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Absorption Band Spectra of Germanous Sulfide: The Isotopic Constitution of Germanium[1,2]

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The absorption spectrum of GeS has been photographed with a 6 foot grating. Two band systems were found in the ultraviolet, the first lying in the region 3358–2709A, the second in the region 2782–2464A. All of the bands are degraded toward the red. The first system consisted of sharp heads, in which the vibrational isotope effect was clearly resolved. Rotational structure could also be observed but only at a considerable distance from the heads. The three abundant isotopes of germanium, 74, 72 and 70, and one of the five less abundant isotopes cited by Aston, 76, were recognized. The vibrational analysis led to the following equation for the bands due to $Ge^{74}S$:—

$$\nu = 32889.5 + 374.99(v'+1/2) - 1.514(v'+1/2)^2 - 575.80(v''+1/2) + 1.80(v''+1/2)^2.$$

The band heads of the second system, for which no isotope analysis was possible because of the low intensity and poor contrast of the bands, can be fitted by the equation:—

$$\nu = 38890.0 + 310.4(v'+1/2) - 1.35(v'+1/2)^2 - 575.8(v''+1/2) + 1.8(v''+1/2)^2.$$

Direct extrapolation of the vibrational constants leads to the following values for the energies of dissociation: for the normal state, common to the two electronic transitions, 5.65 volts and for the two excited states, 2.84 and 2.17 volts respectively. Assuming that the products of dissociation from the normal state are normal atoms, calculation yields for the atomic excitation energy of the dissociation products from the excited state, an average value of 1.27 volts. Both Ge and S have a $^1D_2$ low-lying, metastable level arising from their basic configurations, the energy values for which are 0.88 volts for Ge and 1.18 volts for S (estimated by McLennan).

INTRODUCTION

UP TO the present time, no band spectra of germanium have been reported in the literature, though Hartley and Ramage[4] have mentioned the occurrence of bands in flame spectra of this element without recording their wave-lengths. Some experiments, undertaken by other investigators in our Physics Laboratory, using the flaming arc, have yielded banded spectra in the ultraviolet, presumably due to GeO, while in the Schumann region some unidentified bands have been observed in the spectrum of a Schuler lamp containing metallic germanium and operating with helium.

Germanium, like carbon and silicon, exhibits a primary valence of four, although a few compounds containing the divalent form are known. Recently

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[1] The investigations on which this article is based were supported by grants from the Heckscher Research Foundation, established by August Heckscher at Cornell University.

[2] A preliminary report was presented at the Washington meeting of the American Physical Society, May, 1931. Phys. Rev. **37**, 1709 (1931).

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[4] Hartley and Ramage, Trans. Roy. Dublin Soc. (2) **7**, 339 (1901).

Dennis and Hulse[5] have described the preparation in a pure state of GeO and GeS, samples of which were kindly made available to us. Both of these compounds are solids but can be sublimed at temperatures of 710° and 430°C respectively. The analogous compound of carbon, CO, shows weak, banded absorption[6] near 2000A (Cameron bands) and very strong absorption[7] below 1600A. CS is not a stable molecule in the chemical sense, hence no absorption spectra are known for it. Emission bands attributable to this molecule have been obtained by Jevons[8] in a Geissler discharge through CS_2 vapor. It was to be expected that GeO and GeS would show absorption in the middle ultraviolet, in accordance with the universal observation that in passing down a given column of the periodic table, corresponding electronic transitions, both atomic and molecular, suffer a shift toward longer wave-lengths.

Preliminary experiments with GeO gave weak indications of a banded absorption spectrum between 2900 and 2500A, but the presence of a very strong continuous spectrum over this part of the ultraviolet rendered measurements impossible. It was evident that the quartz windows were being attacked by the GeO at the high temperatures necessary to obtain a sufficient vapor density, 600–650°C, resulting in the formation of a glaze[5] that served to reduce their transmission to a very large degree. It is hoped, however, by the use of a different technique, to obtain this spectrum with better definition. GeS, with its lower subliming temperature, proved more satisfactory under the conditions of the experiment and showed two extensive systems of absorption bands, centering around 3000A and 2500A. There was, nevertheless, some evidence of attack on the quartz windows, which was responsible in part for a continuous absorption beginning at 2800A and extending with increased intensity toward shorter wave-lengths. Doubtless this continuous absorption was also due in part to the continuous spectrum proceeding from the convergence limit of the band system lying at longer wave-lengths.

The isotopic constitution of germanium has been investigated by Aston,[9] who lists 8 species having the following relative abundances:

70	71	72	73	74	75	76	77
56.23	4.36	72.44	26.30	100	6.45	17.37	2.00

The analysis of the band-spectra data below leads to the recognition of the species, 70, 72, 74 and 76. While the bands due to the isotopes 71 and 73 would be somewhat difficult to observe, since they should fall between the very strong bands of the more abundant isotopes, 70, 72 and 74, the bands due to 75 and 77 should be obtainable. It will be necessary, however, to use higher vapor pressures, or longer vapor paths than have been available in the present research in order to bring out these very weak bands, if they exist. In a previous investigation of the isotopes of germanium,[10] Aston has remarked,

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[5] Dennis and Hulse, Jour. Amer. Chem. Soc. **52,** 3553 (1930).

[6] Hopfield, Phys. Rev. **29,** 356 (1926).

[7] Leifson, Astrophys. J. **63,** 73 (1926).

[8] Jevons, Proc. Roy. Soc. **117,** 351 (1928).

[9] Aston, Proc. Roy. Soc. **132,** 487 (1931).

[10] Aston, Nature **122,** 167 (1928). Also Proc. Roy. Soc. **130,** 302 (1930).

in connection with the fact that germanium tetraethyl was used in the discharge chamber of the mass spectrograph, that the possibility of hydride formation "cannot be entirely ruled out" as a source of error in the interpretation of the results. The abundance ratios, quoted above, were obtained by the use of germanium tetramethyl, which also contains hydrogen, but which Aston found to be more satisfactory than the tetraethyl compound.

Experimental

The absorption spectra were obtained by passing the light from a hydrogen discharge tube through the vapor of GeS. The salt was contained in an evacuated quartz tube, 20 cm in length, which was placed in the center of an insulated, cylindrical furnace, 40 cm long, whose ends were closed by quartz windows. The hydrogen discharge tube was patterned after that described by Lawrence and Edlefsen.[11] It was completely immersed in circulating cold water and operated with a current of one ampere at 2000 volts. It was further fitted with a palladium tube, through which hydrogen could be admitted as needed to keep the discharge at its maximum brightness, a condition which is attained when the H_2 pressure is sufficiently high, so that the discharge completely fills the cross section of the tube. The use of the palladium tube does away with the need for bulky ballast bulbs and provides for continuous operation over an indefinite period with a minimum of attention. Spectrograms were obtained in the first order of a 6 foot grating on a Rowland mounting, which gave a dispersion of 4.6 A/mm. An iron arc spectrum served as comparison. The plates were measured on a Gaertner comparator, a few being checked on a new precision comparator built for us by Mr. D. W. Mann of Cambridge, Mass.

The absorption bands of GeS were obtained at a temperature of about 450°C and were distributed between 3360 and 2460A, falling clearly into two groups which overlapped slightly in the vicinity of 2750A. The bands are degraded toward the red and for the most part have sharp edges, although at the short wave-length end of the first system, where overlapping of bands becomes frequent, a number of the heads appear diffuse. A large number of rotational lines were observed but since they were resolved only at relatively large distances from the band origins, with the heads of overlapping bands frequently falling between, no attempt at measurement was made. About 400 band heads were measured, of which approximately 220 have been assigned, among the several isotopes, to the vibrational scheme of the band system whose origin lies at 3040.5A. The bands in this region, which could not be assigned, have for the most part very low intensities, do not show the characteristic isotope resolution of the other bands and do not appear to lend themselves to arrangement in a vibrational scheme. They may be due to impurities. The bands lying further to the ultraviolet and in a separate group show the same vibrational frequencies for the normal state as the first system and so can safely be attributed to the GeS molecule. However, owing to the strong, overlying continuous spectrum, these bands are quite weak and lack-

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[11] Lawrence and Edlefsen, Rev. Sci. Instruments **1**, 45 (1930).

ing in contrast and it has not been possible to recognize the separate heads due to the three abundant isotopes, 70, 72 and 74.

VIBRATIONAL ANALYSIS

In Table I are given the wave-lengths in air, averaged from several plates, wave-numbers in vacuum, calculated wave-numbers and intensities of the band heads constituting the first system. The data are arranged in groups for the sequences $\Delta v = -5$ to $+13$ and in separate columns for the four molecules, $Ge^{76}S$, $Ge^{74}S$, $Ge^{72}S$ and $Ge^{70}S$. Band heads for each isotope for a given vibrational transition have not always been found in the case of many of the weaker bands. This is due, in the majority of instances, to the weak band falling in a region of strong absorption in the vicinity of an intense band or among the rotational lines of such a band. The calculated values were obtained from the following equation for the most abundant molecule, $Ge^{74}S$:—

$$\nu = \nu_e + \omega_e'(v' + \tfrac{1}{2}) - \omega_e'x_e'(v' + \tfrac{1}{2})^2 - \omega_e''(v'' + \tfrac{1}{2}) + \omega_e''x_e''(v'' + \tfrac{1}{2})^2$$

$$Ge^{74}S{:}\nu = 32889.5 + 374.99(v' + \tfrac{1}{2}) - 1.514(v' + \tfrac{1}{2})^2 - 575.8(v'' + \tfrac{1}{2}) + 1.80(v'' + \tfrac{1}{2})^2.$$

The equations for the other three isotopes were computed from the theory of the vibrational isotope effect, as developed by Loomis[12] and others, by means of the relations:

$$\omega_e^i = \rho^i \omega_e^{74} \text{ and } \omega_e^i x_e^i = \rho^{i2} \omega_e^{74} x_e^{74}$$

the superscript, i, referring to the isotope in question. ρ is defined as $(\mu/\mu^i)^{1/2}$, μ being the reduced mass of the reference molecule, $Ge^{74}S$, and μ^i that of the isotopic molecule. The values of ρ and ρ^2 for the several molecules are:

	ρ	ρ^2
$Ge^{70}S$	1.00859	1.01725
$Ge^{72}S$	1.00419	1.00839
$Ge^{76}S$	0.99602	0.99206

The resulting vibrational equations for these molecules are as follows:

$$Ge^{70}S{:}\nu = 32889.5 + 378.21(v' + \tfrac{1}{2}) - 1.54(v' + \tfrac{1}{2})^2 - 580.75(v'' + \tfrac{1}{2}) + 1.831(v'' + \tfrac{1}{2})^2.$$

$$Ge^{72}S{:}\nu = 32889.5 + 376.56(v' + \tfrac{1}{2}) - 1.527(v' + \tfrac{1}{2})^2 - 578.21(v'' + \tfrac{1}{2})^2 + 1.815(v'' + \tfrac{1}{2})^2.$$

$$Ge^{76}S{:}\nu = 32889.5 + 373.489(v' + \tfrac{1}{2}) - 1.502(v' + \tfrac{1}{2})^2 - 573.51(v'' + \tfrac{1}{2}) + 1.786(v'' + \tfrac{1}{2})^2.$$

No evidence of bands due to molecules containing the sulfur isotopes, S^{33} and S^{34}, was obtained but as these two together are present in an abundance of

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[12] Loomis, Bull. Nat. Res. Council **11,** 260 (1926); Birge, Trans. Far. Soc. **25,** 718 (1929), Phys. Rev. **35,** 133 (1930).

TABLE I. *Wave-lengths in air and wave-numbers in vacuum for the* 3040.5 *A band system of GeS*

		Ge^{76}S				Ge^{74}S				Ge^{72}S				Ge^{70}S			
v'	v''	I	λ	ν(obs.)	ν(calc.)	I	λ	ν(obs.)	ν(calc.)	I	λ	ν(obs.)	ν(calc.)	I	λ	ν(obs.)	ν(calc.)
1	6	—	—	—	—	000	3356.32	29786.0	29782.0	00	3358.33	29768.2	29769.3	—	—	—	—
0	5	00	3334.81	29978.3	29975.3	1	3336.34	29964.3	29964.2	0	3337.65	29952.6	29952.2	0	3339.10	29939.6	29939.5
1	5	—	—	—	—	0	3295.45	30336.2	30336.1	—	—	—	—	—	—	—	—
0	4	0	3274.42	30531.0	30531.3	3	3275.34	30522.4	30522.0	1	3276.33	30513.2	30512.3	1	3277.48	30502.5	30501.9
3	6	—	—	—	—	00	3275.96	30516.6	30516.8	—	—	—	—	0	3278.61	30492.0	30496.7
2	5	—	—	—	—	0	3255.98	30703.9	30705.1	—	—	—	—	—	—	—	—
0	3	0	3215.54	31090.0	31090.5	4	3216.13	31084.3	31083.4	2	3216.91	31076.8	31075.9	1	3217.73	31068.9	31068.9
3	5	Bl	3216.91	31076.8	31078.1	Bl	3217.73	31068.9	31071.0	0	3218.44	31062.0	31063.6	1	3219.37	31053.0	31055.6
2	4	—	—	—	—	1	3197.69	31263.6	31262.9	—	—	—	—	—	—	—	—
1	3	—	—	—	—	2	3178.29	31454.4	31455.4	—	—	—	—	0	3179.29	31444.5	31443.2
0	2	0	3158.34	31653.1	31653.3	3	3158.78	31648.7	31648.4	0	3159.16	31644.9	31643.2	2	3159.75	31638.9	31637.8
6	7	Bl	3219.37	31053.0	31052.9	1	3219.89	31048.0	31045.8	1	3221.14	31036.0	31038.3	1	3222.14	31026.3	31030.2
4	5	—	—	—	—	1	3180.10	31436.5	31433.9	0	3181.05	31427.1	31427.9	0	3182.19	31415.8	31421.5
3	4	—	—	—	—	0	3160.35	31632.9	31628.8	0	3161.26	31623.8	31623.6	—	—	—	—
2	3	—	—	—	—	1	3141.28	31825.0	31824.3	—	—	—	—	—	—	—	—
1	2	0	3121.75	32024.1	32023.7	2	3122.12	32020.3	32020.4	2	3123.57	32015.7	32016.7	1	3113.10	32010.2	32012.9
0	1	—	—	—	—	6	3103.02	32217.4	32217.0	1	3103.40	32213.4	32214.2	2	3103.73	32210.0	32211.2
6	6	—	—	—	—	0	3163.97	31596.7	31596.4	—	—	—	—	0	3165.24	31584.1	31585.3
4	4	—	—	—	—	0	3134.70	31991.8	31991.7	—	—	—	—	—	—	—	—
3	3	NR	3105.36	32193.1	32192.9	1	3105.36	32193.1	32190.2	—	—	—	—	—	—	—	—
2	2	NR	3086.28	32392.1	32391.2	1	3086.28	32392.1	32389.3	—	—	—	—	—	—	—	—
1	1	NR	3067.46	32590.8	32590.1	8	3067.46	32590.8	32589.0	NR	3067.46	32590.8	32587.7	4	3068.13	32583.7	32586.3
0	0	NR	3048.91	32789.1	32789.6	5	3048.91	32789.1	32789.2	NR	3048.91	32788.1	32788.8	NR	3048.91	32789.1	32788.3
5	4	NR	3089.77	32355.5	32353.7	1	3089.77	32355.5	32351.5	—	—	—	—	—	—	—	—
4	3	NR	3070.77	32555.7	32554.4	1	3070.77	32555.7	32553.1	—	—	—	—	—	—	—	—
3	2	NR	3051.79	32758.2	32755.7	2	3051.79	32758.2	32755.2	NR	3051.79	32758.2	32754.6	NR	3051.79	32758.2	32753.9
2	1	NR	3033.05	32960.5	32957.6	NR	3033.05	32960.5	32957.9	NR	3033.05	32960.5	32958.1	8	3033.05	32960.5	32958.4
1	0	2	3015.05	33157.3	33160.1	NR	3014.41	33164.4	33161.1	NR	3015.05	33164.4	33162.3	7	3015.05	33164.4	33163.4
5	3	NR	3037.77	32909.3	32912.9	0	3037.77	32909.3	32912.9	NR	3037.77	32909.3	32912.9	NR	3037.77	32909.3	32912.9
4	2	NR	3018.47	33119.8	33117.2	NR	3018.47	33119.8	33118.1	NR	3018.47	33119.8	33118.9	4	3018.47	33119.8	33119.8
3	1	0	3000.33	33320.0	33322.1	NR	2999.83	33325.5	33323.8	3	2999.83	33325.5	33325.5	1	2999.64	33327.6	33327.4
2	0	NR	2982.07	33524.0	33527.6	2	2982.07	33524.0	33530.1	NR	2980.98	33536.3	33532.8	7	2980.98	33536.3	33535.5

8	5	NR	3042.92	32853.7	32855.4	0	3042.92	32853.7	32855.1	NR	3042.92	32853.7	32854.8	NR	3042.92	32853.7	32854.3
7	4	NR	3024.22	33056.8	33061.6	NR	3024.22	33056.8	33062.1	NR	3024.22	33056.8	33062.7	00	3024.22	33056.8	33063.2
6	3	—	—	—	—	NR	3004.45	33274.3	33269.8	NR	3004.45	33274.3	33271.2	2	3004.45	33274.3	33272.6
5	2	NR	2986.59	33473.3	33475.7	1	2986.59	33473.3	33477.9	1	2986.07	33479.1	33480.2	3	2985.55	33485.0	33482.6
3	0	—	—	—	—	7	2949.34	33896.0	33896.0	7	2948.91	33900.9	33900.2	7	2948.47	33906.0	33904.4
8	4	NR	2992.00	33412.8	33411.1	2	2992.00	33412.8	33412.9	2	2992.00	33412.8	33414.8	NR	2992.00	33412.8	33416.7
7	3	—	—	—	—	NR	2972.81	33628.4	33623.5	NR	2972.81	33628.4	33626.3	0	2972.81	33628.4	33629.3
6	2	—	—	—	—	1	2954.60	33835.7	33834.8	NR	2954.17	33840.6	33838.5	1	2954.17	33840.6	33842.4
5	1	—	—	—	—	2	2936.46	34044.7	34046.5	1	2936.06	34049.3	34051.2	2	2935.23	34059.0	34056.1
4	0	00	2918.42	34255.1	34253.5	6	2917.89	34261.4	34258.9	6	2917.52	34265.7	34264.5	4	2916.90	34273.0	34270.3
11	6	—	—	—	—	1	2999.44	33329.8	33335.0	—	—	—	—	—	—	—	—
9	4	—	—	—	—	0	2961.11	33761.3	33760.7	—	—	—	—	—	—	—	—
8	3	—	—	—	—	—	—	—	—	—	—	—	—	00	2941.33	33988.3	33982.8
7	2	NR	2924.48	34184.2	34183.6	1	2924.48	34184.2	34188.5	0	2923.88	34191.2	34193.7	1	2922.62	34205.9	34199.0
6	1	1	2906.56	34394.9	34397.5	2	2905.67	34405.4	34403.4	1	2905.20	34411.0	34409.4	1	2904.45	34419.9	34415.8
5	0	1	2888.26	34612.8	34612.0	7	2887.60	34620.7	34618.7	5	2887.04	34627.4	34625.8	3	2886.40	34635.1	34633.2
13	7	—	—	—	—	1	2988.01	33457.4	33458.7	—	—	—	—	1	2987.36	33464.6	33462.0
11	6	—	—	—	—	00	2950.53	33882.3	33889.2	—	—	—	—	Bl	2949.34	33896.0	33896.5
10	4	—	—	—	—	00	2931.00	34108.1	34105.4	—	—	—	—	—	—	—	—
8	2	—	—	—	—	2	2894.31	34540.5	34539.3	—	—	—	—	1	2892.97	34556.5	34552.6
7	1	—	—	—	—	2	2876.10	34759.1	34757.1	2	2875.39	34767.7	34764.6	1	2874.64	34776.8	34772.4
6	0	1	2858.76	34970.0	34967.5	4	2858.15	34977.4	34975.2	3	2857.39	34986.7	34984.1	3	2856.68	34995.4	34992.9
14	7	—	—	—	—	—	—	—	—	—	—	—	—	1	2957.62	33801.1	33797.1
13	6	—	—	—	—	00	2939.44	34010.2	34009.3	—	—	—	—	—	—	—	—
12	5	—	—	—	—	1	2920.95	34225.4	34227.9	1	2920.26	34233.5	34232.7	1	2919.27	34245.2	34237.8
10	3	—	—	—	—	NR?	2883.17	34673.9	34666.8	NR	2883.17	34673.9	34673.6	1	2883.17	34673.9	34680.7
9	2	0	2866.74	34872.6	34879.6	1	2865.27	34890.5	34887.1	1	2864.68	34897.7	34894.9	1	2864.45	34900.5	34903.1
8	1	0	2848.98	34102.3	34099.5	1	2847.42	34109.2	34107.9	2	2846.62	34119.1	35116.7	1	2845.90	35128.0	35126.0
7	0	—	—	—	—	3	2829.51	34331.4	34329.3	1	2828.86	35339.5	35339.2	3	2827.97	35350.7	35349.5
14	6	—	—	—	—	0	2910.90	34343.6	34341.9	—	—	—	—	—	—	—	—
13	5	NR	2892.97	34556.5	34557.7	Bl	2892.97	34556.5	34563.5	1	2892.01	34567.9	34569.6	—	—	—	—
12	4	NR	2874.64	34776.8	34778.9	1	2874.64	34776.8	34785.7	—	—	—	—	0	2872.52	34802.4	34800.2
11	3	—	—	—	—	1	2855.74	35007.0	35008.4	1	2855.08	35015.0	35016.5	1	2854.10	34027.0	35025.1
10	2	—	—	—	—	—	—	—	—	NR	2836.51	35244.2	35240.9	1	2836.51	35244.2	35250.5
9	1	—	—	—	—	2	2819.43	35457.8	35455.7	1	2818.68	35467.2	35465.8	1	2817.80	35478.2	35476.5
8	0	—	—	—	—	2	2801.84	35680.3	35680.1	1	2800.93	35691.9	35691.4	1	2800.01	35703.7	35703.1

TABLE I. (*Continued*).

		Ge^{76}S				Ge^{74}S				Ge^{72}S				Ge^{70}S			
v'	v''	I	λ	ν(obs.)	ν(calc.)	I	λ	ν(obs.)	ν(calc.)	I	λ	ν(obs.)	ν(calc.)	I	λ	ν(obs.)	ν(calc.)
15	6	—	—	—	—	Bl	2883.17	34673.9	34671.5	—	—	—	—	—	—	—	—
14	5	—	—	—	—	Bl	2864.68	34897.7	34896.1	Bl	2864.45	34900.5	34903.4	1	2863.59	34911.0	34911.0
13	4	—	—	—	—	Bl	2846.62	35119.1	35121.3	Bl	2845.90	34128.0	35129.6	—	—	—	—
12	3	Bl	2828.86	35339.5	35338.1	Bl	2827.97	35350.7	35347.1	—	—	—	—	1	2826.58	35368.0	35366.3
11	2	—	—	—	—	1	2810.33	35572.6	35573.4	1	2809.38	35584.6	35583.9	0	2508.71	35593.1	35594.8
10	1	0	2793.33	35789.0	35789.4	1	2792.41	35800.8	35800.4	1	2791.54	35812.0	35811.8	0	2790.65	35823.4	35823.9
9	0	Bl	2775.78	36015.3	36015.9	1	2774.82	36027.8	36027.8	1	2773.88	36040.0	36040.4	0	2772.81	36053.9	36053.6
16	6	—	—	—	—	Bl	2856.68	34995.4	34998.0	Bl	2855.74	35007.0	35005.4	Bl	2855.08	35015.0	35013.2
15	5	—	—	—	—	1	2838.33	35221.6	35225.7	—	—	—	—	Bl	2836.51	35244.2	35243.0
14	4	—	—	—	—	Bl	2819.43	35457.8	35453.9	Bl	2818.68	35467.2	35463.4	Bl	2817.80	35478.2	35473.5
13	3	—	—	—	—	Bl	2801.84	35680.3	35682.7	Bl	2800.93	35691.9	35693.3	Bl	2800.01	35703.7	35704.5
12	2	00	2785.08	35895.0	35900.9	1	2783.90	35910.3	35912.1	1	2782.84	35924.0	35923.8	—	—	—	—
11	1	0	2766.74	36133.0	36129.8	0	2765.83	36144.9	36142.0	0	2764.99	36155.8	36154.8	0	2764.08	36167.8	36168.2
10	0	00	2749.90	36354.2	36359.3	0	2748.67	36370.4	36372.5	0	2747.42	36387.0	36386.5	0	2746.46	36399.8	36401.0
19	8	—	—	—	—	1	2867.74	34860.5	34861.9	1	2867.29	34865.9	34868.3	—	—	—	—
18	7	—	—	—	—	1	2849.06	35089.0	35091.4	—	—	—	—	—	—	—	—
17	6	NR	2830.98	35313.1	35313.4	0	2830.98	35313.1	35321.5	—	—	—	—	—	—	—	—
16	5	—	—	—	—	0	2812.23	35548.5	35552.2	—	—	—	—	Bl	2810.33	35572.6	35572.0
14	3	—	—	—	—	0	2775.78	36015.3	36015.3	Bl	2774.82	36027.8	36027.1	Bl	2773.88	36040.0	36039.6
13	2	00	2759.14	36232.5	36235.4	0	2758.20	36244.8	36247.7	—	—	—	—	00	2756.08	36272.7	36274.2
12	1	00	2741.27	36468.5	36467.3	0	2740.39	36480.4	36480.7	00	2739.49	36492.3	36494.7	0	2738.41	36506.7	36509.5
11	0	—	—	—	—	00	2723.04	36712.8	36714.2	00	2721.90	36728.2	36729.4	00	2720.74	36743.8	36745.3
20	8	NR	2842.50	35170.0	35169.2	0	2842.50	35170.0	35176.3	—	—	—	—	2	2840.67	34192.6	35191.5
19	7	—	—	—	—	1	2823.45	35407.3	35408.9	1	2822.76	35415.9	35417.4	0	2822.28	35422.0	35426.4
18	6	0	2805.70	35631.3	35632.8	1	2804.56	35645.8	35642.0	1	2804.14	35651.1	35651.7	1	2803.66	35657.2	35661.8
16	4	—	—	—	—	0	2769.11	36102.1	36110.0	1	2768.00	36116.5	36121.9	Bl	2766.74	36133.0	36134.4
15	3	—	—	—	—	0	2750.98	36340.0	36344.9	Bl	2749.90	36354.2	36357.9	Bl	2748.67	36370.4	36371.6
14	2	—	—	—	—	00	2733.38	36573.9	36580.3	—	—	—	—	00	2731.04	36605.3	36609.3
13	1	—	—	—	—	0	2715.62	36813.1	36816.3	—	—	—	—	00	2713.22	36845.7	36847.7
20	7	—	—	—	—	NR	2797.96	35729.8	35723.3	0	2797.96	35729.8	35732.9	—	—	—	—
19	6	—	—	—	—	—	—	—	—	—	—	—	—	00	2778.58	35979.0	35981.5
18	5	—	—	—	—	—	—	—	—	0	2761.03	36207.7	36208.1	0	2759.62	36226.2	36220.6
17	4	NR	2744.75	36422.4	36421.1	00	2744.75	36422.4	36433.5	—	—	—	—	Bl	2741.27	36468.5	36460.3
16	3	—	—	—	—	00	2726.37	36668.0	36671.4	00	2725.65	36677.6	36685.6	Bl	2723.04	36712.8	36700.5
15	2	—	—	—	—	0	2708.81	36905.6	36909.9	—	—	—	—	—	—	—	—
20	6	—	—	—	—	—	—	—	—	—	—	—	—	00	2753.66	36304.6	36298.1

Bl = Blend (with band of different v' v'').
NR = Not resolved (superposition of isotope heads).

but 3 percent as compared to 97 percent for S^{32},[13] higher vapor pressures or longer vapor paths would again be required. The most favorable combination to look for would be $Ge^{74}S^{34}$, whose bands would appear on the high frequency side of the strong bands of the v'' progression ($v'=0$), where there is practically no other absorption. The relatively large values of $\rho=0.9793$ and $\rho^2=0.9589$ would bring these bands well away from even the heaviest of the weak Ge isotopes, 77.

The proper assignment of vibrational quantum numbers to the bands of this system was rendered simple by the existence of the isotope effect, especially since the three chief isotopes have comparable intensities. Theoretically the separation is zero at the origin of the system (v', $v''=-1/2$, $-1/2$) and increases almost proportionately with the distance from this point. The presence of the fairly intense v'' progression ($v'=0$) with six members at the long wave-length end of the system, where overlapping of the vibrational bands was least and in which the isotopes were clearly resolved for all the bands except v', $v''=0$, 0, led at once to the correct assignment. The agreement between the calculated and observed isotope separations for this group is shown in Table II.

TABLE II. *Isotope separations in* cm^{-1} *for the* v'' *progression* ($v'=0$).

v'	v''	$Ge^{74}S-Ge^{76}S$		$Ge^{74}S-Ge^{72}S$		$Ge^{74}S-Ge^{70}S$	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
0	0	−0.4	—	0.4	—	0.9	—
0	1	−2.6	—	2.8	4.0	5.8	7.4
0	2	−4.9	−4.4	5.2	3.8	10.6	9.8
0	3	−7.1	−5.7	7.5	7.5	15.4	15.4
0	4	−9.3	−8.6	9.7	9.2	20.1	19.9
0	5	−11.3	−14.0	12.0	11.7	24.7	24.7

The intensities listed in Table I are visual estimates, averaged from observations on several plates. These estimates are subject to three sources of error: (1) overlapping of bands, (2) blending of isotope heads near the origin of the system and (3) presence of continuous spectrum. The general distribution of intensities, as shown in Table III, is roughly that to be expected on the Franck-Condon theory[14] for transitions where there is a relatively large change in the vibrational frequency in passing from the normal to the excited state, due account being taken of the Boltzmann distribution which governs the proportion of molecules in the several vibrational levels of the initial state. A definite anomaly to be noted, however, is the failure of the 4, 1 band to appear, although the neighboring bands (see Table III) are all strongly developed. Careful search for this band was made on all the plates taken but with no success.

It was of some interest to see how the abundance ratios of the several isotopes, as determined by their intensities in those bands in which they were clearly resolved, agreed with the mass spectrograph results of Aston.[9]

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[13] Aston, Proc. Roy. Soc. **115**, 504 (1927).

[14] Mulliken, Rev. Mod. Phys. **2**, 79–83 (1930). See discussion of his type IV.

In making such an estimate, account must be taken of the fact that on the high frequency side of the system origin the order of the isotopes (counting in the direction of the degradation of the bands, i.e., toward low frequencies) is 70, 72, 74 and 76, while on the low frequency side of the origin, the order is reversed −76, 74, 72 and 70. Hence the error in the intensity estimate due to the overlapping of the bands is in different directions on the two sides of the origin. By averaging the isotope intensities for 30 different bands (30 different values of v', v''), equally distributed on both sides of the origin, the following relative intensities were obtained, comparison being made with rounded figures from Aston's data:

TABLE III. *Intensity distribution of absorption bands of GeS in system I.*

v' \ v''	0	1	2	3	4	5	6	7	8
0	5	6	3	4	3	1			
1	7	8	2	2		0	000		
2	7	8	1	1	1	0			
3	7	3	2	1	0	1	00		
4	6		4	1	0	1			
5	5	2	3	0	1				
6	3	2	1	2					
7	3	2	1	0	00		0	1	
8	2	2	2	00	2	0			
9	1	2	1		0				
10	0	1	1	1	00				
11	00	0	1	1		00	1		
12		0	1	1	1	1			
13		0	0	1	1	1	00	1	
14			00	0	1	1	0	1	
15			0	0		1	0		
16				00	0	0	0		
17					00		)		
18						0	1	1	
19							00	1	1
20							00	0	1

	76	74	72	70
From intensity data	11	100	68	61
From Aston's data	17	100	72	56

The agreement with Aston's results is reasonably good under the circumstances.

Table IV lists the band heads which have been assigned to the second system of absorption in GeS, the calculated values being derived from the frequency equation:

$$\nu = 38890.0 + 310.4(v' + \tfrac{1}{2}) - 1.35(v' + \tfrac{1}{2})^2 - 575.8(v'' + \tfrac{1}{2}) + 1.8(v'' + \tfrac{1}{2})^2$$

Because of the faintness of these bands and the lack of contrast, no structure could be observed at the heads and hence no evidence of the isotope effect obtained. It is clear, however, from the identity of the vibrational frequency of the normal state with that for the first system (see $Ge^{74}S$), that these bands are also due to GeS. Further, the vibrational frequency of the excited state is of the same order of magnitude as in the first system, 309.6 cm^{-1} as com-

TABLE IV. *Wave-lengths in air and wave-numbers in vacuum for the 2579.4A band system of GeS.*

v'	v''	I	λ	ν (obs.)	ν (calc.)
1	5	0	2758.6	36239	36240
0	4	00	2739.4	36493	36490
0	3	0	2697.5	37060	37052
3	5	00	2713.2	36846	36847
2	4	00	2694.3	37104	37103
1	3	2	2675.5	37365	37359
0	2	3	2657.4	37619	37617
4	5	0	2691.6	37142	37147
2	3	3	2653.8	37670	37664
1	2	2	2635.8	37927	37924
0	1	2	2618.0	38186	38185
3	3	2	2632.8	37971	37967
2	2	3	2615.0	38230	38229
1	1	2	2597.0	38494	38493
4	3	00	2612.2	38270	38266
3	2	3	2594.5	38532	38532
2	1	1	2576.7	38797	38798
1	0	0	2559.0	39066	39065
4	2	2	2574.5	38831	38831
3	1	1	2556.7	39101	39100
2	0	1	2539.3	39370	39370
5	2	1	2554.9	39129	39128
4	1	1	2537.4	39399	39400
3	0	00	2520.3	39666	39672
6	2	2	2535.9	39422	39422
5	1	1	2518.2	39699	39697
4	0	00	2501.6	39963	39972
6	1	1	2499.7	39993	39991
10	4	00	2534.2	39449	39446
7	1	0	2481.8	40281	40282
6	0	Bl	2464.3	40568	40563
8	1	0	2464.3	40568	40571
7	0	Bl	2446.9	40856	40855
10	2	Bl	2464.3	40568	40572
9	1	0	2446.9	40856	40857
8	0	Bl	2429.9	41141	41143
11	2	Bl	2446.9	40856	40853
10	1	0	2429.9	41141	41141
9	0	Bl	2413.3	41424	41427
11	1	0	2413.3	41424	41421

pared with 374.99 cm^{-1}. The intensity distribution, Table V, is generally similar, although no reliance can be placed on the individual intensity estimates because of the strong overlying continuous absorption.

TABLE V. *Intensity distribution of absorption bands of GeS in system II.*

v' \ v''	0	1	2	3	4	5
0		2	3	0	00	
1	0	2	2	2		0
2	1	1	3	3	00	
3	00	1	3	2		00
4	00	1	2	00		0
5		1	1			
6	Bl	1	2			
7	Bl	0				
8	Bl	0				
9	Bl	0				
10		0	Bl		00	
11		0	Bl			

ENERGY OF DISSOCIATION

Owing to the relatively small values of "x" in the vibrational equations of the normal and excited states of GeS in both electronic transitions, a direct extrapolation to obtain the energies of dissociation is necessarily a long one and hence quite unreliable.[15] If, however, both the normal and excited states behave similarly in the course of the extrapolation, it should be possible to deduce a reasonably accurate value for the excitation energy of the products of dissociation, since that depends on the difference between D' and D''. Table VI lists the values of $h\nu_0$, D and E for the two electronic transitions, in units of electron-volts. E is the excitation energy of the atoms after dissociation from the excited state on the assumption that dissociation from the normal state results in two normal atoms, and is defined by the relation:

$$E = h\nu_0 + D_0' - D_0'',$$

where $h\nu_0$ is the energy of the electronic transition.

TABLE VI. *Heats of dissociation and excitation energy for GeS.*

	$h\nu_0$	D'	D''	E
Transition I	4.05	2.84	5.65	1.24
Transition II	4.78	2.17	5.65	1.30

The values of E, 1.24 and 1.30 are sufficiently close to indicate that the products of dissociation from transitions I and II may be identical.[16] This energy may exist as atomic excitation energy either of the germanium or of the sulfur, or may be divided between the two. The basic configurations of Ge, (s^2p^2), and of S, (s^2p^4), lead to a similar set of levels for both atoms, *viz.*, ${}^3P_{0,1,2}$ ${}^1D_2$ and ${}^1S_0$, of which the ${}^1D_2$ and ${}^1S_0$ levels are metastable. The ${}^3P$ in sulfur is inverted. Energy values for these levels have been determined by

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[15] Birge, Trans. Far. Soc. **25**, 707 (1929).

[16] In the preliminary report, Ref. 2, E was given as much higher, because of an incomplete analysis of the isotope effect and an incomplete assignment of the bands, which led to a larger value for the anharmonic factor for the normal state than the final one now reported.

Gartlein[17] for Ge and by Hopfield[18] for the ^3P of S, while McLennan and Crawford[19] have suggested values for the $^1D_2$ and $^1S_0$ of S by extrapolation methods which are not very reliable.[20] These results are listed in Table VII.

TABLE VII.

	$^3P_0$	$^3P_1$	$^3P_2$	$^1D_2$	$^1S_0$
S I	0.071	0.049	0	1.18	3.17
Ge I	0	0.069	0.174	0.88	2.02

The average value of E, 1.27 volts, agrees best with the $^1D_2$ of sulfur with the possibility remaining that the germanium atom may be simultaneously excited up to one of the higher levels of its ^3P multiplet.

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[17] Gartlein, Phys. Rev. **31,** 782 (1928).
[18] Hopfield, Nature **112,** 437, 790 (1923).
[19] McLennan and Crawford, Nature **124,** 874 (1929).
[20] Frerichs, Phys. Rev. **36,** 406 (1930).