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The Infra-Red Absorption by Hydrogen Selenide, Deuterium Selenide and Deutero-Hydrogen Selenide

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The infra-red spectra of H_2Se , D_2Se and HDSe have been measured and the positions of the three fundamental frequencies for each molecule have been determined. These are; for H_2Se $\nu_1=2260\text{ cm}^{-1}$, $\nu_2=1074\text{ cm}^{-1}$, $\nu_3=2350\text{ cm}^{-1}$; for D_2Se , $\nu_1=1630\text{ cm}^{-1}$, $\nu_2=745\text{ cm}^{-1}$, $\nu_3=1696\text{ cm}^{-1}$; for HDSe , $\nu_1=1691\text{ cm}^{-1}$, $\nu_2=905\text{ cm}^{-1}$ and $\nu_3=2352\text{ cm}^{-1}$. Interpretation of the observed data has led to the adoption of an obtuse model where the $\text{H}-\text{Se}-\text{H}$ bond angle is slightly in excess of 90° . The $\text{H}-\text{Se}$ distances are evaluated to be 1.6Å and the $\text{H}-\text{H}$ distance is equal to 2.3Å. The product relations of Redlich are made use of as a verification of a correct assignment of frequencies and for a correct determination of the band centers.

I. INTRODUCTION

THE absorption spectra of the hydrides and deuterides of oxygen and sulphur have been studied quite extensively in the infra-red¹ so that the fundamental vibration frequencies of these molecules is known with considerable certainty. Considerable progress has, moreover, been made recently toward a rotational analysis of these spectra; particularly is this true for the bands in the spectrum of water vapor.² Concerning the infra-red spectra of the selenium hydrides very little has hitherto been known. An exploratory prism curve of the spectrum of H_2Se was carried out by Mischke³ and more recently Raman lines due to H_2Se , D_2Se and HDSe have been reported by Dadiou and Engler.⁴ We have considered these preliminary results of sufficient interest to warrant a further investigation of these spectra. Our measurements have been carried out under high dispersion in order that the character of each band might be determined.

II. EXPERIMENTAL

A. Preparation of the H_2Se , D_2Se and HDSe

The gas, hydrogen-selenide, is readily prepared by allowing distilled water to react with alu-

minum selenide, the reaction taking place as follows: $\text{Al}_2\text{Se}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{H}_2\text{Se} + 2\text{Al}(\text{OH})_3$. The aluminum selenide alloy may be prepared by carefully heating together approximately combining weights of finely ground selenium and aluminum in a sealed Pyrex tube over a Bunsen flame. Prior to the sealing of the tube, the air had been removed by evacuation. The combination between the metals takes place as indicated by the equation $2\text{Al} + 3\text{Se} \rightarrow \text{Al}_2\text{Se}_3$. Four different samples of gas were prepared, one using ordinary distilled water, a second using 99.8 percent D_2O , a third using 20 percent heavy water and a fourth from 80 percent heavy water. The first two samples were nearly pure gases while the third and fourth contained approximately 50 percent H_2Se , 40 percent HDSe and 10 percent D_2Se and 10 percent H_2Se , 40 percent HDSe and 50 percent D_2Se , respectively. The purpose of the samples three and four was to make available mixtures of gases rich in HDSe , but containing little D_2Se and H_2Se , respectively, so that the absorption bands due to the hybrid molecule which lay in regions where also H_2Se and D_2Se had absorption bands might be investigated with little falsification due to the presence of these. In all cases before samples of gas were generated the alloy was dried carefully to drive off all occluded water vapor. This precaution is extremely important when preparing pure D_2Se .

B. The spectrometer and the absorption cells

The spectrometer used to make these measurements is the same used by other workers in this

¹ E. K. Plyler and W. W. Sleator, *Phys. Rev.* **37**, 1493-1507 (1931); E. K. Plyler, *Phys. Rev.* **39**, 77 (1932); A. D. Sprague and H. H. Nielsen, *J. Chem. Phys.* **5**, 85 (1937); A. H. Nielsen and H. H. Nielsen, *J. Chem. Phys.* **5**, 277 (1937).

² P. Cross, *Phys. Rev.* **47**, 7 (1935); R. Mecke, *Zeits. f. Physik* **81**, 313, 445, 465 (1933); H. M. Randall, D. M. Dennison, Nathan Ginsburg and L. R. Weber, *Phys. Rev.* **52**, 160 (1937).

³ Walter Mischke, *Zeits. f. Physik* **106**, 67 (1931).

⁴ Armi Dadiou and Wolf Engler, *Wiener Anzeiger* **128**, 13 (1935).

laboratory. Many of the absorption bands in the spectra of these gases lie in regions which have hitherto been almost inaccessible for measurements, namely in the region of the intense CO_2 fundamental band near 4.3μ and in the region of the very intense water vapor fundamental absorption band near 6.2μ . It was consequently found necessary to surround the optical parts of the spectrometer by a box which was made as nearly air tight as possible. When measurements were to be made near 4.3μ , trays containing Ascarite were placed inside to remove as much of the atmospheric carbon dioxide as possible and when measurements near 6.0μ were to be made the trays were filled with phosphoric anhydride to remove as completely as possible all of the atmospheric water vapor. To hasten the removal of the atmospheric gases from the enclosed air the diffusion was enhanced by operating a fan placed inside the box. In all cases it has been found that enough of the CO_2 or water vapor can be removed so that no falsification of the absorption patterns under investigation was detectable.⁵

⁵ The falsification of absorption patterns of bands overlapping badly with atmospheric bands has been especially annoying in the past. The intensity of many of the water vapor lines has necessitated the use of widened spectrometer slits so that enough radiant energy might pass through to give measureable galvanometer deflections. This has made resolution of many such bands practically impossible so that mere envelopes have had to suffice. Almost universally such bands have been found to have an apparent rotational structure which shows itself to be a mirror image of the water vapor absorption pattern, i.e., where ever a strong water vapor line occurs there will manifest itself an apparent deep transmission window in the absorption band of the molecule under investigation. Several explanations have been given for this, but the real reason we believe to be the following one. When the spectrometer is correctly adjusted for measurements in a certain spectral region all higher order radiations should have been eliminated either by a filter or by a monochromator device. It is, however, seldom feasible to remove this higher order radiation completely so that in general about 5 percent of the total galvanometer deflection will be due to higher order. If now a cell containing gas which absorbs in the region for which the spectrometer is set, is placed in the light beam there will be only very slight falsification by these 5 percent if at this setting there is no atmospheric line. Where there occurs a strong atmospheric line, however, all of the first-order radiation may be absorbed by the atmosphere so that the total galvanometer deflection will be due to the 5 percent of higher radiation. This radiation will in general not be absorbed by the molecule being investigated so that at such a point there may very well occur an apparent transmission of nearly 100 percent. It has been possible to remove enough of the atmospheric gases in the above manner so that the second-order radiation represents a rather negligible amount of the total galvanometer deflection even where the atmospheric absorption is most intense.

For the measurements three echelette gratings were made use of, one ruled with 3600 lines per inch for the region near 4.3μ , a second ruled with 2000 lines per inch for the region near 6.5μ and a third with 900 lines ruled to the inch for the region 8.0μ to 14.0μ .

Two lengths of absorption cells were required, one 10 cm long filled to atmospheric pressure and used for the measurements made on the pure gases, and a second 27 cm long filled to atmospheric pressure and used when measurements on the HDSe bands were made. In all cases it was found possible to operate with slit widths equivalent to about 0.5 cm^{-1} . Deflections were recorded with the absorption cell in the light path and with the cell out of the light path at intervals on the circle of the spectrometer equivalent to the above slit widths so that the data could be recorded in terms of percent absorbed.

C. Absorption bands due to H_2Se and D_2Se

Two regions of intense absorption were located when the spectrum of H_2Se was measured with a prism spectrometer of the Wadsworth type. These fall near 4.3μ and 9.0μ . A third peak of less intensity was found near 2.8μ and a much less intense band was detected at 2.1μ . Two regions of intense absorption were likewise found in the prism spectrum of deuterium selenide, these falling near 6.0μ and 13.0μ . Only the regions of most intense absorption by these molecules have been studied under high dispersion; i.e., for H_2Se the regions near 4.2μ and 9.0μ and for D_2Se the bands near 6.0μ and at 13.0μ .

The 4.2μ region in H_2Se and the 6.0μ region in D_2Se .—The 4.3μ absorption region in H_2Se is resolvable into a group of sharp lines on the high frequency side of a strong central line and into a set of double lines on the low frequency side. This region is believed to consist of two overlapping bands. The one of these which has the broad gathered Q branch is interpreted to be the fundamental band ν_3 , using the notation of Dennison.⁶ Its center is taken to be 2350 cm^{-1} . The other of these bands does apparently not have any strong central group of lines and it is believed to be the other fundamental ν_1 , the center of which appears to be at 2260 cm^{-1} . The separations between principal absorption peaks

⁶ D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

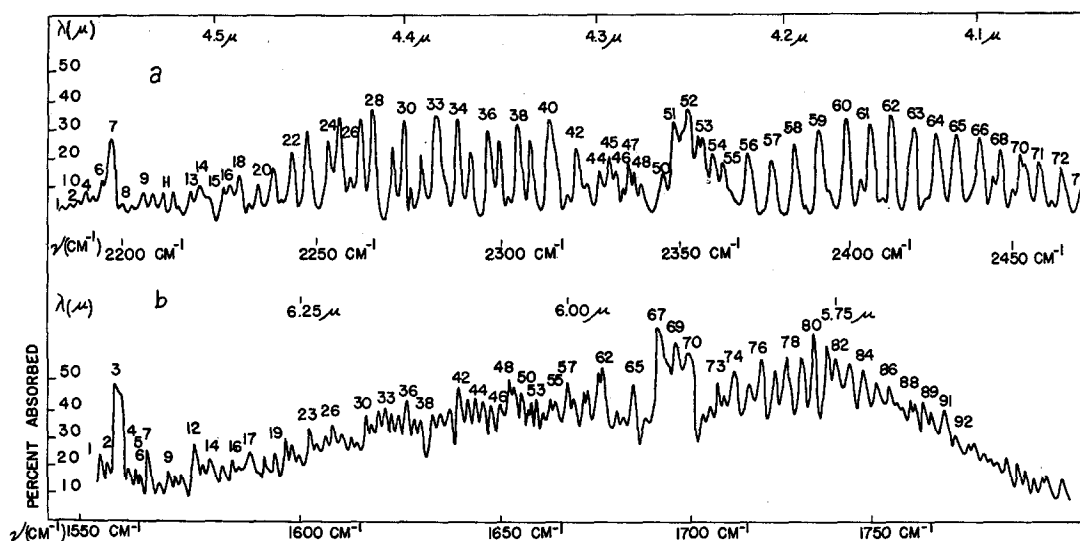


FIG. 1. (a) Absorption by H_2Se at 4.3μ . (b) Absorption by D_2Se at 6.0μ .

is very nearly the same for both bands and is on the average equal to about 7.6 cm^{-1} .

The 6.0μ absorption region in the D_2Se spectrum is undoubtedly the counter part of the 4.3μ bands in the spectrum of H_2Se and to which it bears a striking resemblance. As in the preceding case, resolution shows this region to consist of a set of essentially sharp lines on the high frequency side of a central line and into a set of double lines on the low frequency side. These are again believed to be the fundamental bands ν_3 and ν_1 with centers lying close to 1696 cm^{-1} and 1630 cm^{-1} and on the average the rotational lines in the two bands are separated from each other by an interval of about 3.7 cm^{-1} . The absorption patterns of these regions are shown respectively in Fig. 1, (a) and (b), original circle settings having been replaced by abscissae of wave-lengths and frequencies. In Tables I and II are set down the frequency positions of the principal absorption lines as determined from these measurements.

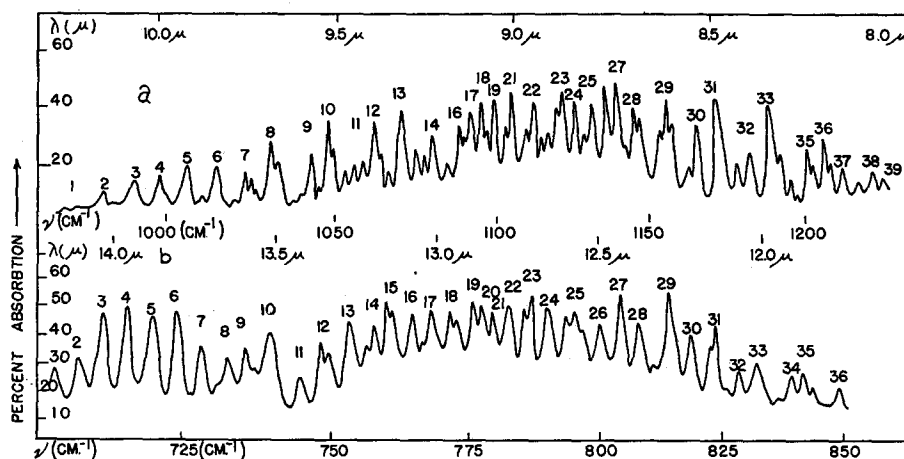
The 9.0μ region in H_2Se and the 13.0μ region in D_2Se .—The region near 9.0μ is the most intense in the spectrum of H_2Se and must almost certainly be attributed to the fundamental deformation frequency ν_2 . When examined under high dispersion and resolving power it splits up into a rotational structure which is quite irregular in appearance near the middle of the band, but which at the extremities consists of rather sharp

lines separated quite uniformly from each other by a spacing which on the average is close to 7.8 cm^{-1} . This band has no strong central line (as is the case in ν_3 at 2350 cm^{-1}) but there is a noticeable dip in the envelope of the absorption pattern near 1074 cm^{-1} and this point is identified as the center. A more exact determination of the center can hardly be affected before a complete rotational analysis of this region is feasible.

The corresponding region in the spectrum of D_2Se lies near 13.0μ and when it is examined under high dispersion it resembles in general structure and appearance the 9.0μ band in the H_2Se spectrum. As in that spectrum so also here

TABLE I. Frequency positions of principal H_2Se absorption lines.

LINE No.	FREQUENCY POSITION	LINE No.	FREQUENCY POSITION	LINE No.	FREQUENCY POSITION	LINE No.	FREQUENCY POSITION
1	2184.0 cm^{-1}	19	2232.7 cm^{-1}	37	2299.6 cm^{-1}	55	2362.5 cm^{-1}
2	2186.8	20	2235.0	38	2304.5	56	2369.8
3	2188.3	21	2238.9	39	2308.0	57	2376.8
4	2190.2	22	2244.1	40	2312.8	58	2383.8
5	2192.7	23	2247.3	41	2319.1	59	2391.2
6	2195.2	24	2253.6	42	2320.5	60	2398.3
7	2197.0	25	2256.6	43	2322.5	61	2405.5
8	2200.2	26	2259.6	44	2326.0	62	2412.3
9	2205.2	27	2261.8	45	2329.6	63	2419.1
10	2207.7	28	2265.2	46	2331.7	64	2426.0
11	2210.2	29	2270.5	47	2336.7	65	2432.9
12	2213.1	30	2273.9	48	2338.0	66	2439.9
13	2217.2	31	2275.9	49	2343.1	67	2443.4
14	2219.4	32	2279.0	50	2344.8	68	2446.1
15	2222.6	33	2282.6	51	2348.1	69	2450.0
16	2225.5	34	2287.4	52	2351.7	70	2453.2
17	2227.4	35	2290.8	53	2355.6	71	2459.4
18	2230.0	36	2296.3	54	2359.6	72	2465.4
						73	2471.8

FIG. 2. (a) Absorption by H_2Se at 9.0μ . (b) Absorption by D_2Se at 13.0μ .

is the rotational structure near the center quite complex, but a small distance away from the center a fairly uniform spacing of 3.9 cm^{-1} manifests itself. The center of this band is taken to be at 745 cm^{-1} where again there is a minimum in the envelope of the band; this time much more

discernible than in the H_2Se band. A diagram of the absorption bands ν_2 for H_2Se and D_2Se is given in Fig. 2, (a) and (b), respectively, where as before percent absorption has been plotted against a scale of frequencies and wave-lengths. Frequency positions of the principal absorption lines in these two bands are listed in Tables III and IV.

TABLE II. Frequency positions of principal D_2Se absorption lines at 6.2μ .

LINE No.	FREQUENCY POSITION	LINE No.	FREQUENCY POSITION	LINE No.	FREQUENCY POSITION
1	1554.2	32	1619.3	63	1679.8
2	1555.9	33	1620.6	64	1681.8
3	1558.7	34	1622.0	65	1684.4
4	1560.9	35	1624.2	66	1687.7
5	1562.0	36	1626.0	67	1691.7
6	1563.6	37	1628.5	68	1693.7
7	1564.9	38	1630.3	69	1695.7
8	1567.7	39	1632.8	70	1699.1
9	1569.9	40	1635.3	71	1703.1
10	1571.1	41	1637.1	72	1705.1
11	1572.8	42	1639.6	73	1707.8
12	1575.7	43	1641.5	74	1711.9
13	1577.4	44	1644.0	75	1716.0
14	1579.7	45	1645.9	76	1718.7
15	1582.0	46	1647.8	77	1722.8
16	1584.3	47	1649.6	78	1726.0
17	1588.4	48	1651.5	79	1729.8
18	1591.9	49	1652.8	80	1735.0
19	1594.8	50	1654.7	81	1736.8
20	1596.6	51	1656.0	82	1740.3
21	1598.4	52	1657.3	83	1743.8
22	1600.2	53	1658.8	84	1747.3
23	1602.5	54	1660.4	85	1751.6
24	1604.9	55	1663.0	86	1754.8
25	1607.3	56	1664.3	87	1758.8
26	1608.5	57	1666.9	88	1762.4
27	1610.3	58	1668.8	89	1765.3
28	1612.7	59	1670.7	90	1767.5
29	1614.5	60	1672.0	91	1771.1
30	1615.7	61	1674.6	92	1774.0
31	1617.5	62	1675.9		

D. Absorption bands due to HDSe

In the spectrum of deuterio-hydrogen selenide three rather intense absorption regions appear. Their presence is determined in the following manner: first, measurements are made on a mixture of selenide containing 50 percent H_2Se , 40 percent HD_2Se and 10 percent D_2Se and then measurements are made on a mixture of the gases containing 10 percent H_2Se , 40 percent HDSe and 50 percent D_2Se . The first mixture shows intense bands where absorption occurs due to H_2Se and HDSe and very faint absorption where there are bands due to D_2Se ; the second sample exhibits strong absorption bands due to HDSe and D_2Se and only weak bands due to H_2Se . The regions of absorption which occur intensely in both cases must be ascribed to HDSe . The three regions already referred to lie near 4.3μ , 6.0μ and 11.0μ .

The 4.3μ region in HDSe .—This region when investigated under high dispersion becomes at least partially resolved into rotational structure. In this band a strong minimum of absorption is found at the center and it has been identified as

ν_3 of the HDSe molecule. The center of this band lies at 2352 cm^{-1} , almost exactly coincident with the center of the 4.3μ absorption band in H_2Se . The absorption curve for HDSe in this region has been carefully compared with the curve obtained earlier for H_2Se at these wave-lengths to guard against falsification by the small amount of H_2Se present and absorbing here. No consistent coincidence of absorption lines in the two patterns could be detected and it is believed that the falsification due to the absorption by H_2Se must be negligibly small. At some distance from the center on either side the rotational structure becomes quite uniform and an average spacing of about 5.0 cm^{-1} between adjacent lines seems to prevail. When relative intensities of the absorption are plotted against a scale of frequencies, the curve in Fig. 3(a) is obtained. Frequency positions of the more prominent lines, to which arbitrary numbers have been affixed, are set down in Table V.

The 6.0μ region in HDSe.—The region near 6.0μ has been measured and has also been, at least partially, resolved into rotational structure. In contrast to the band at 4.3μ in this spectrum this one shows a very intense and sharp central line as may be seen by referring to Fig. 3(b). This band has been identified as the fundamental frequency ν_1 of the HDSe. Its central line lies at 1691 cm^{-1} , almost exactly coincident with the center of the 6.0μ band in the spectrum of H_2Se .

TABLE III. Frequency positions of principal H_2Se absorption lines at 9.0μ .

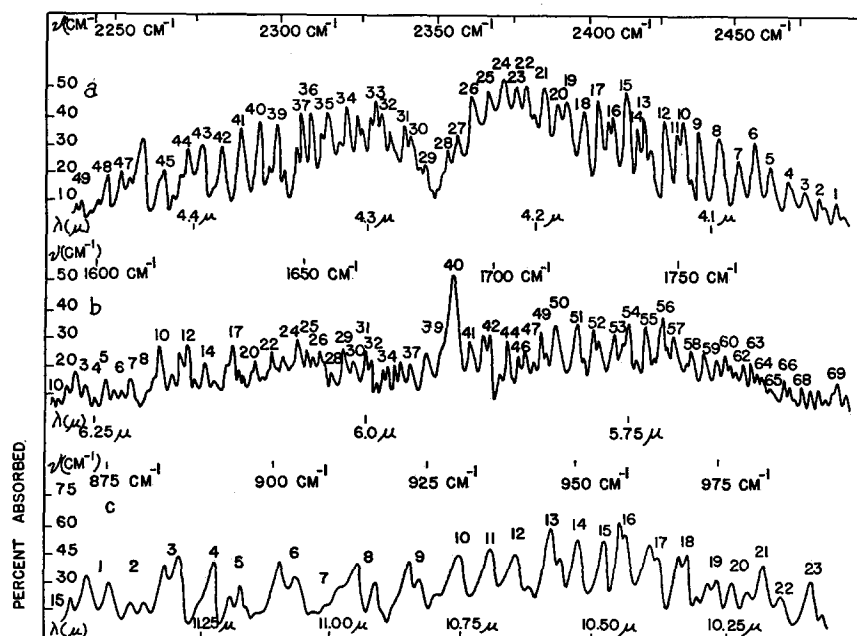
LINE No.	FREQUENCY POSITIONS	LINE No.	FREQUENCY POSITIONS
1	974.9 cm^{-1}	21	1104.9
2	982.7	22	1112.8
3	991.5	23	1122.0
4	998.7	24	1126.8
5	1005.6	25	1132.9
6	1013.9	26	1137.9
7	1021.9	27	1140.7
8	1030.2	28	1147.4
9	1041.6	29	1158.9
10	1048.1	30	1170.0
11	1057.7	31	1176.5
12	1063.5	32	1188.6
13	1069.0	33	1195.9
14	1078.7	34	1199.6
15	1083.8	35	1209.6
16	1086.8	36	1214.7
17	1091.4	37	1224.3
18	1094.5	38	1234.7
19	1098.6	39	1238.0
20	1102.8		

Also here a careful comparison has been made with the absorption band in the spectrum of D_2Se in this region to verify that no major falsifications in the absorption pattern have arisen because of the small amount of D_2Se present and absorbing here. No consistent coincidence could be established here either and it is felt that any such falsification is certainly small. In Table VI is given the frequency positions of the principal peaks of this band.

The 11.0μ region in HDSe.—This region has been investigated under high resolving power and at least to some extent it has been split up into rotational structure. The envelope of this band has the same general appearance as the envelope of the one measured near 4.3μ , there being a minimum discernible near 905 cm^{-1} . This point has been chosen as the center of the band which has been identified as the frequency ν_2 of the HDSe molecule. On the high frequency side of the center is found a series of fairly sharp lines separated quite uniformly from each other by an interval of about 5 cm^{-1} . The absorption curve is reproduced in Fig. 3(c) where as in other cases percent absorption has been plotted against a scale of frequencies and wave-lengths. The positions of the principal lines in the bands are set down in Table VII.

TABLE IV. Frequency positions of principal D_2Se absorption lines at 13.0μ .

LINE No.	FREQUENCY POSITIONS	LINE No.	FREQUENCY POSITIONS
1	704.6		
2	708.5	19	775.7
3	712.4	20	777.6
4	716.4	21	779.5
5	720.5	22	782.3
6	724.3	23	785.2
7	728.3		786.8
8	732.7	24	790.1
9	736.4	25	793.9
10	739.9		795.7
11	744.9		797.3
12	748.4	26	800.4
	750.4	27	804.1
13	752.4	28	808.0
14	756.3	29	813.9
	757.7	30	818.5
15	760.5	31	822.4
16	764.4		823.7
17	768.3	32	828.2
18	772.2	33	832.0
		34	839.7
		35	842.1
		36	850.5

FIG. 3. Absorption bands of HDSe .

III. DISCUSSION OF THE RESULTS

The absorption bands in asymmetric molecules of this kind are of two types. One type arises when the electric moment alternates along the axis of the smallest moment of inertia and frequently has a gathered Q branch at the center. The other kind originates with alternations of the electric moment parallel to the intermediate moment of inertia and has a Q branch where the components spread out from the center away from each other leaving the middle of the band free from lines. This difference in general character of their rotational characters gives an important clue toward fixing which frequencies are which and, indeed, ultimately determining the shape of the molecular model.

The oscillations of the nonlinear XY_2 type molecule divide themselves into two symmetry classes. The frequencies ν_1 and ν_2 make up the one of these symmetry classes and give rise to alternations of the electric moment parallel to the axis of symmetry while the frequency ν_3 which belongs to the other symmetry class produces a change of electric moment perpendicular to the symmetry axis. ν_1 and ν_3 are oscillations of the molecule where the atoms move essentially along the XY bonds; in the first case they are oscillating in the same phase, in the second case

their motions are out of phase. The masses and restoring forces being essentially the same in each case, one may expect the frequencies ν_1 and ν_3 to take very nearly the same values. The frequency ν_2 , on the other hand, which originates principally from a deformation of the YXY bond angle only may be expected to take a value appreciably less than ν_1 or ν_3 . Since, however, ν_1 and ν_2 both produce an electric moment parallel to the same

TABLE V. Frequencies of principal HDSe absorption lines at 4.3μ .

LINE NO.	FREQUENCY POSITION	LINE NO.	FREQUENCY POSITION	LINE NO.	FREQUENCY POSITION
1	2488.4	20	2389.1	39	2299.8
2	2482.8	21	2384.6	40	2293.6
3	2477.1	22	2379.1	41	2288.1
4	2471.1	23	2376.5	42	2282.0
5	2465.2	24	2371.0	43	2275.3
6	2458.8	25	2367.0	44	2272.0
7	2452.9	26	2361.9	45	2266.0
8	2446.3	27	2357.5	46	2258.7
9	2440.0	28	2352.5	47	2255.4
10	2433.8	29	2346.0	48	2252.7
11	2431.5	30	2341.0	49	2248.8
12	2426.9	31	2339.6	50	2241.6
13	2420.7	32	2332.5		
14	2417.7	33	2330.4		
15	2413.1	34	2321.9		
16	2407.8	35	2315.3		
17	2403.3	36	2310.8		
18	2398.8	37	2306.6		
19	2384.6	38	2304.6		

TABLE VI. Frequencies of principal HDSe absorption lines at 6.2μ .

LINE No.	FREQUENCY POSITION	LINE No.	FREQUENCY POSITION	LINE No.	FREQUENCY POSITION
1	1594.0 cm^{-1}	24	1650.0	47	1710.5
2	1596.6	25	1653.4	48	1712.6
3	1599.3	26	1656.0	49	1714.6
4	1600.2	27	1657.9	50	1718.7
5	1603.1	28	1659.8	51	1724.9
6	1606.9	29	1662.4	52	1729.8
7	1609.1	30	1665.2	53	1735.0
8	1612.7	31	1668.1	54	1739.6
9	1614.5	32	1670.1	55	1743.8
10	1616.3	33	1671.4	56	1748.8
11	1619.3	34	1674.0	57	1752.3
12	1622.4	35	1675.3	58	1757.3
13	1624.8	36	1677.9	59	1760.9
14	1627.6	37	1680.1	60	1767.5
15	1630.0	38	1683.8	61	1769.6
16	1632.8	39	1685.8	62	1772.6
17	1633.7	40	1691.1	63	1774.0
18	1635.9	41	1696.4	64	1775.5
19	1637.1	42	1700.4	65	1781.4
20	1639.3	43	1703.1	66	1785.1
21	1642.1	44	1704.8	67	1786.6
22	1644.6	45	1707.1	68	1789.9
23	1647.1	46	1708.5	69	1797.8

TABLE VII. Frequency positions of principal absorption lines in HDSe at 11.0μ .

LINE No.	FREQUENCY POSITIONS	LINE No.	FREQUENCY POSITIONS
1	874.0	13	945.5
2	879.8	14	950.0
3	885.8	15	954.3
4	892.3	16	958.3
5	898.3	17	963.4
6	903.5	18	968.9
7	910.3	19	974.5
8	915.2	20	979.2
9	922.5	21	983.5
10	930.0	22	988.0
11	935.0	23	992.7
12	939.9		

axis their rotational character should be the same, whereas the rotational characteristics of the band ν_3 might well be quite different. This supplies an important clue toward determining without ambiguity which frequencies are which, and indeed, ultimately toward fixing the shape of the molecular model.

In the case of the spectrum of H_2Se we have attributed the 4.3μ region to two overlapping bands of considerable intensity, one near 2350 cm^{-1} which has a rather prominent gathered Q branch and another at 2260 cm^{-1} which has no gathered Q branch. The band in the H_2Se spectrum at 9.0μ gives, moreover, no evidence of a gathered Q branch and it may therefore be

inferred that it is similar in rotational structure to the band at 2260 cm^{-1} . Similarly in the spectrum of D_2Se two bands have been found with no gathered Q branches, one lying at 1630 cm^{-1} , and the other at 745 cm^{-1} , and a third band showing a distinct gathered Q branch has been located at 1696 cm^{-1} . Thus we believe to have observed in the spectra of H_2Se and D_2Se the three fundamental bands and in each case two of these are essentially alike while the third is different. In view of the above argument we feel justified in making the assignments of these as indicated in Section II. These assignments are summarized in Table VIII together with positions of observed Raman lines, these latter being set in parentheses.

On the basis of a molecule oscillating with simple harmonic motion Redlich⁷ has shown that the frequencies of two isotopic molecules belonging to the same symmetry classes must obey certain product relations. For the H_2Se and D_2Se molecules these will be:

$$\left(\frac{\nu_1\nu_2}{\nu_1'\nu_2'}\right)^2 = \left(\frac{m_{\text{D}}m_{\text{Se}}}{m_{\text{H}}^2m_{\text{Se}}}\right) \times \left(\frac{M_{\text{H}_2\text{Se}}}{M_{\text{D}_2\text{Se}}}\right)$$

and

$$\left(\frac{\nu_3}{\nu_3'}\right)^2 = \left(\frac{m_{\text{D}}m_{\text{Se}}}{m_{\text{H}}^2m_{\text{Se}}}\right) \times \left(\frac{M_{\text{H}_2\text{Se}}}{M_{\text{D}_2\text{Se}}}\right) \left(\frac{A}{A'}\right).$$

TABLE VIII. Assignment of vibrational frequencies in H_2Se , D_2Se and HDSe.

	H_2Se	D_2Se	HDSe
ν_1	2260 cm^{-1}	1630 cm^{-1}	912 cm^{-1}
ν_2	1074 cm^{-1}	745 cm^{-1}	1691 cm^{-1} (1671)
ν_3	2350 cm^{-1} (2312)	1696 cm^{-1} (1665)	2352 cm^{-1} (2313)

The value of such relations is, of course, that they serve as a check on the manner in which the observed vibration bands are identified and indeed also serve as a guide as to where the centers of bands are to be chosen. To be able to apply these to any advantage the moments of inertia of the molecules must be known. The values of these may be estimated from the frequency intervals between rotational lines in the

⁷ O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).

bands ν_1 and ν_3 at 4.3μ in the H_2Se spectrum and at 6.0μ in the spectrum of D_2Se . In these bands the frequency intervals between lines is quite uniform from one end to the other save just at the centers. This leads one to conclude that the molecule is very nearly a symmetric molecule where $B \approx C = A/2$. When this approximation is made and one remembers that prominent lines occur in the spectrum when the molecule makes the transitions corresponding to $\Delta J = 0$, $\Delta K = \pm 1$

TABLE IX. Values of $\Pi(\nu_i/\nu_i')^2$.

Computed values	1.98	3.92
Experimental values	1.92	3.95

we obtain for A the value 7.3×10^{-40} g cm² and $C = 3.6 \times 10^{-40}$ g cm². Applying the same methods to the bands at 6.0μ in the D_2Se spectrum one obtains the value $A' = 14.6 \times 10^{-40}$ g cm² and $C' = 7.3 \times 10^{-40}$ g cm². With the aid of these and the values assigned to ν_1 , ν_2 and ν_3 for the two molecules we may make use of the product relations of Redlich. The calculated values are compared with the values determined from the spectrum in Table VIII and it will be seen that the agreement is well within 10 percent. Better agreement can probably not be expected in as much as the development by Redlich assumes the oscillational motion to be harmonic which of course is true only in first approximation. Having adopted the above assignment of vibrational frequencies it is possible to draw certain conclusions concerning the forces binding the molecule together. In order to do so it is in general necessary to make certain assumptions concerning the nature of these forces. One assumption which has justified itself in a great

many instances is the one, that to a satisfactory approximation the interatomic forces may be replaced by the so-called valence forces. This is a very useful approximation since the results obtained are so readily translated into physical and chemical notation. Lechner⁸ has treated the problem of the nonlinear $X-Y-X'$ with three different masses (of which the XY_2 type is a special case) oscillating harmonically using a potential energy relation consistent with the valence forces. On this basis he has arrived at certain equations which relate the frequencies to the force constant f associated with the displacements of the particles X , X' and Y relative to each other along the XY and $X'Y$ distances, the force constant d associated with the deformation of the $X-Y-X'$ bond angle and the equilibrium value of the bond angles $(\pi - \alpha)$ itself. These equations are in principle sufficient for each individual molecule to determine the constants f , d and α .

The positions of the fundamental bands in the spectrum are all displaced, slightly toward smaller frequencies, essentially because of the anharmonicity of the oscillational motion, so that the vibration frequencies themselves are only approximately given by the band centers. The constant α depends in a very critical manner upon the exact values of the frequencies so that the equations of Lechner do not, unfortunately, constitute a reliable method for determining this constant. Conversely the values f and d are very insensitive to the value of α . We have therefore determined the values of f and d from the equations of Lechner which are most consistent with the data of the three molecules H_2Se , HDSe and D_2Se entirely without regard to the value

⁸ E. Lechner, Wien Bericht. **141**, 291 (1932).

TABLE X.

FORCE CONSTANTS IN DYNES/CM	COMPUTED FREQUENCIES			MEASURED FREQUENCIES		
	H_2Se	D_2Se	HDSe	H_2Se	D_2Se	HDSe
$f = 3.12 \times 10^6$	$\nu_1 = 2300 \text{ cm}^{-1}$	$\nu_1 = 1645 \text{ cm}^{-1}$	$\nu_1 = 1639 \text{ cm}^{-1}$	$\nu_1 = 2260 \text{ cm}^{-1}$	$\nu_1 = 1630 \text{ cm}^{-1}$	$\nu_1 = 1691 \text{ cm}^{-1}$
$d = 3.17 \times 10^4$	$\nu_2 = 1060 \text{ cm}^{-1}$	$\nu_2 = 745 \text{ cm}^{-1}$	$\nu_2 = 914 \text{ cm}^{-1}$	$\nu_2 = 1074 \text{ cm}^{-1}$	$\nu_2 = 745 \text{ cm}^{-1}$	$\nu_2 = 905 \text{ cm}^{-1}$
	$\nu_3 = 2305 \text{ cm}^{-1}$	$\nu_3 = 1652 \text{ cm}^{-1}$	$\nu_3 = 2320 \text{ cm}^{-1}$	$\nu_3 = 2350 \text{ cm}^{-1}$	$\nu_3 = 1696 \text{ cm}^{-1}$	$\nu_3 = 2352 \text{ cm}^{-1}$

for the angle α . With these constants, f and d , so determined we have re-evaluated the frequencies ν_1 , ν_2 and ν_3 from Lechner's equations, this time putting in for α the value 90° , the value which seems most consistent with the regularity of the rotational structure of ν_1 and ν_3 .⁹ The re-

⁹ These frequencies have been chosen as most indicative of what the bond angle really is since the molecule suffers

sults of this recalculation of frequencies is given in Table X for comparison with the experimentally observed frequencies. The agreement seems to be satisfactory when one considers that no correction whatever has been made for the anharmonicity of the oscillational motion.

less distortion when it is oscillating in these modes than when it is oscillating with the frequency ν_3 .

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Line Absorption Spectra of Rare Earth Ions in Crystals

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Absorption spectra of the sulfate octahydrates of Er^{+++} , Dy^{+++} , Ho^{+++} and Tm^{+++} have been obtained at temperatures ranging from 14°K to 300°K . From the study of the variation in intensity of the absorption lines with temperature, energy levels have been found, in Er^{+++} , at 19, 41 and 86 cm^{-1} above the normal state. Similar levels have been found in Dy^{+++} at 22 and 57 cm^{-1} above the lowest. No such low energy states have been found in Ho^{+++} and Tm^{+++} .

INTRODUCTION

NUMEROUS studies of the absorption spectra of rare earth ions have been made in the last few years, in the temperature interval $20^\circ\text{--}300^\circ\text{K}$.¹ In this paper data are presented for the sulfate octahydrates of Er^{+++} , Dy^{+++} , Ho^{+++} and Tm^{+++} in the region $7000\text{--}3500\text{\AA}$.

A great deal has been written about the absorption spectra of rare earth ions in crystals. It is sufficient here to say that these ions (excepting

Ce^{+++} and Yb^{+++}) have absorption spectra containing numerous unusually sharp lines. From the absorption spectrum at a very low temperature we obtain an energy level diagram of the excited states, since the lines observed originate in the one lowest level. It is believed that, for the strong and sharp lines, the excited states as well as the normal state involve only $4f$ electrons which occupy a relatively sheltered position in the ion. Many of the observed terms are produced by crystal splitting of the terms of the free ion.

According to Van Vleck² the transitions between levels of the same $4f^x$ configuration, which would be forbidden as dipole radiation, may be quadrupole, magnetic dipole or electric dipole radiation induced by crystal fields. Probably the radiation contains some elements of the three types. Ewald,^{1c} working with Nd^{+++} , showed that the strong and sharp lines are pure electron transitions but that anion and lattice vibrations are also concerned in producing the lines which are weaker and less sharp.

The normal states of these ions are important in determining magnetic susceptibilities and other low temperature thermal and magnetic

¹ (a) Ce^{+++} ; S. Freed, *Phys. Rev.* **38**, 2122 (1931).

(b) Pr^{+++} ; F. H. Spedding, J. P. Howe and W. H. Keller, *J. Chem. Phys.* **5**, 416 (1937); A. Merz, *Ann. d. Physik* [5] **28**, 569 (1937); P. Lehmann, *Ann. d. Physik* [5] **34**, 389 (1939).

(c) Nd^{+++} ; F. H. Spedding, H. F. Hamlin and G. C. Nutting, *J. Chem. Phys.* **5**, 191 (1937); H. Ewald, *Ann. d. Physik* [5] **34**, 14 (1939).

(d) Sm^{+++} ; S. Freed and J. G. Harwell, *Proc. Acad. Sci. Amsterdam* **35**, 979 (1932); F. H. Spedding and R. S. Bear, *Phys. Rev.* **46**, 308, 975 (1934).

(e) Gd^{+++} ; G. C. Nutting and F. H. Spedding, *J. Chem. Phys.* **5**, 33 (1937).

(f) Eu^{+++} ; E. J. Meehan, *J. Chem. Phys.* **3**, 621 (1935). (The conclusions advanced in this paper with respect to the spectrum of Eu^{+++} must be withdrawn. It has since been discovered that the sample contained sufficient impurities to account for many of the lines.) H. Lange, *Ann. d. Physik* **32**, 361 (1938).

(g) Yb^{+++} ; S. Freed and R. Mesirow, *J. Chem. Phys.* **5**, 22 (1937).

(h) H. Gobrecht has studied many rare earth spectra. Most of his results are summarized in *Ann. d. Physik* [5] **31**, 755 (1938).

² J. H. Van Vleck, *J. Phys. Chem.* **41**, 67 (1937).