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Thomas F. Anderson and Anton B. Burg

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The Raman Spectrum of Liquid Diborane

THOMAS F. ANDERSON, *Botany Department, University of Wisconsin, Madison, Wisconsin*

AND

ANTON B. BURG, *George Herbert Jones Chemical Laboratory, University of Chicago, Chicago, Illinois*

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The Raman spectrum of $B_2H_6(l)$ is found to contain an isotopic triplet (ν_1) 793, 806, 821 cm^{-1} , a broad line (ν_2) 1108 cm^{-1} and a very intense doublet (ν_3 ?) 2102, 2523 cm^{-1} as well as several weaker lines. Abnormally large values for the B—B, C—C, and Si—Si bond force constants in B_2H_6 , C_2H_6 , and Si_2H_6 suggest that these bonds are compressed in these molecules by forces which may be associated with those which restrict internal rotation. The value of 55.3 ± 1.5 cal./deg. is calculated for the entropy of $B_2H_6(g)$ at 25°. Combined with the known heat of formation this value leads to a free energy of formation of $-30,000 \pm 4000$ cal. for $B_2H_6(g)$ at 25°. This large value does not truly indicate high stability, for diborane decomposes easily to form other boron hydrides.

THE x-ray¹ and electron diffraction² patterns of diborane (B_2H_6) show that its atomic arrangement is analogous to that in ethane. However, the formulation of its electronic structure is made difficult by the deficiency of two electrons.³ In the hope of contributing toward the solution of this problem, we have obtained the Raman spectrum of diborane in the liquid condition.

EXPERIMENTAL METHOD

Preparation of the substance

Diborane was prepared by the method of Schlesinger and Burg,⁴ and purified with great care. The vapor tensions of the first and last fractions corresponded to that previously recorded for the pure substance: 225 mm at -111.8° . The quantity employed was slightly more than three liters of the gas at standard conditions. The sample was completely condensed (by the aid of liquid nitrogen) in the Raman tube, which was sealed off and at once put to use.

Optical arrangements

The apparatus in which the diborane received and scattered the light from a mercury lamp, is

¹ H. Mark and E. Pohland, *Zeits. f. Krist.* **62**, 103 (1925).

² S. H. Bauer, *J. Am. Chem. Soc.* **59**, 1096 (1937).

³ A review of the literature on this subject is given by Wiberg, *Ber.* **69B**, 2816 (1936).

⁴ Schlesinger and Burg, *J. Am. Chem. Soc.* **53**, 4321 (1931).

shown in Fig. 1. The Raman tube was made from a 12.5 cm length of standard wall, 10 mm diameter Pyrex tubing, sealed at the lower end to a Wood light trap of black Pyrex glass, and at the upper end to a wider (18 mm) tube carrying a horizontal plane window and the side tube for introducing and removing the sample. This Raman tube was surrounded by a 19×4 cm copper cylinder, out of whose wall (2 mm thick) a 13×3 cm window had been cut. The piece cut out was soldered to the inner wall to make a well for receiving liquid nitrogen, by whose aid

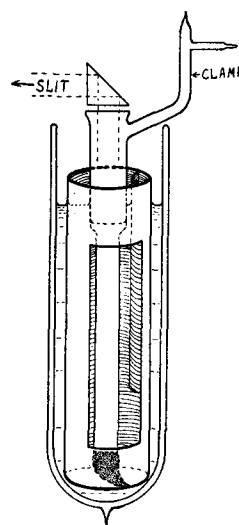


FIG. 1. Schematic drawing of Raman tube assembly. The alcohol is kept at $-100^\circ C$ with liquid nitrogen to liquify the low boiling material in the Raman tube.

the required low temperature (in the neighborhood of -100° or lower) could be maintained. The entire inner surface of the copper cylinder was silver plated to minimize the loss of light.

The Raman tube and reflecting cylinder were immersed in an alcohol bath, contained in a cylindrical Dewar vessel which had been silvered only around two-thirds of its circumference. As a safety device, in case of an accidental rise of temperature, solid carbon dioxide was placed in the space below the window of the copper cylinder.

The mercury vapor lamp used in this work was of the very convenient design shown in Fig. 2. In the use of this relatively simple type of lamp, the current passes through the Torricellian vacuum in the water-jacketed tube. The arc is struck by forcing the mercury to the top of the

TABLE I. Observed frequencies in the Raman spectrum of B_2H_6 (l) with displacements from the exciting Hg lines $\lambda 3984(l)$, $\lambda 4047(k)$, $\lambda 4077(i)$, $\lambda 4339(g)$, $\lambda 4347.5(f)$, and $\lambda 4358(e)$, $d = \text{diffuse}$.

I (ARB.)	ν (CM^{-1})	PROBABLE $\Delta\nu$ (CM^{-1})	ALTERNATE $\Delta\nu$ (CM^{-1})
9	22603.9	2101.5 <i>k</i>	
3	22571.1	2527 <i>l</i>	
3	22414.2	2101.9 <i>i</i>	
10	22182.0	2523.4 <i>k</i>	
5	22145.6	792.5 <i>e</i>	
4	22131.9	806.2 <i>e</i>	
3	22116.7	821.4 <i>e</i>	
4	21993.2	2522.9 <i>i</i>	
2 <i>d</i>	21930.0	2775.4 <i>k</i>	1008.1 <i>e</i>
2	21757.7	1180.4 <i>e</i>	2947.7 <i>k</i>
3	20933.1	2106 <i>g</i>	
1	20898	2101 <i>f</i>	
10	20836.6	2101.5 <i>e</i>	
0	20517	2522 <i>g</i>	
0	20478	2521 <i>f</i>	
3	20449.6	2488.5 <i>e</i>	4255.8 <i>k</i>
8	20416.2	2521.9 <i>e</i>	
7	20155.3	2782.8 <i>e</i>	Hg 4960.3A
2	20070.3	2867.8 <i>e</i>	4635.1 <i>k</i>
4	19818.4	3119.7 <i>e</i>	4887.0 <i>k</i>

discharge tube, where it makes contact with the mercury in the closed end, and then releasing the pressure. The discharge tube has an internal diameter of 7.5 mm and the connecting "barometer" tube has a bore of 2.5 mm. Connected to a source of 110-volt direct current, through a six-ohm resistance, this lamp draws a current of 11 amperes, and produces mercury spectrum lines quite sufficiently sharp for accurate Raman studies.

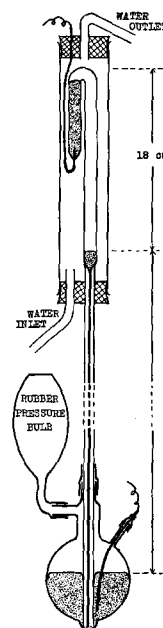


FIG. 2. Water-cooled mercury lamp. The arc is struck in the 18 cm long Torricellian vacuum.

This mercury lamp was placed against the window of the Dewar cylinder, and the two were wrapped with bright aluminum foil, in order to save as much of the light as was feasible. The scattered light was taken off through a right-angle prism into the slit of a three-prism Steinheil spectrograph, set for a dispersion of 18.7Å per mm at a wave-length of 4350Å. The instrument was in sharp focus between 4350Å and 5100Å. Three photographs were obtained: the first was exposed half an hour, the second, two hours, and the third, five hours, on Eastman DC *ortho* plates. The spectrum of an iron arc was photographed upon each plate for comparison; on the third plate the spectrum of the mercury lamp itself also was photographed, with an intensity of exposure almost the same as that of the scattered mercury spectrum.

EXPERIMENTAL RESULTS

Seven Raman lines were obtained with the half-hour exposure, sixteen with the two-hour exposure which had a low background, and sixteen or more with the five-hour exposure which gave a uniform background. In Table I are given the estimated intensity (I) and frequency (ν) of each of the observed lines together with

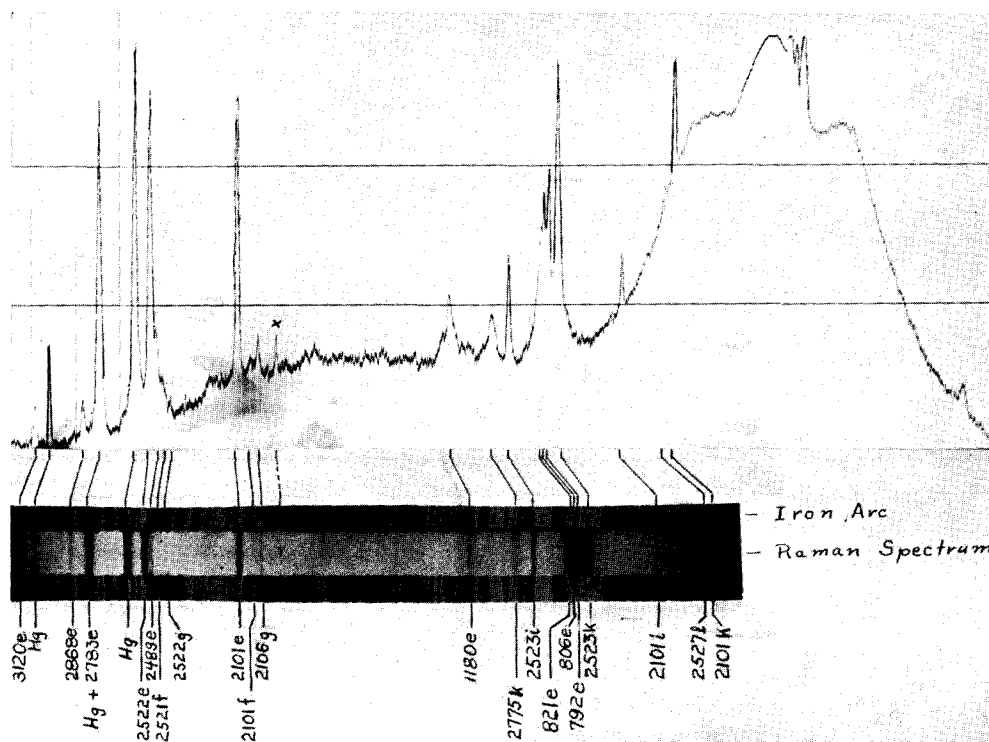


FIG. 3. The Raman spectrum of $B_2H_6(l)$ and its microphotometer tracing.

the displacements from the various exciting lines. In Fig. 3 the five-hour exposure is reproduced together with the iron comparison spectrum, the observed frequency shifts, and a microphotometer tracing of the Raman spectrum.

The lines 2101 *k, e* and 2523 *k, e* are most intense and exceedingly sharp; these frequencies have also been scattered from the Hg *i, f*, and *g* and the Hg *l* and *i* lines, respectively. The pair 792*e* and 806*e* are sharp and the former is considerably stronger than the latter. The line 821*e* is broad, however, and its integrated intensity is probably greater than that of 792*e*.

As indicated in Table I, in a number of cases it is uncertain whether the exciting line is $\lambda 4358$ or $\lambda 4047$. We feel, however, that $\lambda 4358$ is responsible for most of these lines since if they were of higher frequency (i.e., scattered from $\lambda 4047$) they should also be observed as scattered from $\lambda 4358$. The broad line at $21,930\text{ cm}^{-1}$ may be an exception for if it were 2775*k*, 2775*e* would be obscured by the mercury line $\lambda 4960$. The fuzzy appearance of the line Hg 4960 causes us

to favor this latter possibility. Note that the apparently sharp line marked *x* on the microphotometer tracing is in reality only a dust mark on the plate.

ASSIGNMENT OF FREQUENCIES

Selection rules for this type of molecule have been given by Stitt and Yost.⁵ They allow 6 frequencies for the D_{3d} configuration (center of symmetry), 9 for the D_{3h}' configuration (in which internal rotation is unrestricted) and 9 Raman active frequencies for the D_{3h} configuration (plane of symmetry perpendicular to the central bond). Howard⁶ has worked out the normal coordinates using a three-constant valence-force potential function with restricted internal rotation.

The symmetrical stretching vibration ν_1 ,⁶ for each of the three isotopic molecules containing

⁵ Stitt and Yost, J. Chem. Phys. 5, 90 (1937).

⁶ J. B. Howard, J. Chem. Phys. 5, 442 (1937). We have used the notation used in this paper to designate the frequencies. We are indebted to Dr. Howard for sending us the unpublished formulae for the ν_9 , ν_{10} , and ν_{11} vibrations.

$B^{11}-B^{11}$, $B^{11}-B^{10}$, and $B^{10}-B^{10}$, are readily identified as the lines 793, 806, and 821 cm^{-1} , respectively. The calculated isotopic shifts in frequency agree within 1 cm^{-1} with the observed shifts, and the relative intensities are of an order of magnitude corresponding to the relative abundance, 4 to 1, of the boron isotopes except for the line 821 cm^{-1} which is more intense than corresponds to this ratio. It has been noted, however, that the line at 821 cm^{-1} is broad and therefore doubtless derives its principal intensity from another frequency, possibly ν_9 .

A comparison of the spectrum of B_2H_6 with those of the analogous compounds C_2H_6 and Si_2H_6 aids in making further assignments. In Table II are listed our results together with those for $C_2H_6(l)$,⁷ $C_2H_6(g)$,⁸ and $Si_2H_6(g)$.⁵ The frequency at 1180 cm^{-1} apparently corresponds to the 1463 cm^{-1} line for C_2H_6 and the 933 cm^{-1} band for Si_2H_6 which have been assigned to ν_2 , associated with the symmetrical bending of the B-H, C-H, and Si-H bonds, respectively. Likewise the intense pair 2102, 2523 cm^{-1} would correspond to the pair 2884, 2941 cm^{-1} of $C_2H_6(l)$ and the line 2163 in $Si_2H_6(g)$ which have been assigned to ν_3 , the frequency associated with the symmetrical stretching of the six bonds to the hydrogen atoms. These frequencies lie close to the B-H stretching frequency 2535 cm^{-1} in $B_3N_3H_6$.⁹ In $C_2H_6(l)$ the 57 cm^{-1} split in the vibration is supposed to arise through coincidence and consequent resonance¹⁰ of this mode with one of the overtones $2\nu_7$, or $2\nu_{10}$. It is difficult at this time to imagine another explanation for the appearance of such an intense pair of lines in this region; yet a resonance splitting of 421 cm^{-1} seems so abnormally large that we make this assignment only tentatively.

The frequency 2489 cm^{-1} might be tentatively assigned to ν_{11} in analogy with the assignment¹¹ of the line of $C_2H_6(g)$ at 2940 cm^{-1} ; the latter assignment is confirmed by the appearance of the rotation lines associated with it which were

observed by Lewis and Houston.⁸ The meaning of the remaining frequencies is uncertain; a knowledge of the infra-red frequencies would probably help in assigning them.

THE FORCE CONSTANTS

With the assignment of the three parallel frequencies ν_1 , ν_2 , ν_3 , and Howard's formulae⁶ for the normal modes of vibration derived from a valence force potential function it is possible to calculate the force constants of the molecule. We obtain 3.0×10^5 dynes/cm for K_1 associated with stretching the B-H bond, 0.26×10^5 dynes/cm for K_2 associated with bending the B-H bond and 3.6×10^5 dynes/cm for K_3 associated with stretching the B-B bond and determined principally by ν_1 . The two B-H force constants are in satisfactory agreement with the B-H force constants in the triborine triamine molecule $B_3N_3H_6$ in which the B-H stretching constant is 3.42×10^5 dynes/cm and the B-H bending constants are 0.35 and

TABLE II. Raman Frequencies of B_2H_6 , C_2H_6 , and Si_2H_6 .

$B_2H_6(l)$	$C_2H_6(l)^7$	$C_2H_6(g)^8$	$Si_2H_6(g)^5$
792.5(5)			
806.2(4)	979(1)		
821.4(3)	994(10)	993(10)	435(7)
1180.4(2)	1463(5d)	1344(0)	910
		1460	to } (2)
			955
	2733(2)	2744(2)	
	2768(2)	2778(0)	
2102(10)	2884(10)	2899(10)	
2489(3)	2922(1d)	2940(1)	2163(10)
2523(10)	2941(10)	2955(10)	
2775(3)	2963(1d)	2969	
2868(2)		2979	
3120(2)		2989	
		2999	
		3009	

0.23×10^5 dynes/cm for the planar and out-of-plane bending, respectively.⁹

INTRAMOLECULAR FORCES IN B_2H_6 , C_2H_6 , AND Si_2H_6

A comparison of the internuclear distances for B_2H_6 and analogous molecules as calculated from the force constants and Badger's rule¹² with the

⁷ P. Daure, Ann. de physique **12**, 375 (1929); Glockler and Renfrew, J. Chem. Phys. **6**, 295 (1938).

⁸ Bhagavantam, Ind. J. Phys. **6**, 596 (1931); Lewis and Houston, Phys. Rev. **44**, 903 (1933).

⁹ B. L. Crawford, Jr. and J. T. Edsall, private communication of unpublished results.

¹⁰ E. Fermi, Zeits. f. Physik **71**, 250 (1931).

¹¹ Bartholomé and Karweil, Zeits. f. physik. Chemie **B39**, 1 (1938).

¹² a, R. M. Badger, J. Chem. Phys. **2**, 128 (1934); b, **3**, 710 (1935).

TABLE III. Comparison of internuclear distances calculated from force constants and those observed by electron diffraction.

COMPOUND	K_3 (DYNES/CM $\times 10^{-6}$)	R (CALC.) (Å)	R (OBS.) (Å)	R (OBS.) $-R$ (CALC.) (Å)	K_1 (DYNES/CM $\times 10^{-6}$)	r (CALC.) (Å)	r (OBS.) (Å)	r (OBS.) $-r$ (CALC.) (Å)
B ₂ H ₆	3.57	1.48	1.86 ²	0.38	3.0	1.19	1.27 ²	0.08
C ₂ H ₆	5.62	1.37	1.55 ¹³	0.18	4.79	1.06	1.09 ¹³	0.03
Si ₂ H ₆	1.7	2.13	2.32 ¹⁴	0.19	—	—	—	—

internuclear distances as measured by electron diffraction, leads to interesting indications concerning intramolecular forces. In Table III are given in column II the values of the force constants K_3 for the B—B, C—C, and Si—Si bonds in the compounds B₂H₆, C₂H₆, and Si₂H₆ listed in column I. The corresponding internuclear distances R calculated from Badger's rule are given in column III for comparison with the values from electron diffraction given in column IV; differences between observed and calculated values are given in column V. Columns VI, VII, VIII, and IX contain the values for the B—H and C—H force constants K_1 , the calculated distances r , the observed distances, and the differences between observed and calculated distances, respectively.

The fact that the calculated values of R are much smaller than the observed values for all three compounds strongly suggests that the bonds between the central atoms are compressed, in analogy with Badger's association^{12b} of the apparent stretching of the bonds in tetrachlorides and hexafluorides by repulsion between halogen atoms. If the magnitude of the compressional forces indicated here depend upon the internal angle, internal rotation would be hindered.

The results for the central atom-hydrogen distances indicate that these bonds, too, are under compression. An effective attraction between hydrogen atoms of one CH₃ group in ethane with the C—H bonding orbitals of the other group possibly arising through consideration of the terms suggested by Penney¹⁵ might give rise to just such compressional forces.

Any such attraction between hydrogen atoms would give the molecule a plane of symmetry perpendicular to the central bond (D_{3h}) rather

than a center of symmetry (D_{3d}). In fact Bartholomé and Karweil¹¹ recently have obtained an infra-red spectrum for ethane which they could interpret using D_{3h} selection rules, but not with D_{3d} selection rules. They concluded that ethane has a plane of symmetry perpendicular to the C—C bond rather than a center of symmetry.

It is difficult at this time to make an estimate of the magnitude of the restricting potential,¹⁶ or the magnitude of the dependence of the compressional forces on the internal angle.

THE STABILITY OF DIBORANE

Since the heat of formation is known¹⁷ and it is now possible to calculate an approximate value for the entropy, it seems desirable to discuss the stability of diborane at this time. From electron diffraction results² the moments of inertia are calculated to be $A=B=55.2 \pm 2.0$ and $C=14.3 \pm 0.5 \times 10^{-40}$ g cm², on the assumption of tetrahedral distribution of bonds about boron atoms. The contribution of rotation and translation to the entropy of the gas at 25°C is thus 50.94 ± 0.1 cal./deg. including the symmetry term with the symmetry number equal to 18. The maximum contribution of internal rotation is 3.26 cal./deg. for no restricting potential, $V_0=0$, while for $V_0=3000$ cal. the contribution would be about 2.0 cal./deg.¹⁸ A safe estimate of this contribution would probably be 2.4 ± 0.8 cal./deg. We have calculated the approximate values for the missing frequencies using Howard's formulae⁶ and from them find

¹⁶ American authors favor a value of 3000 cal. in the case of ethane (see Kistiakowski, Lacher, and Stitt, J. Chem. Phys. **6**, 407 (1938) for references) while Eucken and co-workers estimate the height of the barrier to be about 350 cal. (W. Hunsmann, Zeits. f. physik. Chemie **B39**, 23 (1938)).

¹⁷ Roth and Börger, Ber. **70**, 48 (1937).

¹⁸ K. S. Pitzer, J. Chem. Phys. **5**, 469 (1937).

¹³ Pauling and Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

¹⁴ Brockway and Beach, J. Am. Chem. Soc. **60**, 1836 (1938).

¹⁵ W. G. Penney, Proc. Roy. Soc. **A144**, 166 (1934).

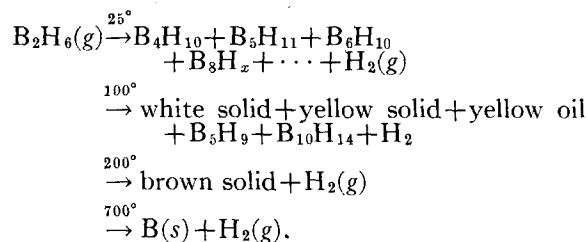
the contribution of vibration to the entropy to be only 1.9 ± 0.6 cal./deg., allowing a wide margin of uncertainty for the missing frequencies. We thus have the approximate value of 55.3 ± 1.5 cal./deg. for the entropy of $B_2H_6(g)$ at 25° .

The heat of formation of $B_2H_6(g)$ from the elements has recently been determined to be $44,000 \pm 3000$ cal.¹⁷ We may make an estimate of the entropy of solid boron and write the following equations:

$$\begin{aligned} 2B(s) + 3H_2(g) &= B_2H_6(g), \\ S^*_{298.1, H_2(g)} &= 31.23 \text{ cal./deg.}, \\ S^*_{298.1, B(s)} &= 4 \pm 1 \text{ cal./deg.}, \\ S^*_{298.1, B_2H_6(g)} &= 55.3 \pm 1.5 \text{ cal./deg.}, \\ \Delta S^\circ_{298.1} &= -50.4 \pm 3.5 \text{ cal./deg.}, \\ \Delta H_{298} &= -44,000 \pm 3000 \text{ cal.}, \\ \Delta F^\circ_{298} &= -30,000 \pm 4000 \text{ cal.} \end{aligned}$$

The uncertainty in the entropy of diborane is indeed rather large, but it is to be pointed out that this uncertainty can at most lead to an error of only 1000 cal. in the standard free energy while the uncertainty in the measured heat of formation is estimated¹⁷ to be 3000 cal. The total of 4000 cal. uncertainty in the free energy cannot possibly invalidate the following conclusions regarding the stability of diborane.

Namely, at room temperature diborane is stable with respect to decomposition into the elements and will not begin to decompose into the *elements* until about 500°C . Actually this process is not analytically complete short of 700° . It is well known, however, that diborane is unstable at room temperature and above, decomposing to form other hydrides in a complicated set of reactions:



It will, of course, be impossible to relate the stability of diborane with respect to these products without a knowledge of their thermodynamic properties.

We are indebted to Professor H. I. Schlesinger for the use of large amounts of diborane prepared with his material aid. We are also grateful to members of the staff of the California Institute of Technology for the use of equipment to evaluate the plates.