

Vibrational Analysis of the Emission Bands of Germanous Oxide

R. WILLIAM SHAW, *Department of Physics, Cornell University, Ithaca, N. Y.*

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Twenty-one bands degraded to the red and associated with GeO have been observed in the region $\lambda 2500$ to $\lambda 2900$. The wave numbers of the band heads are expressed by the equation

$$\nu = 37763.7 + 649.4(v' + \frac{1}{2}) - 3.81(v' + \frac{1}{2})^2 - 985.0(v'' + \frac{1}{2}) + 4.36(v'' + \frac{1}{2})^2.$$

Attention is called to the regular variation of the dissociation energies for the normal states of the monoxides and monosulphides of the fourth periodic column. It is shown that the electronic transition ${}^1\Pi \rightarrow {}^1\Sigma$ for the GeO system seems to agree best with the available evidence. It is found that the quantity $\omega_e'' r_e^2 \cdot 10^{-16}$ cm is very nearly constant for the fourth column monoxides. From this it is concluded that $1.65 \pm 0.06 \text{ \AA}$ is a good value of r_e for GeO. The dense structure due to overlapping bands and isotope effect makes rotational analysis extremely difficult.

ABSORPTION bands arising from black germanous oxide were observed by Shapiro¹ in certain experiments on the isotopes of germanium. These bands, which are degraded towards the longer wave-lengths, lie in the spectral region $\lambda 2500$ to $\lambda 2900$. Because of the tendency of hot GeO vapor to attack the quartz windows of the absorption tube with the formation of a non-transparent glaze, it was impossible to obtain spectrograms of sufficient intensity for precise measurement.

Somewhat later a preliminary report was made by the author² concerning emission bands, lying in the same spectral region and degraded toward the red, which were observed in a flaming arc charged with the dioxide of germanium. Similar results in experiment and analysis were obtained by W. F. G. Ferguson³ of New York University. The present paper is concerned with the details of the observations on the emission bands.

EXPERIMENTAL PART

The flaming arc used for the excitation of the emission bands consisted of a vertical positive electrode of graphite, cored with germanium dioxide, and a horizontal negative electrode also of graphite. The horizontal electrode was ground to a long point by means of a pencil sharpener. This pointed electrode was found advantageous in causing the arc (8–10 amp.) to play on the oxide in the positive electrode. When the pointed

electrode was drawn well away from the vertical one there resulted a high flame in which the GeO bands were well developed—an essential result since very limited quantities of the oxide were available. Light from only the higher portions of the flame was used. The spectrograms were obtained by means of a Hilger E I Littrow quartz spectrograph with an iron arc for the standard comparison. Inasmuch as the rotational structure of the GeO bands is extremely dense due to overlapping and isotope effect it seemed inadvisable to attempt a rotational analysis. Hence the measurements were confined to the *R* heads of the bands. Measurements were made both by comparator and by microphotometer tracings.

TABLE I. Band heads in the GeO system. Last column is the difference between observed and calculated wave numbers.

v'	v''	ν (VAC)	INTENSITY	O - C
7	1	40954.9	0	+2.6
5	0	40729.2	2	+0.3
4	0	40117.9	2	+0.3
5	1	39752.1	2	-0.5
3	0	39498.9	5	+0.2
2	0	38872.0	8	-0.4
1	0	38237.4	5	-0.5
2	1	37897.0	2	-0.1
0	0	37596.1	4	0.0
1	1	37261.3	10	-0.3
2	2	(36928.6)*		
0	1	36619.0	8	-0.8
1	2	(36294.1)*		
2	3	35968.7	2	-1.1
0	2	35651.5	10	-0.8
1	3	(35335.3)*		
2	4	35018.2	0	-1.0
0	3	34692.6	10	-0.9
1	4	34384.8	4 <i>d</i>	+0.1
0	4	33742.9	4 <i>d</i>	0.0
1	5	33443.4	6 <i>d</i>	-0.5

* Present but with head obscured by atomic line.

¹ Shapiro, Gibbs and Laubengayer, Phys. Rev. **40**, 354 (1932).

² R. W. Shaw, Phys. Rev. **43**, 104 (1933).

³ Private communication.

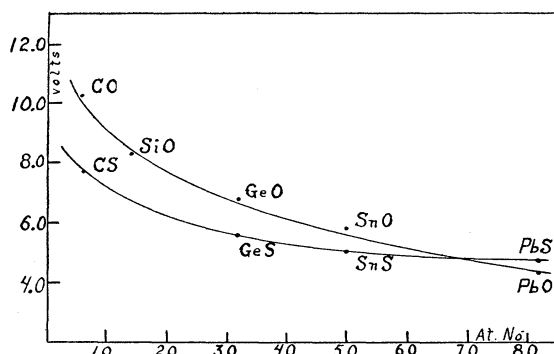


FIG. 1. Heats of dissociation of the diatomic oxides and sulphides of the fourth periodic column.

The latter were especially helpful in the cases of the fainter bands.

OBSERVATIONS AND DISCUSSION

Twenty-one bands were observed of which three heads were obscured by atomic germanium lines. The wave numbers, vibrational assignments and intensities are given in Table I. Analysis of these data leads to the following vibrational equation for the *R* heads of the bands.

$$\nu = 37763.7 + 649.4(v' + \frac{1}{2}) - 3.81(v' + \frac{1}{2})^2 - 985.0(v'' + \frac{1}{2}) + 4.36(v'' + \frac{1}{2})^2.$$

The column of observed minus calculated wave numbers (O-C) in Table I shows that this equation expresses the observations satisfactorily.

The intensities are eye estimates and are perhaps none too reliable because of excessive overlapping of the bands. However the intensity distribution indicates a wide Condon curve in keeping with similar observations of the typical

TABLE II. Heats of dissociation.

MOLECULE	AT. NO.	D_e'' (VOLTS)	SOURCE
CO	6+8	10.3	Kaplan ¹
SiO	14	8.4	Saper ²
GeO	32	6.8	Present work
SnO	50	5.8	Connelly ³
PbO	82	4.3	Shawhan-Morgan ⁴
CS	6+16	7.7	Crawford-Shurcliff ⁵
GeS	32	5.6	Shapiro ⁶
SnS	50	5.0	Shawhan ⁷
PbS	82	4.7	Rochester-Howell ⁸

¹ Kaplan, Phys. Rev. **35**, 957 (1930).

² Saper, Phys. Rev. **42**, 498 (1932).

³ Connelly, Proc. Phys. Soc. London **46**, 571 (1934).

⁴ Shawhan and Morgan, Phys. Rev. **47**, 377 (1935).

⁵ Crawford and Shurcliff, Phys. Rev. **45**, 860 (1934).

⁶ Shapiro, Phys. Rev. **40**, 354 (1932).

⁷ Shawhan, Phys. Rev. **48**, 521 (1935).

⁸ Rochester and Howell, Proc. Roy. Soc. **A148**, 157 (1935).

TABLE III. Internuclear distances.

MOLECULE	ω_e''	$r_e'' \cdot 10^{-8}$ CM	$\omega_e''/r_e''^2 \cdot 10^{-16}$ CM
CO	2169.3	1.13	2770.2
SiO	1242.0	1.50	2794.5
GeO	985.0	(1.69)	
SnO	821.9	(1.82)	
PbO	722.3	1.92	2662.4
		Mean	2742.3

and *B* sub-group monoxides of the fourth periodic column and with the observed harmonic constants, $\omega_e'' > \omega_e'$.

The coincidence of wave-lengths and the direction of degradation of the present bands with those observed by Shapiro in the absorption spectrum of germanous oxide indicate clearly that the emission bands are due to the monoxide and, moreover, that the observed lower state is the normal state of the molecule. That it is the normal state which is observed is demonstrated further by the heats of dissociation. While it is generally unsatisfactory to use the Birge-Sponer⁴ extrapolation of vibrational levels for heats of dissociation in cases with few observed vibrational states, values of the correct order of magnitude may often be obtained. Values of dissociation energies for the normal states of the typical and type *B* group monoxides of the fourth periodic column are given in Table II. These values, when plotted against atomic number as in Fig. 1, give a remarkably smooth curve. Similar data⁵ for the corresponding monosulphides are included for the sake of comparison.

The normal state of GeO is then a $^1\Sigma$ state since the molecule has an even number of electrons and sub-shells are all closed. From analogy with similar molecules the normal state should be considered as arising from Ge (3P) and O (3P) states. When allowance is made for the fact that linear extrapolations of vibrational levels for heats of dissociation usually give values which are too large, it appears that the GeO molecule dissociates in the excited state with the products

⁴ Birge and Sponer, Phys. Rev. **28**, 259 (1926).

⁵ All the data included in Table II have been computed on the same basis. The recent value, 8.41 volts for CO by Brons, Nature **136**, 796 (1935) and others, does not agree well with the data given unless the value for SiO be changed to 7.8 volts, which is a more probable value for SiO at least as compared with its isoelectronic molecules. The CO value has been arrived at by a detailed study of perturbations in the various CO band systems. These studies are difficult or impossible in the other less complete molecular systems.

Ge (1D) and O (3P). The electronic transitions $^1\Pi \rightarrow ^1\Sigma$ and $^1\Sigma \rightarrow ^1\Sigma$, are therefore possibilities. A comparison of the values of ν_e of the fourth column monoxides shows that the $^1\Pi \rightarrow ^1\Sigma$ transition is the more likely. The observed band system of GeO is then similar to the fourth positive system of CO.

It is interesting to note that the quantity, $\omega_e'' r_e^2 \cdot 10^{-16}$ cm, as evaluated from the data on CO, SiO and PbO, is very nearly a constant. The essential data, which are given in Table III, show that the deviations of individual values from the mean, 2742.3 cm, are less than three percent. This produces in the case of a calculated value of r_e for PbO a deviation of 0.02 unit or about one percent which is within usual experimental error in determinations of r_e . The corresponding calculated values of r_e for GeO and SnO are 1.69Å and 1.82Å, respectively. The internuclear distance 1.69Å for GeO is in good agreement with the Ge—O distance, 1.65Å, observed by Warren⁶ in GeO₂.

⁶ B. E. Warren, Phys. Rev. **45**, 657 (1934).

It is well known⁷ that there is only a small change in the C—O distance⁸ in CO₂ (1.05—1.2Å depending on the physical state) and CO (1.13Å) and in SiO₂ (1.60Å) and SiO (1.50Å). Moreover, while the character of binding gradually changes as one goes downward in a periodic column as is shown by chemical properties, it has not varied so greatly at germanium that one would expect any pronounced peculiarities of internuclear distance. It seems reasonable, therefore, to consider 1.65 ± 0.06 Å as a good value of r_e for GeO pending the possibility of a rotational analysis of some of the individual bands.

The author wishes to express appreciation to Professor R. C. Gibbs for his interest in the problem and to Professor A. W. Laubengayer of the Chemistry Department for supplying the GeO₂ and for many helpful discussions on the properties of the oxides of the fourth periodic column.

⁷ R. Kronig, *Optical Basis of the Theory of Valency* (1935), p. 164.

⁸ H. A. Stuart, *Molekulstruktur* (1934), p. 77.

Helium I Like Spectra

HOWARD A. ROBINSON,* *University of Uppsala, Sweden*

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New measurements of the $1s^2\ ^1S_0 - 1s \cdot np\ ^1P_1$ series of the Helium I isoelectronic sequence for Be III, B IV and C V together with previously published data on He I, Li II, N VI and O VII are critically examined and values for the $1s^2\ ^1S_0$ terms for these spectra obtained. A slightly modified Hylleraas type extrapolation formula is used to calculate these same values. When relativity, spin, mass and mass polarization corrections are applied the agreement between observed and calculated values is very good for the heavier elements. A small discrepancy appears in the case of Li II.

IT has been possible for some time to calculate the ground states of the helium I like spectra by means of the formulae first given by Hylleraas.¹ The experimental data have, however, been meager due mainly to the inaccessibility of the region below 100Å where most of the necessary lines lie. A new 4° grazing incidence spectrograph designed by Professor Siegbahn² and built in the workshops of this institute has proved

unusually well suited to this region and it is now possible for the first time to measure lines below 100Å with an accuracy of a few thousandths of an angstrom. The spectra Li II, Be III, B IV, and C V are, in addition, useful as wave-length

TABLE I. *Data for Li II.*

n	2	3	4
λ (Å)	199,280 \pm 0.003	178,014 \pm 0.003	171,575 \pm 0.004
ν cm ⁻¹	501,807 \pm 5	561,754 \pm 10	582,835 \pm 14
T cm ⁻¹	108,263 \pm 10	48,330 \pm 3	27,247 \pm 4
$1s^2\ ^1S_0$	= 610,070 \pm 15	610,084 \pm 13	610,082 \pm 18
$1s^2\ ^1S_0$	= 610,079 \pm 25 cm ⁻¹	I.P. = 75,2593 \pm 0.0031 volts	

* Irving Langmuir Fellow, American Scandinavian Foundation. Now at Ohio State University.

¹ E. Hylleraas, Zeits. f. Physik **65**, 209 (1930).

² B. Edlén, Zeits. f. Physik **100**, 621 (1936).