TABLE II. *Experimental values of the isotope coefficient.*

v	ΔG	α	ΔG^i	α^i
$\frac{3}{2}$	2016.127	0.01723	1974.874	0.01617
$\frac{1}{2}$	2042.416	0.01738	2000.047	0.01620
$-\frac{1}{2}$	$2068.705=\omega_e$ $13.144=x\omega_e$		$2025.220=\omega_e{}^i$ $12.586=x^i\omega_e{}^i$	

$$\rho=(\mu/\mu^i)^{\frac{1}{2}}=\omega_c{}^i/\omega_e=0.97898\pm0.00002$$
$$\rho^2=x^i\omega_e{}^i/x\omega_e=0.9576$$
$$\rho^3=\alpha^i/\alpha=0.932(v=\tfrac{1}{2})$$
$$=0.938(v=\tfrac{3}{2})$$

can be done. The anharmonicity correction[15] can be found accurately, since the constants of the potential function are here well known. Using the function

$$U=5.622\times10^5\xi^2(1-2.653\xi+4.186\xi^2-4.607\xi^3+1.075\xi^4)\ \mathrm{cm}^{-1},$$

derived from the constants of the normal state, to obtain the correction $\delta_a{}^i-\delta_a$ in the equation

$$\omega_e{}^i/\omega_e=(\mu/\mu^i)^{\frac{1}{2}}(1+\delta_a{}^i-\delta_a),$$

we obtain $+4.5\times10^{-7}$. This is negligible compared to the probable error in ρ.

The correction for diagonal elements can also be evaluated, assuming pure precession and a value $L=1$ for the united atom. This gives $\delta_b{}^i-\delta_b=+7.2\times10^{-7}$, which is also negligible. The correction for L-uncoupling does not apply to vibrational constants ($\delta_c=0$ for both molecules). The last correction, due to interaction between states of equal Λ, cannot be found without a knowledge of the wave function, but it should be smaller than $2(B^i-B)/\nu=-6.2\times10^{-6}$. In this expression ν is the separation of the two $^2\Sigma$ states. This correction is again so small that it should have no influence on our experimental result. In view of these considerations, it thus appears that the accuracy of the comparison of isotope masses from band spectra of such molecules as CN is limited only by the accuracy of the wave-length measurements.

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[15] In comparing the formulas for γ_a and δ_a given by Van Vleck with the original equations of Dunham (Phys. Rev. **41**, 721 (1932)), we find that the term $41a_1$ in the expression for γ_a should read $14a_1$, and that an extra term $-1155a_1{}^4/8$ should be included in that for δ_a.

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Band Spectra of PbSe, SnSe and PbTe in Absorption

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(Received November 15, 1937)

A vibrational analysis has been made of band systems in the visible region due to PbSe, to SnSe and to PbTe. These bands were observed in absorption. In each case the band heads degrade toward the red. The vibrational coefficients ω_e and $\chi_e\omega_e$ for the ground state and for the first excited state are compared with those of the band systems in PbO, SnO, PbS and SnS. The expected trend in these vibrational constants is observed in each case, namely a decrease in ν_h, ω_e, and $\chi_e\omega_e$ with increasing number of electrons in the molecule.

THE similarity of band spectra produced by diatomic molecules formed by the combination of a given element with different elements in the same group in the periodic table is generally recognized. A number of investigations have been made of band spectra produced by the diatomic molecules, PbO,[1-4] SnO,[5-7] PbS[8] and SnS.[9-11] The band spectra due to PbSe, SnSe, PbTe and SnTe have been observed by Rochester and Howell[12] but no analyses seem to have been

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[1] Bloomenthal, Phys. Rev. **35**, 34 (1930). PbO.

[2] Christy and Bloomenthal, Phys. Rev. **35**, 46 (1930). PbO.

[3] Shawhan and Morgan, Phys. Rev. **47**, 377 (1935). PbO.

[4] Howell, Proc. Roy. Soc. **A153**, 683 (1935). PbO.

[5] Mahanti, Zeits. f. Physik **68**, 114 (1931). SnO.

[6] Connelly, Proc. Phys. Soc. **45**, 780 (1933). SnO.

[7] Loomis and Watson, Phys. Rev. **45**, 805 (1934). SnO.

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

[9] Buktow and Tschassowenny, Zeits. f. Physik **90**, 815 (1934). SnS.

[10] Rochester, Proc. Roy. Soc. **A150**, 608 (1935). SnS.

[11] Shawhan, Phys. Rev. **48**, 821 (1935). SnS.

[12] Rochester and Howell, Univ. of Durham Phil. Soc. Proc. **9**, 126 (1934).

made. Since oxygen, sulfur, selenium and tellurium belong to group VI of the periodic table, this investigation was undertaken to extend our knowledge of these sequences and to make possible a comparison of the vibrational coefficients of these bands.

EXPERIMENTAL

The three diatomic compounds, PbSe, PbTe and SnSe, were prepared from the purest chemicals available. Convenient masses of the two elements entering into one of these compounds were chosen in the ratio of their atomic weights, pulverized and then mixed together intimately in a closed glass tube. The tube was subsequently evacuated and heated until both constituents were melted and thoroughly mixed. The tube was then cooled and the conglomerate consisting of the compound and residues of the uncombined elements were introduced into a carbon tube which could be heated by means of a compressional carbon ring electric furnace with a current of about three hundred amperes at twenty-five volts. The carbon tube was about 50 cm long and 2 cm in diameter. It was heated to sufficiently high temperatures to produce the desired vapor density of the compounds. These temperatures ranged from 300° to 1500°C. The tube was open at both ends and nitrogen was passed into each end to prevent the oxidation of the metals. A five-hundred watt projection lamp was used as a source of continuous radiation. The light after passing along the axis of the tube and through the vapor to be examined was focused on the slit of the spectrograph.

The spectrograms were made with a concave grating in an eagle mounting with a radius of curvature of 10 ft. The grating was ruled with 14,400 lines to the inch. The observations were made in the first order where the dispersion was about 5.5A per millimeter. An iron comparison spectrum was superimposed on one edge of the absorption spectrum without displacing the photographic plate. The intensities were estimated visually taking into consideration the difference in the times of exposure. Average values of the intensities and wave-lengths from different plates were used.

PBSE

In the region between 4000 and 6000A three band systems have been observed and analyzed in the vapor of PbSe. They are designated as the A, B and C systems. One hundred and eighty-four bands have been assigned to these three systems. Bands evidently belonging to a D system and to an E system were also observed, but these systems were not sufficiently well developed to make it possible to analyze them. The presence of the isotopes of Se and Pb made the band heads diffuse and difficult to measure accurately. In the analysis band heads due to such impurities as Se_2, Pb_2, and PbO were identified and eliminated. The presence of other impurities gave rise to band heads which it was not possible either to identify or to analyze.

Table I gives the vibrational quantum numbers, the observed intensities, the observed wave numbers and the difference between the observed and the calculated wave numbers for these band systems. The B system was the most completely developed of the systems.

The following formulae represent the band heads within the error of observation. The intensities in each of the three systems form a well established Frank and Condon parabola.

$$A \text{ system},\ \nu_h = 18716.8 + 166.91u' - 0.144u'^2 - 277.78u'' + 0.452u''^2,$$

$$B \text{ system},\ \nu_h = 21005.8 + 184.82u' - 0.427u'^2 - 277.78u'' + 0.452u''^2,$$

$$C \text{ system},\ \nu_h = 23315.7 + 183.00u' - 0.250u'^2 - 277.78u'' + 0.452u''^2,$$

where $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$.

SNSE

Tin selenide presented more experimental difficulties than were found in lead selenide. It is probably less stable than lead selenide and band heads due to such impurities as Se_2, SnO and SeO were more prominent. The bands due to these impurities could, however, be identified and eliminated. Three imperfectly developed systems of bands have been observed and analyzed. They are similar to the three systems observed in lead selenide and are designated as the A, B and C systems. Table II gives the vibrational

TABLE I. *Bands in PbSe.*

I	v'	v''	$\nu_{\text{(Observed)}}$	$\nu_{\text{obs.}}-\nu_{\text{cal.}}$	I	v'	v''	$\nu_{\text{(Observed)}}$	$\nu_{\text{obs.}}-\nu_{\text{cal.}}$
				A System					
4	0	8	16471.0	−1.1	7	3	1	18884.8	+1.1
4	1	8	16638.7	+0.2	7	13	7	18884.8	−1.2
4	0	7	16741.3	−2.1	10	5	2	18938.7	−0.2
8	1	7	16909.3	+0.3	4	12	6	18994.0	−0.4
6	0	6	17011.9	−2.0	4	2	0	18994.0	−0.4
2	1	6	17180.0	−0.5	8	4	1	19049.4	−0.1
2	3	7	17241.7	+0.3	4	11	5	19103.2	−0.1
5	0	5	17283.4	−2.8	4	6	2	19103.2	−1.6
5	2	6	17344.7	−2.2	6	13	6	19158.0	+0.5
2	4	7	17405.2	−2.0	6	3	0	19162.4	+2.0
7	1	5	17450.6	−2.2	10	10	4	19213.5	+0.7
4	3	6	17509.3	−3.6	10	5	1	19216.0	+1.1
2	5	7	17570.0	−2.6	3	12	5	19266.3	−0.4
3	0	4	17557.0	−2.5	4	4	0	19327.6	+1.4
9	2	5	17618.4	−0.8	7	11	4	19376.8	+0.2
1	4	6	17679.7	+1.0	10	6	1	19379.7	−1.1
8	1	4	17724.7	−1.4	5	5	0	19492.9	+1.3
3	3	5	17783.3	−1.9	2	12	4	19539.2	−0.8
2	5	6	17844.1	00	8	7	1	19545.3	−0.6
8	2	4	17891.8	−0.7	3	9	2	19598.7	+0.8
2	1	3	17999.1	−1.2	1	11	3	19647.8	−3.0
5	3	4	18058.7	+0.2	7	6	0	19656.6	−0.9
3	5	5	18117.0	+0.6	3	8	1	19708.8	−0.9
8	2	3	18166.5	−0.2	6	10	2	19761.7	−0.3
1	4	4	18225.3	+1.0	2	12	3	19812.6	−1.6
2	1	2	18275.8	+0.5	6	7	0	19820.3	−2.3
7	3	3	18332.1	−0.6	3	11	2	19925.4	−0.4
5	2	2	18440.1	−1.6	1	13	3	19979.4	+2.1
7	4	3	18500.1	+1.6	8	8	0	19988.2	+1.9
5	1	1	18553.3	+2.0	2	10	1	20039.4	+1.4
1	6	4	18556.1	+0.5	4	14	3	20143.0	+2.8
10	3	2	18607.8	+0.1	8	9	0	20152.3	+1.7
5	5	3	18663.7	−0.2	10	10	0	20314.5	−0.2
3	2	1	18719.4	+1.7	3	12	1	20365.4	+0.2
3	12	7	18720.3	−0.6	2	14	2	20419.7	+4.5
10	4	2	18773.7	+0.2	7	11	0	20480.4	+1.9
1	11	6	18834.2	+3.3	3	13	1	20530.2	+1.9
					4	12	0	20641.2	−0.7
					3	14	1	20691.8	+0.6
					3	13	0	20806.1	+1.1

quantum numbers, the observed intensities, the observed wave numbers and the differences between the calculated and the observed wave numbers.

Within the errors of observation the wave numbers of these band heads are represented by the following equations:

$$A \text{ system}: \nu_h = 19354.3 + 223.82u'' - 0.879u'^2 - 333.16u'' + 1.247u''^2,$$

$$B \text{ system}: \nu_h = 22579.4 + 218.84u' - 0.500u'^2 - 333.16u'' + 1.247u''^2,$$

$$C \text{ system}: \nu = 26906.3 + 216.14u' - 0.525u'^2 - 333.16u'' + 1.247u''^2,$$

when $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$.

PBTE

Three systems of bands were also observed in lead telluride but only two of them have been analyzed. These systems correspond to the *A* system and to the *B* system of lead selenide but they are displaced toward the red, when compared to the corresponding systems of lead selenide. As in the case of lead selenide the presence of isotopes rendered the bands diffuse and difficult to observe accurately. The bands due to diatomic lead and to diatomic tellurium could be identified and were eliminated. No bands which could be unambiguously assigned to PbO or to TeO were observed.

TABLE I.—*Continued.*

I	v'	v''	ν(Observed)	$\nu_{\text{obs.}}-\nu_{\text{cal.}}$	I	v'	v''	ν(Observed)	$\nu_{\text{obs.}}-\nu_{\text{cal.}}$
B System									
8	0	9	18497.7	−2.4	2	12	2	22558.1	+0.3
1	0	7	19041.6	+1.3	2	20	7	22558.1	+1.1
3	2	8	19135.3	−1.6	4	9	0	22586.3	+2.1
1	3	8	19315.9	−3.3	3	17	5	22598.5	+3.4
5	1	6	19493.2	−2.6	1	14	3	22631.2	+2.1
5	4	8	19498.7	−1.9	6	11	1	22660.2	+1.0
3	0	5	19582.2	−1.9	4	19	6	22660.2	−0.6
4	0	4	19855.2	−2.2	2	21	7	22727.5	+3.7
3	1	4	20039.4	−2.0	3	13	2	22731.8	+0.4
4	0	3	20130.4	−1.2	3	10	0	22762.4	+1.9
10	1	3	20314.5	−1.1	2	18	5	22763.9	−0.7
7	0	2	20406.2	−0.4	2	15	3	22805.2	+4.0
4	2	3	20495.5	−3.2	4	12	1	22833.9	+0.1
10	1	2	20587.8	−2.8	4	20	6	22832.7	+4.2
2	3	3	20677.9	−4.7	4	14	2	22903.8	−0.5
2	0	1	20678.0	−3.0	3	19	5	22936.7	+3.6
10	2	2	20770.7	−3.0	3	11	0	22937.7	+1.8
10	1	1	20865.2	−1.4	3	16	3	22971.5	−0.9
5	3	2	20953.5	−1.5	4	13	1	23006.8	−0.6
10	2	1	21051.2	+1.5	3	18	4	23039.2	+1.3
10	3	1	21232.8	+0.8	4	15	2	23075.9	−0.3
6	2	0	21327.6	+1.2	1	12	0	23110.1	−0.4
6	4	1	21412.5	−0.9	2	17	3	23141.2	−1.4
1	6	2	21496.2	−1.4	2	14	1	23179.2	−1.1
8	3	1	21509.5	+0.8	2	19	4	23205.3	−1.1
1	5	1	21594.0	+0.1	1	13	0	23284.6	+0.5
1	7	2	21678.1	+1.7	1	16	2	23247.2	−0.2
7	4	0	21690.5	+0.4	2	18	3	23310.9	−1.2
2	8	2	21856.5	+2.1	1	15	1	23352.2	0
9	5	0	21871.5	+0.9	2	20	4	23373.9	−0.2
1	9	2	22033.8	+2.3	4	17	2	23419.5	+1.9
8	6	0	22050.8	+0.5	3	19	3	23481.3	+0.7
4	8	1	22131.6	+1.2	2	16	1	23522.1	−1.3
1	13	4	22179.3	−2.9	1	21	4	23543.2	−2.3
2	18	7	22221.5	+0.7	2	15	0	23631.0	+2.2
8	7	0	22229.8	+0.7	1	20	3	23651.6	+3.3
3	9	1	22308.8	+1.3	2	19	2	23755.5	−0.1
1	11	2	22381.8	−1.4	1	21	3	23816.8	+1.7
7	8	0	22405.5	−1.6	2	18	1	23861.4	−1.7
1	13	3	22456.1	−0.3	1	20	2	23923.1	−0.2
1	10	1	22485.1	+1.3	2	17	0	23973.3	+3.0
1	15	4	22530.4	+3.4	1	19	1	24031.2	−0.4
C System									
2	2	5	22258.6	+0.9	2	1	0	23450.6	−0.3
2	1	4	22350.1	+1.1	2	3	1	23537.8	+0.1
1	2	4	22530.4	−0.6	3	2	0	23633.7	+0.8
2	2	3	22805.2	0	4	3	0	23815.6	+1.2
2	1	2	22902.3	+4.1	2	5	1	23902.3	+3.1
3	2	2	23077.0	−3.2	6	4	0	23997.5	+2.1
2	1	1	23170.4	−3.8	2	6	1	24080.8	+1.6
2	3	2	23260.5	−1.2	7	5	0	24177.8	+1.9
1	0	0	23270.6	+2.2	3	7	1	24260.2	+1.8
3	2	1	23354.3	−1.9	6	6	0	24354.3	−1.6
1	4	2	23443.4	+0.7	2	7	0	24534.6	−0.8
					1	9	1	24611.4	−4.8

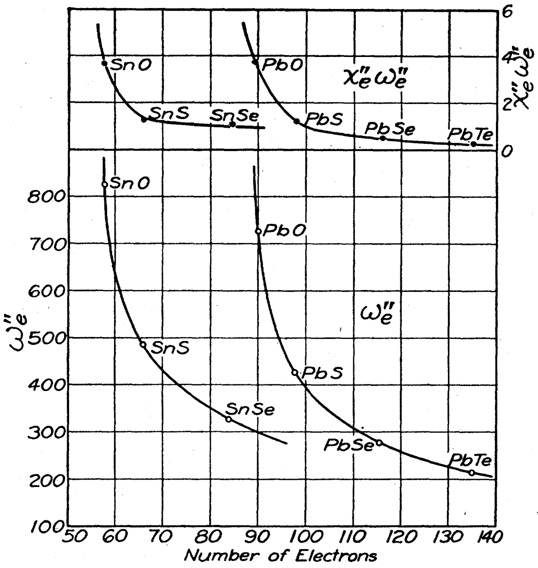

FIG. 1. Variations of the vibrational constants in the ground state of monoxides, monosulphides, monoselenides and monotellurides of lead and tin.

Table III gives the vibrational quantum numbers, the observed intensities, the observed wave numbers and the difference between the observed and calculated wave numbers for these two systems of bands.

The wave numbers of the band heads of these systems are represented within the error of observation by the following equations:

$$A \text{ system}: \nu_h = 16362.3 + 141.37u' - 0.224u'^2 - 211.79u'' + 0.119u''^2,$$

$$B \text{ system}: \nu_h = 19736.4 + 145.51u' - 0.464u'^2 - 211.79u'' + 0.119u''^2,$$

where $u' = (v' + \frac{1}{2})$ and $u'' = (v'' + \frac{1}{2})$.

DISCUSSION OF RESULTS

In Fig. 1 ω_e and $\chi\omega_e$ have been plotted for the ground state against the number of electrons in the molecule. These curves show how the vibrational constants of these molecules for the ground state are related to each other. Similar curves

TABLE II. *Band heads in SnSe.*

I	v'	v''	$\nu_{(\text{Observed})}$	$\nu_{\text{obs.}} - \nu_{\text{cal.}}$	I	v'	v''	$\nu_{(\text{Observed})}$	$\nu_{\text{obs.}} - \nu_{\text{cal.}}$
				A System					
4	1	4	18211.9	−2.5	8	2	2	19083.8	+0.3
3	0	3	18315.5	0	6	1	1	19191.9	+0.5
10	1	3	18538.0	+0.4	6	3	2	19301.9	+0.2
5	0	2	18641.1	0	4	2	1	19412.0	+0.3
10	2	3	18756.4	−1.5	4	4	2	19518.9	0
6	1	2	18863.5	−0.2	3	5	2	19737.1	+2.7
5	0	1	18971.1	+1.8	4	3	1	19630.4	+0.1
5	3	3	18976.4	−0.1	5	3	0	19958.4	−2.3
				B System					
3	1	6	20796.8	+2.5	10	0	2	21864.0	−0.2
7	1	5	21114.0	+1.5	1	1	2	22081.9	−0.2
10	1	4	21433.1	−0.2	10	0	1	22192.3	−0.1
6	0	3	21538.8	+0.2	8	1	1	22410.6	+0.3
2	2	4	21654.7	+5.4	4	0	0	22523.4	+0.6
7	1	3	21755.9	−0.6	10	1	0	22740.0	−0.7
				C System					
2	1	7	24800.1	−1.0	6	0	3	25863.9	+0.4
4	0	6	24901.4	+0.1	9	0	2	26189.0	+0.1
5	1	6	25116.4	−0.4	4	0	1	26517.0	−0.3
5	0	5	25219.9	+0.4	5	1	1	26731.7	−1.1
2	1	5	25436.2	+1.2	3	1	0	27062.5	−0.7
	0	4	25541.5	+1.2					

TABLE III. *Bands in PbTe.*

I	v'	v''	$\nu_{\text{(Observed)}}$	$\nu_{\text{obs.}}-\nu_{\text{cal.}}$	I	v'	v''	$\nu_{\text{(Observed)}}$	$\nu_{\text{obs.}}-\nu_{\text{cal.}}$
A System									
3	2	5	15555.8	+2.6	2	8	2	17020.0	−0.9
3	0	3	15695.6	+2.4	4	5	0	17026.9	−0.3
6	2	4	15763.9	+0.1	1	10	3	17081.4	−0.8
5	1	3	15835.6	+1.5	3	7	1	17093.8	+1.2
5	0	2	15906.4	+2.1	3	9	2	17155.0	−1.5
3	2	3	15977.2	+2.6	4	6	0	17166.5	+0.6
4	1	2	16043.4	−1.8	1	11	3	17220.3	+1.6
5	0	1	16114.7	−0.9	3	8	1	17230.1	−0.3
4	2	2	16182.3	−3.4	5	10	2	17296.0	+2.7
5	1	1	16255.4	−1.1	7	7	0	17304.2	+0.1
5	2	1	16394.3	−2.7	1	12	3	17353.3	−1.4
4	3	1	16533.1	−3.9	1	9	1	17369.6	+1.8
3	2	0	16607.1	−1.5	2	11	2	17430.8	+1.0
2	4	1	16677.9	+1.3	8	8	0	17442.0	−0.1
4	3	0	16745.5	−3.0	7	9	0	17579.8	+0.6
2	5	1	16815.5	−0.2	1	11	1	17640.5	−0.6
2	7	2	16882.7	+1.4	2	10	0	17715.5	−0.6
4	4	0	16890.6	+2.5	2	12	1	17777.1	0
B System									
3	0	8	18018.5	−1.3	2	4	2	19852.2	−0.7
2	0	7	18228.0	+0.9	2	9	5	19915.6	+0.1
2	0	6	18438.3	+1.1	8	3	1	19922.6	+0.2
1	0	5	18648.4	+0.8	2	11	6	19977.1	+0.4
4	0	4	18859.4	+1.2	2	2	0	19992.3	+1.2
2	2	5	18936.5	+0.7	6	5	2	19992.4	−1.4
2	1	4	19001.0	−1.8	2	10	5	20051.5	−0.2
5	0	3	19070.3	+1.3	5	4	1	20063.1	−1.1
1	3	5	19077.1	−1.5	8	3	0	20134.1	+0.4
1	2	4	19147.1	+0.7	1	11	5	20188.7	+1.6
3	1	3	19214.4	+0.8	2	8	3	20199.8	+0.1
4	0	2	19280.7	+0.6	2	5	1	20203.3	−1.8
2	3	4	19287.0	−2.2	10	4	0	20275.0	−0.7
2	2	3	19359.2	+2.0	2	9	3	20336.8	−0.1
1	5	5	19363.2	+1.9	10	5	0	20417.3	+0.7
6	1	2	19423.5	−1.2	1	9	2	20545.7	−2.3
1	4	4	19429.7	−1.3	9	6	0	20556.2	−0.3
2	0	1	19490.2	−1.2	3	8	1	20621.7	−0.4
2	3	3	19502.8	+2.8	2	10	2	20684.1	−0.1
5	2	2	19567.5	−0.8	7	7	0	20695.4	−0.1
2	5	4	19572.4	+0.5	4	9	1	20759.6	+0.3
6	1	1	19636.0	0	5	8	0	20833.2	−0.4
4	4	3	19641.9	+0.1	4	10	1	20895.8	+0.3
2	3	2	19709.3	−1.8	4	9	0	20971.0	+0.2
2	11	7	19766.6	0	3	11	1	21031.8	+0.9
10	2	1	19779.4	−0.2	1	10	0	21107.6	+0.6
2	5	3	19785.9	+3.2	3	12	1	21165.5	+0.3
1	10	6	19842.9	+1.6	1	11	0	21242.3	−0.1
					2	13	0	21508.6	−1.1

were obtained for the excited states. The variations of these vibrational constants are similar to those obtained by Jevons, Bashford and Briscoe[13] for the monoxides and monosulphides of the group IVb elements.

Since a rotational analysis of these spectra has not been possible, the electronic transitions cannot be determined with certainty. Howell has ascribed the corresponding bands in PbO and PbS to $^{1}\Sigma\rightleftarrows{}^{1}\Sigma$ electron transitions. The similarity of the observed band spectra and the electron configurations of PbO, PbS, PbSe and PbTe suggest that these bands in PbSe and PbTe also arise from $^{1}\Sigma\rightleftarrows{}^{1}\Sigma$ transitions. A similar comparison of the band spectra and the electron configurations of SnO, SnS and SnSe also suggests that the observed bands in SnSe arise from $^{1}\Sigma\rightleftarrows{}^{1}\Sigma$ transitions.

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[13] Jevons, Bashford and Briscoe, Proc. Phys. Soc. **49**, 543 (1937).