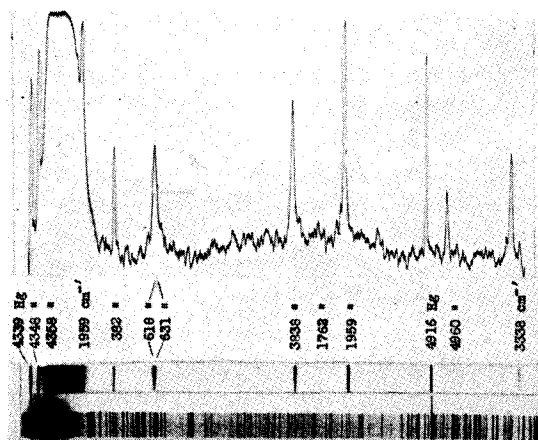
FIG. 3. Raman spectrum of diiodoacetylene.

Dideuteroacetylene

This substance was obtained from Professor Taylor of Princeton University.³ Its exact purity was unknown but was undoubtedly quite high. No lines were found which could not readily be attributed to the C_2D_2 molecule. The gas was confined and exposed in a 280-cc tube at 763 mm pressure.

Monodeuteroacetylene

The spectra of gaseous C_2H_2 and C_2HD molecules were obtained from a mixture of the two substances confined at a total pressure of 2.8 atmospheres. The mixture was supplied by Dr. L. H. Reyerson³ and was prepared from ordinary acetylene and 19 percent heavy water. It contained about 12–15 percent of monodeuteroacetylene at a partial pressure of about 0.4 atmosphere.

FIG. 4. Raman spectrum of liquid acetylene (C_2H_2) excited by 4046 Hg and 4358 Hg.

III. EXPERIMENTAL RESULTS

The Raman frequencies of the substances investigated are given in Tables I–III and shown in Figs. 3 and 4.

TABLE I. *Diiodoacetylene (alcohol solution)*. Twenty-four hours exposure; sodium nitrite filter. Exciting line: 4358A Hg.

$\Delta\nu(cm^{-1})$	INTENSITY	NATURE
191.3	7	broad, diffuse
310.2	5	sharp
627.0	3	very diffuse
688.2	2	diffuse
2109.4	10	sharp

TABLE II. *Liquid acetylene; ten hours exposure*. No filter, exciting lines: 4047 and 4358A Hg.

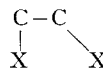
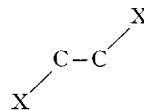
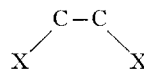
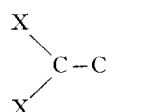
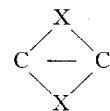
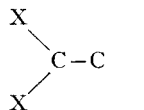
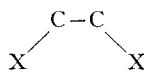
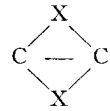
$\Delta\nu(cm^{-1})$	INTENSITY	NATURE
1931.4*	1.5	sharp
1959.5*	10	sharp
381.6	5	sharp
618.0	2	diffuse
630.7	5	sharp
3338.0*	7	diffuse
1761.9	1	diffuse
1813.7	0.1	very faint
1855.8	0.1	very faint
1877.8	0.1	very faint
1903.2	1	slightly diffuse
1929.9	1	slightly diffuse
1958.0	10	sharp
3336.8	5	diffuse

* Excited by 4047A Hg.

TABLE III. *Gaseous acetylenes; valency vibrations*. Seventy hours to one week exposure; no filter. Exciting lines: 4047 and 4358A Hg.

TRIAL	C_2H_2		C_2HD		C_2D_2	
	ν_1	ν_2	ν_1	ν_2	ν_1	ν_2
1	1974.2	3374.2	1851.1	3334.8	1762.3	2700.9
2	1973.3	3373.1	1851.3		1762.6	2699.2
3	1974.4	3373.8			1762.2	
4	1973.3					
5	1973.8					
Ave.	1973.8	3373.7	1851.2	3334.8	1762.4	2700.5

TABLE IV. Application of Placzek's selection and polarization rules to the spectra of a number of different space configurations of the molecule C_2X_2 ($X=I$ or H).

CONFIGURATION			TYPE OF FREQ.	<i>s</i>	<i>a</i>	TOTAL NO. OF FREQ.	RAMAN EFFECT	ρ	ALLOWED NO. OF FREQ.	
I. Linear forms										
<i>a</i>	$D_{\infty h}$	X—C—C—X	A_1	C_{∞}	σ_v	i	2	$c_{ik}=0$	$0-\frac{3}{4}$	
			A_2	C_{∞}	σ_v	i	1	forbidden	—	
			B_1	σ_v	i	C_{∞}	1	only $c_{xz}=c_{yz}\neq 0$	$\frac{3}{4}$	
			B_2	σ_v	C_{∞}	i	1	forbidden	—	
II. Planar forms										
<i>b</i>	C_{1h}		A	σ			5	$c_{xz}=c_{yz}=0$	$0-\frac{3}{4}$	
			B		σ	1	$c_{ii}=c_{xy}=0$	$\frac{3}{4}$		
<i>c</i>	C_{2h}		A_1	C_2	σ_h		3	$c_{xz}=c_{yz}=0$	$0-\frac{3}{4}$	
			A_2	C_2		σ_h	1	forbidden	—	
			B_1	σ_h		C_2	2	forbidden	—	
			B_2		C_2	σ_h	0	$c_{ii}=c_{xy}=0$	$\frac{3}{4}$	
<i>d</i>	C_{2v}		A_1	C_2	σ_x	σ_y	3	$c_{ik}=0$	$0-\frac{3}{4}$	
			A_2	C_2		σ_x	σ_y	0	only $c_{xy}\neq 0$	$\frac{3}{4}$
			B_1	σ_y		C_2	σ_x	2	only $c_{xz}\neq 0$	$\frac{3}{4}$
			B_2	σ_x		C_2	σ_y	1	only $c_{yz}\neq 0$	$\frac{3}{4}$
<i>e</i>	C_{2v}		A_1	C_2	σ_x	σ_y	3	$c_{ik}=0$	$0-\frac{3}{4}$	
			A_2	C_2		σ_x	σ_y	0	only $c_{xy}\neq 0$	$\frac{3}{4}$
			B_1	σ_y		C_2	σ_x	2	only $c_{xz}\neq 0$	$\frac{3}{4}$
			B_2	σ_x		C_2	σ_y	1	only $c_{yz}\neq 0$	$\frac{3}{4}$
<i>f</i>	D_{3h}		A	σ_x	σ_y	σ_z	3	$c_{ik}=0$	$0-\frac{3}{4}$	
			B_1	σ_x	σ_y		σ_z	1	forbidden	—
			B_2	σ_x	σ_z		σ_y	1	forbidden	—
			B_3	σ_y	σ_z		σ_x	1	forbidden	—
III. Nonplanar forms										
<i>g</i>	C_{1h}		A	σ			4	$c_{xz}=c_{yz}=0$	$0-\frac{3}{4}$	
			B		σ	2	$c_{ii}=c_{xy}=0$	$\frac{3}{4}$		
<i>h</i>	C_2		A	C_2			4	$c_{xz}=c_{yz}=0$	$0-\frac{3}{4}$	
			B		C_2	2	$c_{ii}=c_{xy}=0$	$\frac{3}{4}$		
<i>i</i>	C_{2v}		A_1	C_2	σ_x	σ_y	3	$c_{ik}=0$	$0-\frac{3}{4}$	
			A_2	C_2		σ_x	σ_y	1	only $c_{xy}\neq 0$	$\frac{3}{4}$
			B_1	σ_y		C_2	σ_x	1	only $c_{xz}\neq 0$	$\frac{3}{4}$
			B_2	σ_x		C_2	σ_y	1	only $c_{yz}\neq 0$	$\frac{3}{4}$

IV. DISCUSSION OF RESULTS

Symmetry considerations

For the discussion of these spectra it will be convenient to determine the symmetry classes possible for molecules of the type studied and to ascertain the number of possible Raman vibration frequencies from Placzek's theory and his selection rules.⁸ These molecules must possess

for purely dynamical reasons, six fundamental frequencies. All possible configurations of these molecules will be considered: linear, planar, and space models. In Table IV are listed the Schoenflies designations for the class of symmetry, the configuration pictorially represented, the types of frequencies denoted by capital A or B with appropriate subscripts, the symmetry elements to which the type of frequency is symmetric (s) or antisymmetric (a), the number of distinct fundamental frequencies belonging to a given

⁸ Placzek, *Handbuch der Radiologie* (Leipzig, 1934), Vol. II, p. 205.

type, the selection rules for the Raman effect stated in terms of the magnitudes of the components of the scattering tensor c , the degree of depolarization ρ and the number of allowed Raman frequencies. If all the components of the scattering tensor are zero for a given type of vibration, then this vibration cannot be active in the Raman effect. The letters C , σ , i represent, respectively, an axis of rotational symmetry, a plane of symmetry and a center of symmetry. The term σ_v represents a plane of symmetry passing through an axis of symmetry. C_{1h} , C_2 , and C_{2v} represent systems containing a single plane, a twofold axis and a twofold axis with a σ_v plane of symmetry. The system D_{3h} contains $3C_2$ axes and $3C_v$ planes. The system C_{2h} contains a center of symmetry, a twofold axis of symmetry and a plane of symmetry perpendicular to this axis. In cases where the symmetry planes are designated by the rectangular coordinates x , y , and z , the z axis is taken as the axis of symmetry. The letter X in the first column represents either hydrogen or iodine.

The gaseous acetylenes

From Table III it is seen that only two types of Raman frequencies have been observed. Most previous studies⁹⁻¹⁴ show the same results. However from the selection rules (Table IV) these molecules should show three frequencies if they are linear. The two frequencies found are the valency vibrations ν_1 and ν_2 of Mecke's¹⁵ assignment. The deformation frequency δ_2 , Raman-allowed by Placzek's selection rule has never been found. It must mean that the components of the polarization tensor are very weak and the intensity of this line is very small. However δ_2 can be deduced from the infrared combination bands (Table VI). There is a great deal of evidence that gaseous acetylene (C_2H_2) is linear. The rotational structure of the bands is similar to that of a diatomic molecule. The individual rotation lines have alternating intensity showing that the molecule has a center of symmetry.

⁹ Daure, Ann. de physique **12**, 375 (1929).

¹⁰ Segrè, Rend. Linc. **12**, 226 (1930).

¹¹ Venkatesachar and Sibaiya, Ind. J. Phys. **5**, 319 (1931).

¹² Bhagavantam, Nature **127**, 817 (1931) and Ind. J. Phys. **6**, 319 (1931).

¹³ Daure and Kastler, Comptes rendus **192**, 1721 (1931).

¹⁴ Lewis and Houston, Phys. Rev. **44**, 903 (1933).

¹⁵ Mecke, Zeits. f. physik. Chemie **B17**, 1 (1931).

Recently monodeuteroacetylene (C_2HD) has been investigated in the near infrared by McKellar and Bradley¹⁶ and Herzberg, Spinks and Patat.¹⁷ The parallel bands observed show a rotational structure which must be attributed to a linear oscillator. Dideuteroacetylene is most likely also linear in the gaseous state. It may then be said that *in the gaseous state acetylene molecules are linear*.

Liquid acetylene (C_2H_2)

The failure to find the deformation frequency δ_2 at 614 cm^{-1} (predicted from the infrared) in the gas lead to an investigation of the liquid. A frequency was indeed found at 618 cm^{-1} (Table II) but it has a companion at 631 cm^{-1} . Moreover a very low frequency is shown on our plates at 382 cm^{-1} and a very weak line at 1762 cm^{-1} . These four frequencies are excited by 4358Å Hg and not by 4047Å Hg, for if the latter were the exciting line, then their frequencies would be 2149 (382), 2385 (618), 2398 (631), and 3629 (1762). It would be expected that 4358Å Hg would excite the lines 2149, 2385, 2398, and 3629 cm^{-1} . They are not found and hence it is certain that 4358Å Hg is the exciting line. *In liquid acetylene six lines are found instead of three* as expected from Placzek's rules! The possibility must be considered that these selection rules are not valid for the closely crowded molecules of the liquid. Then the frequencies expected would be the ones of the gaseous molecule as given by Mecke¹⁵ and summarized in Table V. But the new lines found are not the fundamentals of ordinary acetylene. They might be due to an impurity. However from the preparation and purification this possibility seems most unlikely. Moreover any sensible impurity would have a more complicated spectrum which should show in its entirety. Furthermore the lines 382, 618, and 631 are much too

TABLE V. Fundamental frequencies of acetylene (C_2H_2).

ν_1	H→	C→	←C	←H	1975 cm^{-1}
ν_2	H→	←C	C→	←H	3370
ν_3	H→	←C	←C	H→	3277
δ_1	H↓	C↑	C↑	H↓	729
δ_2	H↓	C↑	C↓	H↑	614

¹⁶ McKellar and Bradley, Phys. Rev. **46**, 664 (1934).

¹⁷ Herzberg, Spinks and Patat, Zeits. f. Physik **92**, 87 (1934).

strong to be ascribed to an impurity. These new lines might be due to some strange reflections produced in the set-up due to improper alignment. However if such were the case then it would be expected that a great deal of general background would show on the photographic plates. However the photographs are remarkably free from such background.

A possible explanation of the appearance of these six Raman lines is the assumption that the acetylene molecules are not linear in the liquid state. Then six fundamental frequencies would be expected. They are: 381.6, 618, 631, 1762, 1959 and 2338 cm^{-1} . The lines 1813.7 to 1929.9 cm^{-1} are thought to be due to a rotation phenomenon and will be discussed below. Referring to Table IV it is seen that models *a*, *c* and *f* need not be considered because only three frequencies should appear in the Raman effect. Models *b*, *d*, *e*, *g* and *h* may perhaps be excluded because these structures would have an appreciable dipole moment. Liquid acetylene has most likely only a small dipole moment although no experimental evidence exists. The dipole moment of gaseous acetylene is zero. Model *i* can be thought of as a plane formed by two carbon atoms and one hydrogen atom with the other hydrogen atom not in this plane. Only slight displacements of the hydrogen atoms need to occur in the usual linear structure to remove them from the figure axis determined by the carbon atoms. Such distortions may conceivably occur in the liquid state due to the close interactions of the liquid molecules. Model *i* would quite possibly have only a small dipole moment. The important result of our findings is the suggestion that the molecules of a liquid may suffer deformations which affect their symmetry properties.

The possibility of association in the liquid state must also be considered but it does not seem possible to explain the present results on this basis. If a definite polymer were formed, more lines are expected than are actually found. For example $(\text{C}_2\text{H}_2)_2$ as a four-membered ring would be a polymer belonging to the point-group D_{4h} with seven Raman allowed frequencies and if the same polymer were of a linear configuration with methylene groups at the ends (D_{2h}) then nine frequencies should be observed

in the Raman effect. As only six lines are found it might be said that the others are of low intensity and they might be discovered on longer exposure. While this possibility exists it must be said that other physical properties of liquid acetylene speak against association. Substances which do polymerize have large dipole moments, they do not behave like normal liquids regarding their surface-tension variation with temperature. Such molecules as water and ammonia have broad Raman bands. Liquid acetylene has probably only a small dipole moment, the constant *K* in the Ramsey-Shields-Eötvös equation has the value of a normal liquid and the Raman lines are sharp, i.e., not bands. However, some sort of special interaction between the acetylene molecules in the liquid state appears to take place for it should be noted that nitrogen and acetylene although isoelectronic boil about 100°C apart and C_2H_2 boils at a higher temperature.

These results indicate that a difference may exist in the structure of acetylene molecules depending on the state of aggregation. It appears that similar differences may be found with many other substances. For in many cases the number of Raman lines expected on the basis of Placzek's selection rules is not in agreement with published data.

Diiodoacetylene

From Table I it is seen that five Raman lines are found whereas only three would be expected if the molecule is linear, i.e., if the selection rules hold. Again it appears that the molecule may be nonlinear in solution, the interaction due to the solvent molecules causing the deformation. Consideration as made in the case of liquid acetylene would indicate model *i* of Table IV. There should be found a sixth frequency for this molecule. The fact that these molecules are conceivably nonlinear recalls to mind the arguments of organic chemists who have often put forward the idea that the symmetrical structures given these compounds do not explain all their reaction possibilities.¹⁸

¹⁸ E. H. Ingold, J. Chem. Soc. **125**, 1528 (1924); and **127**, 1199 (1925); Nieuwland *et al.*, J. Am. Chem. Soc. **53**, 4197 (1931); Nef, Ann. **296**, 332 (1897); Ber. **34**, 2718 (1901), etc.

Calculated frequencies of the acetylenes

Both Mecke¹⁹ and Olson and Kramers²⁰ have derived expressions for the fundamental frequencies of acetylene in terms of the masses of the atoms and Hooke's law constants on the theory of small vibrations. The calculated values are compared with the experimental frequencies in Table VI from various sources.^{1, 16}

TABLE VI. *The fundamental frequencies of the acetylenes: $k_{C-H} = k_{C-D} = 5.868 \times 10^5$; $K_{C \equiv C} = 15.49 \times 10^5$ dynes/cm.*

	TYPE OF VIBRATION	C ₂ H ₂		C ₂ HD		C ₂ D ₂	
		calc.	obs.	calc.	obs.	calc.	obs.
ν_1	H → C ← C ← H	(1974)	1974	1846	1851	1757	1762
ν_2	H → C ← C → H	(3374)	3374	3326	3335	2678	2700
ν_3	H → C → C → H	3281	3277	2556	2570	2410	—
δ_1	H ↓ C ↑ C ↑ H ↓	—	729	—	679	—	520
δ_2	H ↓ C ↑ C ↓ H ↑	614	—	—	541	392	—

Free energies of C₂H₂, C₂HD, and C₂D₂

The possibility of calculating the thermodynamic properties of the simpler gaseous substances from spectrographic data was suggested by Urey²¹ and Tolman and Badger.²² The fundamental equations for such computations have been adequately outlined by Giauque.²³ For ordinary acetylene (C₂H₂) Kassel²⁴ has derived some simple expressions which have been used to calculate the free energy of the deuterio-acetylenes. The fundamental frequencies are shown in Table VI. The moments of inertia (I) of these molecules are taken as: I(C₂H₂) = 23.509×10^{-40} , I(C₂HD) = 27.412×10^{-40} , and I(C₂D₂) = 31.616×10^{-40} .^{16, 17} The effect of the spin terms in the acetylene molecules can be taken care of at higher temperatures by adding to the free energy the quantity $-RT \ln \mu$ where μ has the value

$$\mu = (2i_1 + 1)^2 / 2$$

for the symmetrical molecules C₂H₂ and C₂D₂ and the value

$$\mu = (2i_1 + 1) \times (2i_2 + 1)$$

for the asymmetrical molecule C₂HD.²⁵ The

¹⁹ Mecke, Zeits. f. Physik **64**, 173 (1930).

²⁰ Olson and Kramers, J. Am. Chem. Soc. **54**, 136 (1932).

²¹ Urey, J. Am. Chem. Soc. **45**, 1445 (1923).

²² Tolman and Badger, J. Am. Chem. Soc. **45**, 2277 (1923).

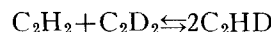
²³ Giauque, J. Am. Chem. Soc. **52**, 4808 (1930).

²⁴ Kassel, J. Am. Chem. Soc. **55**, 1351 (1933).

²⁵ Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933).

quantities i_1 and i_2 are the spin numbers of the hydrogen and deuterium nuclei. The spin of the deuterium nucleus is assumed to be unity. The carbon atoms have no spin. Although the values of the free energy (F°) of both C₂HD and C₂D₂ depend on the spin, the values of any equilibrium constants calculated for reactions into which these molecules enter, does not depend on the spin chosen. This independence is due to the very general fact that the nuclear spins are unchanged during chemical reactions at temperatures considerably removed from absolute zero. The quantity E_0° is the energy content of a species of molecules at standard condition at absolute zero.

From the values of Table VII equilibrium constants for the reaction



can readily be calculated by the following equation:

$$\Delta F^\circ = -RT \ln K = \Delta(F^\circ - E_0^\circ) + \Delta E_0^\circ.$$

On account of the great similarity of all the molecules taking part in the reaction the quantity ΔE_0° can be considered as the difference between the zero-point vibrational energies of the product and the reactants. With the frequencies given in Table VI $\Delta E_0^\circ = 519.01$ cal.

The above values for the equilibrium constant are undoubtedly more accurate than the free

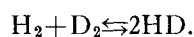
TABLE VII. *Values of $-(F^\circ - E_0^\circ)/T$ for the acetylene gases at one atmosphere pressure. (Calories/degree/mole.)*

TEMP. (°K)	C ₂ H ₂	C ₂ HD	C ₂ D ₂
273.18	42.034	44.790	45.017
298.18	42.728	45.493	45.811
373.18	44.597	47.426	47.951
500.00	47.270	50.195	51.003
600.00	49.083	52.074	53.039
700.00	50.710	53.756	54.874

TABLE VIII. *Free energy changes and equilibrium constants for the reaction: C₂H₂ + C₂D₂ \rightleftharpoons 2C₂HD.*

TEMP. (°K)	$-\Delta(F^\circ - E_0^\circ)$ (cal.)	$-\Delta F^\circ$ (cal.)	K
273.18	690.87	171.86	1.373
298.18	729.65	210.64	1.427
373.18	860.18	341.17	1.584
500.00	1058.50	539.49	1.722
600.00	1215.60	696.59	1.794
700.00	1349.60	834.09	1.822

energy values. The errors in the quantities $(F^\circ - E_0^\circ)$ arise not only from inaccuracies in the values of the fundamental frequencies but also from the failure to consider the stretching and anharmonicity terms in the formation of the Q sums. The values of ΔF° and K are not so much affected because errors which arise from these sources cancel out during the process of subtracting the individual free energy values. The curve obtained by plotting K as a function of temperature has the same general shape as that obtained by Urey and Rittenberg²⁵ for the reaction



Rotation effects in liquid acetylene

A series of faint lines was observed on the short wave-length side of 1959 cm^{-1} . Similar lines have been observed previously in pinene²⁶ and in dimethylacetylene²⁷ and have been interpreted as the members of a P branch of a rotation-vibration band. The individual lines are so spaced that their displacements (cm^{-1}) from 1959 cm^{-1} can be represented quite accurately by means of the following equation:

$$\Delta\nu = 6.99(4m+4) - 0.014 \times 16\left(\frac{1}{2}m^3 + \frac{3}{2}m^2 + 2m + 1\right)$$

$$m = 0, 1, 2, \dots$$

This equation may be regarded as the difference between the $(m+2)$ th and m th term of

$$E_m/(hc) = 6.99m^2 - 0.014m^4$$

$$m = 0, 1, 2, \dots$$

of a nonrigid rotator with fixed axis. In Table IX are recorded the measured and calculated values of the displacements $\Delta\nu = 1959 \text{ cm}^{-1}$. The con-

TABLE IX. *The faint companion lines as displacements from $\Delta\nu = 1959 \text{ cm}^{-1}$.*

TRANSITION	m	$\nu(\text{calc.})$ (cm^{-1})	$\nu(\text{obs.})$ (cm^{-1})
2 \rightarrow 0	0	27.8	28.1
3 \rightarrow 1	1	54.8	54.9
4 \rightarrow 2	2	80.5	80.2
5 \rightarrow 3	3	(104.2)	104.2
6 \rightarrow 4	4	125.2	—
7 \rightarrow 5	5	(142.9)	142.9

stant 6.99 must be equal to $h/(8\pi^2 I_0 c)$, where I_0 is the moment of inertia of the assumed rotator. The calculated value is $3.96 \times 10^{-40} \text{ g cm}^2$. The only conceivable type of rotation involving such a small moment of inertia is a spinning of the non-linear molecule about the line of the carbon atoms.

The lines appear from visual observation, to show alternating intensity, the ones corresponding to odd values, being stronger. In spite of the good agreement between the measured and the calculated displacements of Table IX, there are a number of important objections to the interpretation as a rotation effect. It is difficult to understand why the nonlinear acetylene molecule should not act as a space rotator rather than as a plane rotator even in the liquid state. The complete absence of a corresponding R branch is also at variance with the expectations of theory.

In the case of diiodoacetylene we also find a companion to the Raman line $\Delta\nu = 2109 \text{ cm}^{-1}$. While the line is quite easily visible on a magnified spectrogram we have been unable to measure its position. The displacement appears to be about 20 cm^{-1} . It apparently has the same origin as the faint lines in acetylene. On account of the large masses of the iodine atoms, the possibility of this line being a member of a P branch seems difficult to understand.

²⁶ Bonino, *Nature* **126**, 915 (1930).

²⁷ Glockler and Davis, *J. Chem. Phys.* **2**, 881 (1932).