AUGUST 15, 1933 PHYSICAL REVIEW VOLUME 44

Absorption Spectra of the Samarium Ion in Solids. III. Absorption of $Sm(BrO_3)_3 \cdot 9H_2O$ and a Partial Energy-Level Diagram for the Sm^{+++} Ion as It Exists in Crystalline $Sm(BrO_3)_3 \cdot 9H_2O$

FRANK H. SPEDDING AND RICHARD S. BEAR, *Chemical Laboratory, University of California*

(Received March 7, 1933)

The absorption spectrum of $Sm(BrO_3)_3 \cdot 9H_2O$ has been studied at four temperatures between 20° and 298°K. The temperature variation in the absorption intensities is used to determine the location of excited lower levels situated at 39 and 68 cm^{-1} above the basic one. Other levels from 100 to 230 cm^{-1} above the normal state are probable. Between 78° and 20° many lines show a marked change, becoming double at the lower temperature. This is shown to be compatible with a splitting of the levels into new ones at 0, 37, 45, 67 and 82 cm^{-1}. Selection rules are indicated which show two apparently independent sets of these levels; 0, 37, 82 and one group of high levels; and 0, 45, 67 and another group of upper levels. This low-temperature splitting may be due either (1) to actual removal of degeneracy or (2) to development of two types of Sm^{+++} ion, differing in crystal environments. Either effect could presumably be caused by small changes in the crystal dimensions and symmetry. The hexagonal bromate shows less extension and complexity of upper multiplets and the excited lower levels are closer to the basic one than in the less symmetrical monoclinic chloride previously studied.

THIS is the third of a series of papers describing the effects of chemical composition and crystal symmetry on the energy levels of Sm IV (Sm^{+++} ion) in the solid state. In the previous papers[1] the absorption spectra of monoclinic crystals of $SmCl_3 \cdot 6H_2O$ have been described. It was demonstrated at that time that the absorption lines result from transitions between several lower levels and higher ones, the latter being grouped in multiplets. The behavior of these multiplets with temperature variation strongly indicates that they are composed of components which have resulted from the splitting of one or more excited levels by the electric fields of the neighboring ions in the crystal (a crystal Stark effect). This conclusion is in excellent agreement with the discoveries of Spedding and Nutting[2] concerning the nature of the excited levels of the Gd^{+++} ion in various salts. It will also be substantiated in this and subsequent papers.

The lines arising from the excited lower levels are readily distinguished, not only by the frequently occurring constant energy differences of the spectrum, but also by the behavior of the lines with temperature variation. As is well known, the intensity of a line is proportional to the number of atoms in the energy state from which it originates, and that number in turn depends on the temperature according to the Boltzmann relation. Because of this fact, as the temperature is lowered the intensities of lines arising from excited lower levels become less, and below a certain critical temperature, which depends on $\Delta\nu$, such lines become too faint to be observed.

This paper deals with the absorption spectra of hexagonal crystals of $Sm(BrO_3)_3 \cdot 9H_2O$ as shown by single crystals and by conglomerates of small crystals. In general the spectra resemble those described for the chloride and behave in a similar manner with regard to temperature shifts of multiplets and lines within them, changes in distinctness and intensity, etc. We shall describe only the points wherein the two spectra differ and shall refer the reader to the previous paper for general details.

EXPERIMENTAL PART

The bromate was prepared by the addition of a $Ba(BrO_3)_2$ solution to one of $Sm_2(SO_4)_3$ in a slightly less than equivalent amount. The $Sm(BrO_3)_3$ solution was then evaporated and the hydrated crystals extracted and purified by re-

---

[1] Spedding and Bear, Phys. Rev. **42**, 58 (1932); **42**, 76 (1932).

[2] Spedding and Nutting, Phys. Rev. **38**, 2294 (1931); J. Am. Chem. Soc. **55**, 496 (1933).

crystallization. The crystals were measured by Dr. A. Pabst of this university. His preliminary results were as follows: The crystals are hexagonal prisms with very ragged multiple terminations by hexagonal pyramid faces. From the measurement of four crystals the angle $(10\bar{1}0):(10\bar{1}1)$ was found to be 57°1′. This gives an axial ratio of 0.5620.

The samarium was from the same lot that had been used for the chloride preparation and was of such purity that no lines of other rare earths were observed. In addition to photographing single crystals with 3 to 6 mm absorbing paths, conglomerates of 5 to 10 mm in thickness were used. The differences between the spectra for the two cases were less than with the chloride, since the low-lying levels are much closer to the basic one. Even at hydrogen temperatures (20°) the population in these states is appreciable, making extreme absorbing layers unnecessary.

The apparatus and methods used in photographing the spectra at low temperatures have been described previously.[1]

RESULTS

In Fig. 1 are reproduced the photographs of the spectra observed at 20°, 78°, 169° and 298°K, and in Table I are given measurements of the positions of lines and bands at these temperatures. Between 78° and 20° occurs a remarkable phenomenon which we have observed so far only for the bromate. Practically all the lines split into two components, the red one of which is almost certainly complex (see Fig. 2). Above 78° the spectra behave similarly to the other samarium salts that we have studied.[3] The shift in position with temperature variation and the widening of the multiplets at lower temperatures may perhaps be slightly greater in the bromate case than in the chloride.

The multiplets of excited energy levels, and consequently the low-temperature multiplets of the spectrum, on the whole obey rules that are similar to those found by Spedding and Nutting[2] for the Gd^{+++} ion. In crystals of higher symmetry the over-all spread of the spectral multiplets is less and frequently the number of components fewer than in crystals of less symmetry. The samarium bromate multiplets, however, are shifted to the red with respect to those of the chloride, while with the gadolinium salts the opposite is true. In some cases the samarium bromate multiplets seem to have more components than the corresponding ones in the chloride. This is almost certainly an illusion, since the extra lines may arise from the excited lower levels. In the case of the chloride these lines are absent at 20°K, while in the bromate they can be quite intense at that temperature as a result of the smaller separations between these low levels. Another factor which tends to complicate matters is an apparent difference in the selection rules that are effective in the two salts. Thick conglomerates (long optical path) of the chloride tend to bring out many faint lines, causing the appearance of the spectrum to be markedly changed from that of a single crystal. In the bromate only a few new lines appear.

The lower levels of the ion in the bromate are also "pulled-in" from their chloride position.[4] Fig. 3 shows an energy-level diagram of several of the multiplets whose individual lines could be most satisfactorily studied. Lines arising from the low excited levels were identified, as before with the chloride, not only by their constant energy differences but also by their temperature

---

[3] This is also true below 78° if only the red components of the doublets at 20° are considered. On the other hand, the violet components shift quite markedly to the shorter wave-lengths, which is contrary to the usual behavior. As a result, at 20° the "center of gravity" of a doublet frequently appears to have reversed the direction of temperature shift. This phenomenon may account for an apparent reversal between 78° and 20° in the direction of displacement of several diffuse lines that are probably unresolved doublets of this type.

[4] The close proximity of the low excited levels to the basic one makes the bromate spectrum an excellent example of a type whose temperature variation has frequently been erroneously reported in the literature. When spectroscopic instruments of low dispersion are employed related high and low-temperature lines appear to form an unresolved band. On account of the fading of the former and the increasing intensity of the latter type of line as the temperature is lowered, such a band may appear to shift to shorter wave-lengths, whereas the individual lines themselves may be actually displaced in the opposite direction. That the movement of multiplets and most lines is to longer wave-lengths at low temperatures has now been confirmed in this laboratory for quite a few gadolinium and samarium salts.

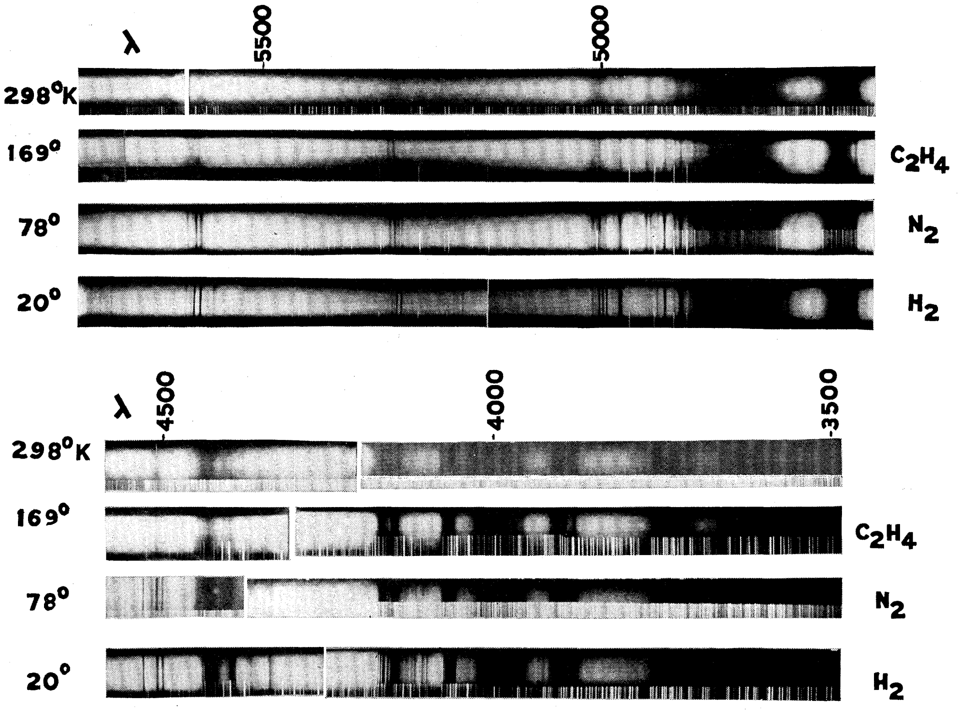

FIG. 1. Conglomerate absorption of $Sm(BrO_3)_3 \cdot 9H_2O$. The substances at whose boiling points the spectra were photographed are indicated on the right, the corresponding temperatures on the left. The three conspicuously simple multiplets on the long wave-length end are considered in more detail in Figs. 2 and 3.

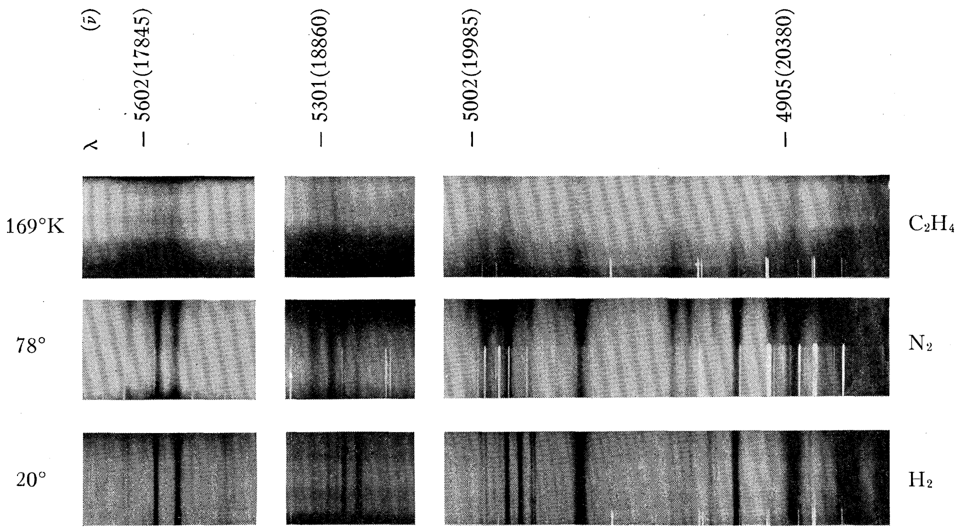

FIG. 2. Selected multiplets of $Sm(BrO_3)_3 \cdot 9H_2O$ absorption. Several of the multiplets of simplest structure are shown here magnified. The temperatures are given on the left, these being the boiling points of the substances on the right. Above are quoted wave-lengths and wave numbers for purposes of orientation with respect to the other figures and tables.

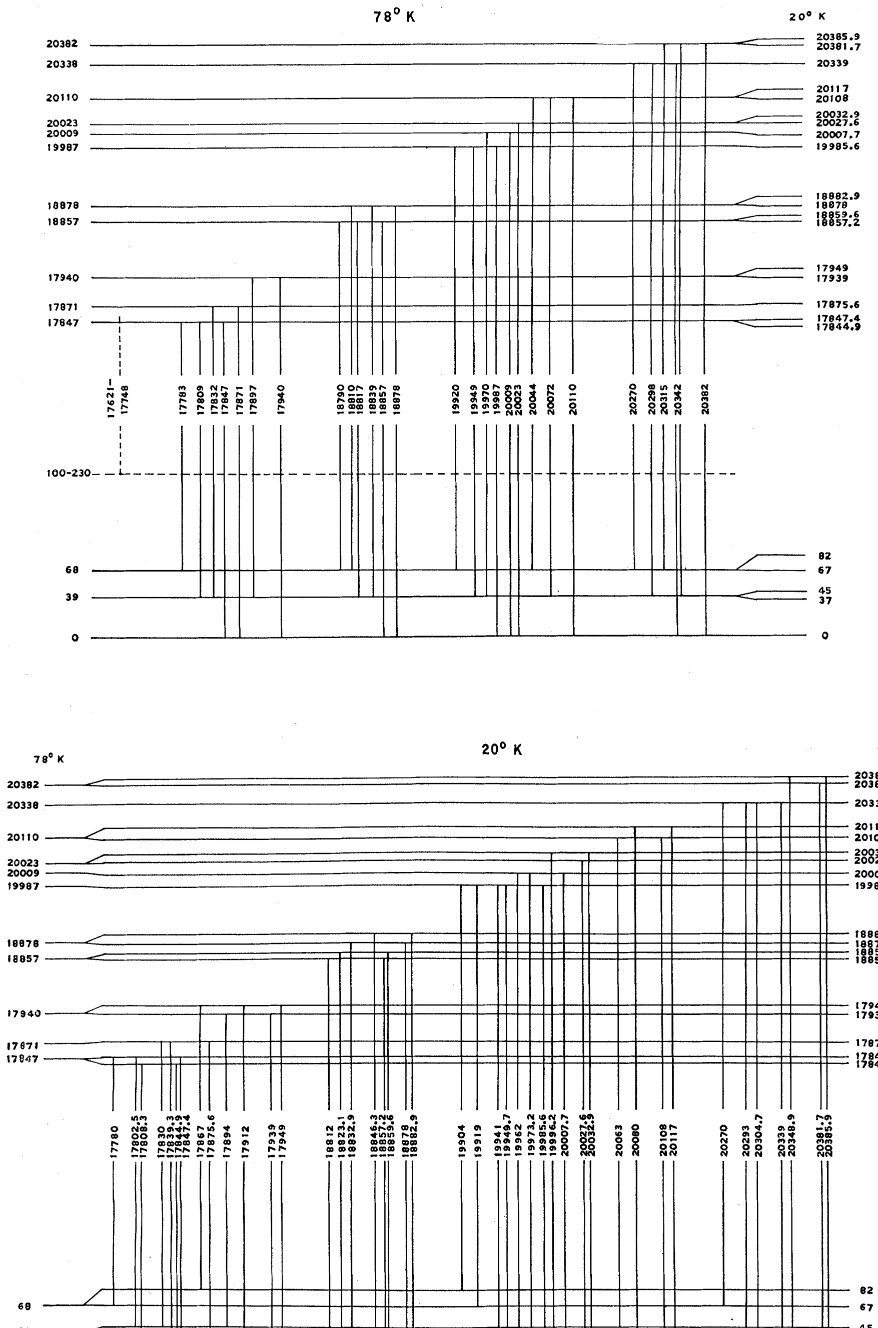

FIG. 3. Energy levels of $Sm(BrO_3)_3 \cdot 9H_2O$. Fig. 3a shows the levels needed to account for the multiplets of Fig. 2 at 78°K. The dotted lines indicate indistinct levels and transitions which are most evident at ethylene temperature (for other examples see text). In Fig. 3b are given the same levels after the changes which occur between 78° and 20°. The figures are wave numbers (cm^{-1}).

TABLE I. *Conglomerate absorption lines and bands of* $Sm(BrO_3)_3\cdot 9H_2O$.

H (Type) = high-temperature line; L (Type) = low-temperature line; HL (Type) = probably both types overlap; R. T., E. T., N. T., H. T. = columns for room, ethylene, nitrogen, and hydrogen temperatures, respectively; Int.=columns of intensity and character of the lines. Intensity is estimated very roughly on a scale of 10, with very faint or doubtful lines given as 0; s, vs, indicate degrees of increasing sharpness; se, indicates that a line that is somewhat broader than a truly single line would be expected to be has sharp edges; nd, d, vd = degrees of increasing diffuseness; b = broad line or band, used most frequently with bands; "2," "3" = possibly double or triple, respectively. Primed values represent band edges; c, centers.

R. T. $\tilde{\nu}$ (cm^{-1})	E. T. $\tilde{\nu}$ (cm^{-1})	N. T. $\tilde{\nu}$ (cm^{-1})	Int.	Type	H. T. λ (A)	H. T. $\tilde{\nu}$ (cm^{-1})	Int.
	17621′	17308	2d	L	5776.0	17309	3s
	17637′	17352	0d	H?			
	17649′	17374	2d	L	5754.2	17374	3d
	17734′	17415	2d	L	5740.7	17415	3d
	17749′	17465	2d	L	5724.1	17465	3d "2"
	17782′	17783	1d	H	5622.6	17780	0
	17792′			H	5615.65	17802.5	2nd
	17804′	17809	4d	H	5613.80	17808.3	2s
				?	5611.6	17815.3	0
				?	5609.1	17823.5	0
	17819′	17832	3d	H	5606.9	17830	2d
17836′	17835c			H	5604.05	17839.3	1s
	17845′	17845′			5602.6′	17844′	
				L	5602.30	17844.9	10s
		17847	9d	L	5601.50	17847.4	10s
	17853′	17850′			5601.0′	17849′	
				?	5598.8	17856	0
	17866′	17867′		?	5595.35	17867.1	1nd
17877′		17871	9d	L	5592.65	17875.6	10se
	17886′	17875′					
		17897	2d	H	5588.5′	17889′	1d
					5585.7′	17898′	
	17905′			H	5582.0′	17910′	1d
					5580.4′	17915′	
	17930′				5574.1′	17935′	
		17940	2d	L	5572.9	17939	4d
					5572.0′	17942′	
				L	5569.8	17949	3d
	17952′	18790	0	H			
	18786′	18810c	4d	H	5314.3	18812	2d
	18797′	18817c	4d	H			
18811′	18807′			H	5311.15	18823.1	2s
18824′	18818′	18839	8d	H	5308.40	18832.9	4d
18840′	18836′			H	5304.60	18846.3	4s
	18845′				5302.7′	18853′	
18852′		18857	4d	L	5301.55	18857.2	9s "3"
	18859			L	5300.85	18859.6	9s
					5300.5′	18861′	
				?	5298.5	18868	0
	18879	18878	4d	L	5295.8	18878	9d "2"
				L	5294.35	18882.8	9s
	19012.6	19008.4	2nd	?	5260.4	19005	0s
	19020.7	19018.1	1nd	?			
	19166	19163.9	3nd	L	5216.85	19163.0	4s
				?	5212.8′	19178′	0vd
					5210.0′	19189′	
	19209	19211.6	4nd	L	5203.40	19212.7	5s
		19650	0s	L	5087.5	19651	0nd
				H	5022.7	19904	0d
	19918′	19920	3d	H	5018.9	19919	2d
19931′		19938′					
	19941′			H	5013.4	19941	3d
19956′		19949	5vd	H	5011.20	19949.7	3s
	19957′	19958′		H	5008.0	19962	2d
		19970	4d	H	5005.30	19973.2	2s
19986′	19983′	19987	9d	LH	5002.20	19985.6	9se
	19996′			H	4999.55	19996.2	1nd
20003′		20009	1d	L	4996.70	20007.7	9se "2"
	20023	20023	4d	L	4991.70	20027.6	7s
				L	4990.40	20032.9	7s
		20044	0d	H			
	20065′	20067′		H	4983.0	20063	1vd
		20072	3d	H			
	20083′	20076′		H	4978.7	20080	1vd
20107′	20106′	20105′			4972.8′	20104′	
				L	4971.8	20108	10d "2"
		20110	8d	L	4970.9′	20111′	
20125′	20120′	20117′		L	4969.6	20117	9d
20269′	20269′	20270	4d	H	4931.9	20270	1d
20290′	20279′	20298	4d	H	4926.5	20293	2d
	20303			H	4923.60	20304.7	2nd
20322′		20315	1d "3"	H			
	20338′	20342	2d	LH	4915.4	20339	3d
	20352′			H	4912.90	20348.9	2nd
20378′	20379′	20378′			4905.70′	20378.7′	
		20382	9d	L	4905.00	20381.7	10s
20394′	20389′	20387′			4904.00	20585.9	10s
					4903.60′	20387.5′	
				L	4896.5′	20417′	0d
					4893.5′	20430′	
20438′	20442′	20439′	8	H	4890.9	20440	1d
20457′	20452′	20450′	8d	H	4889.1	20448	2d
		20472′		L	4884.3	20468	2d
20475′	20478′		9vd		4882.2′	20477′	
20495′	20489′	20492′		L	4878.6′	20492′	9d "2"
					4876.9′	20499′	
				L	4872.95	20515.7	3nd
	20526′	20526′			4870.6′	20526′	
	20536′		4db	H	4866.6	20543	3d
		20550′			4863.8′	20554′	
				L	4863.0	20558	1d
20559′	20563′	20563′			4861.4′	20565′	
	20583′		8db	L	4858.0′	20579′	10vd
20591′		20593′		L	4855.3	20590	9vd
					4852.0′	20604′	
20612′	20614′	20611′	4d	H	4849.6	20615	2d
	20626′	20623′			4845.8′	20631′	
		20637′		H	4844.7	20636	3vd
20644′			5d	H	4842.7	20644	4vd
		20650′			4841.4′	20649′	
20667′	20666′	20664′		L	4837.8	20665	3d
	20682′		9db		4835.5′	20675′	
20693′		20683′		L	4834.4	20679	10vd
	20700′	20695′		L	4830.1	20698	10vd
	20719′		9db	L	4828.2′	20706′	10vd
		20723′			4822.3′	20731′	
20762′	20765′	20745	2d	L	4818.9	20746	7d
20802′	20799′	20768′	9db	L	4814.7′	20764′	10vd
	20829′	20800′			4804.8′	20807′	
	20858′	20829′	9vdb	L	4797.7′	20838′	10vd
	20878′	20864′			4790.1′	20871′	
	20898′	20872′	7vdb	L	4787.8′	20880′	8vd
	20915′	20896′			4784.1′	20897′	
	20931′	20909′	6vdb	L	4780.0′	20915′	7vd
	20947′	20930′			4776.8′	20929′	
	20967′	20945′	9vdb	L	4773.6′	20943′	10vd
		20962′			4767.5′	20970′	
	20990′	20978′		L	4764.2′	20984′	9vd
21004′					4760.5′	21000′	
	21016′		8wvd	L	4758.1′	21011′	8vd
		21024′			4752.7′	21035′	
	21046′	21047′			4749.2′	21050′	6vd
			5wd	L	4745.4′	21067′	
	21089′	21091′		L	4740.5	21089	4vd
21104′	21116′	21115′			4736.4′	21107′	
	21133′	21135′	8vd	L	4733.2′	21121′	9vd
					4729.3′	21139′	
		21173′	3d	L	4720.9′	21176′	5vd
		21186′			4718.5′	21187′	
				L	4713.7′	21209′	1vd
					4708.9′	21252′	
21254′				L	4704.0	21252	1vd
				L	4693.3	21301	1vd
				L	4682.2′	21351′	1vd
					4677.4′	21374′	

TABLE I. (*Continued*).

R. T. $\tilde{\nu}$ (cm^{-1})	E. T. $\tilde{\nu}$ (cm^{-1})	N. T. $\tilde{\nu}$ (cm^{-1})	Int.	Type	H. T. λ (A)	H. T. $\tilde{\nu}$ (cm^{-1})	Int.
					4669.3′	21411′	
21438′	21439′	21442c	9d	H	4661.7	21445	2vd
	21456′	21472	10d	H	4657.5c	21465c	7d
	21471′			H	4653.9	21481	7d
	21486′			HL	4650.5	21497	5vd
21512′	21518′	21509	8vd	L	4647.5	21511	10vd
21539′	21530′	21532′	8vd	L	4643.4	21530	10vd
	21541′	21548′					
	21547′				4636.3′	21563′	
21578′	21573′	21567	8d	L	4634.2′	21573′	10d
	21585′	21585	8d	L	4631.5′	21585′	
21594′		21600	8d	H	4629.4	21595	5d
21614′	21608′			H	4626.6	21608	7d
		21622′			4623.6′	21622′	
21635′	21634′	21634′	10vd	L			10vd
	21645′	21648′					
21656′		21659′			4616.7′	21654′	
	21707′	21719	0	L	4605.4′	21707′	1vd
	21734′				4600.1′	21733′	
		21812	1d	L	4583.7′	21810′	2d
					4581.4′	21821′	
		21833′	0	L	4578.2′	21837′	1d
		21852′			4575.6′	21849′	
		21872′					
		21891′	0	L	4568.2	21885	1d
		21904′					
		21921′	0	L	4562.0	21914	1d
				L	4555.3	21946	1d
				H	4551.4	21965	1d
	21974′	21974.7	2nd	H	4549.0	21977	1d
21983′	21985′	22003.3	2nd	H	4544.6	21998	1d
22002′	22004′			H	4541.8	22011	1d
22016′	22016′			L	4535.80	22040.7	8s
22028′		22043.0	6nd	L	4535.10	22044.0	8s
22049′	22048			L	4534.30	22048.5	8s
22072′	22075′	22076	2d	H	4531.2′	22063′	0
	22086′				4528.2′	22078′	
22106′	22104′	22104	3d	H	4523.75	22099.4	2nd
				H	4521.20	22111.8	2nd
22122′	22117′	22117	1d	H	4519.5	22120	0
22142′	22142′	22136′			4515.2′	22141′	
		22144	8d	LH	4514.3	22145	9d "2"
22159′	22152′	22152′			4513.5′	22150′	
22176′	22181′	22179′			4506.9′	22182′	
		22185	6d	L	4505.9	22187	8d
22197′	22193′	22191′			4504.9′	22191′	
		22242	0	H?			
		22276	0	H?			
		22319	0	H?			
		22341′	0	?	4473.5′	22348′	0
		22367′			4469.3′	22369′	
				L	4466.2′	22384′	0
					4463.2′	22399′	
	22426′	22420′		H	4459.2′	22419′	1d
22449′					4457.2′	22430′	
		22446′		H	4454.1	22445	1s
	22462′		8db	H	4452.4	22453	1s
				H	4451.3	22459	1s
		22470′		H	4449.7	22467	1s
					4448.5′	22473′	
	22477′			H	4448.3	22474	2d
	22490′	22480′		H	4447.2	22480	2d
			8d	L	4445.30c	22489.3c	9s
22508′	22507′			L	4442.50	22503.5	9s
		22512′		L	4440.85	22511.9	8s
22527′	22527′		8d	L	4438.85c	22522.0c	8nd
		22528		L	4437.90c	22526.8c	8nd
					4436.3′	22535′	
	22548′			L	4435.4	22540	10d
22558′		22545	8d	L	4433.3	22550	10d
					4432.5′	22554′	
		22568	8d	L	4430.4c	22565c	8d
				L	4429.1c	22572c	8d
22581′	22587′	22581′	8d	L	4426.35	22585.6	9nd
		22601′		L	4423.95	22597.8	8nd
				L	4421.6	22610	2d
22643′	22639′			L	4418.80	22624.3	4nd
		22642	6wd	H	4412.5	22657	0
		22661′					
		22669	7d	H	4410.6	22666	2d
22676′	22680′	22674′					
22702′	22700′	22699′			4405.0′	22695′	
		22708	8d	L	4403.7	22702	10d
	22715′	22712′		L	4401.8	22712	10d
					4400.8′	22717′	
		22726′	8d		4398.7′	22728′	
22737′					4397.7	22733	d
		22742′			4396.6′	22739′	
22809′	22802′	22798′		L	4386.4	22791	1d
				L	4382.4	22812	1d
		22829′		L	4379.1	22829	2d
					4375.4′	22849′	
22860′	22856′		3wvd	L	4374.1	22856	3d
		22872′		L	4371.2c	22871c	2vd
				L	4368.3	22886	1d
				L	4363.1	22913	1d
22930′	22929′	22931c	3d	H	4359.6	22931	2d
	22939′			H	4357.0	22945	3d
	22952′	22960	3d	H	4352.6	22968	2d
	22966′	22976c	3d	H	4350.0	22982	0
22985	22983′	Faintly evident		L	4347.2	22997	2d
23011′	23007′				4345.1′	23008′	
		23012	6d	L	4344.2	23013	7d
	23018′				4343.3′	23017′	
23031′		Faintly evident		L	4340.7c	23031c	2d
	23660′				4338.7′	23042′	
	23701′	23391.6	1vs	L	4274.10	23390.3	1vs
	23742′	23744	0	H			
	23783′	23776	0	H			
	23818′	23830	1d	H			
	23843′	23859	2d	H	4190.45	23857.2	2nd
	23859′			H	4188.60	23867.6	2nd
23877′	23877′	23898.8	8nd	L	4182.70c	23901.4c	9s
	23900′	23908′		L	4182.15c	23904.5c	9s
	23908′		10db	L	4179.45c	23919.9c	9nd
		23928′		L	4178.70c	23924.3c	9nd
	23925′	23940′		L	4175.4	23943	10d
23943′	23933′		10db	L	4173.6	23953	10d
	23943′	23962′		L	4171.95	23962.8	3nd
	23964′			L	4170.85	23969.3	2nd
		23980.9c	8nd	L	4168.75	23981.2	9nd
23987′	23982	23987.3c	8nd	L	4167.40	23988.9	10nd
				L	4165.55c	23999.8c	3nd
24013′	24015′	24006′			4163.2′	24013′	
			9db	L	4162.5	24017	10d
	24029′	24028′		L	4160.7	24028	10d
					4159.8′	24033′	
	24041′	24038′		L	4158.7′	24039′	10b
			10db		4156.4′	24053′	
	24060′	24060′		L	4155.3	24059	10d
				L	4153.6	24069	10d
24080′	24076′			L	4151.6	24080	8d
	24093′	24082′			4150.8′	24085′	
		24101	3vd	L	4147.8	24103	3d "2"
					4147.3′	24105′	
	24111′			L	4146.00c	24112.8c	4nd
		24119′		L	4144.95c	24119.0c	4nd
	24134′			L	4143.30	24128.6	3nd
			4db	L	4140.95	24142.3	4nd
24148′				L	4139.3	24152	4d
	24161′	24168′		L	4137.4	24163	4d
				L	4135.90	24171.9	2nd
				L	4132.60c	24190.9c	3nd
	24197′	24199	4d	L	4131.25	24198.8	4nd
24203′	24213′			L	4129.80c	24207.4c	3nd
	24220′			L	4128.15c	24217.2c	3nd
24234′	24233′	24226	5d	L	4126.90	24224.5	5nd
					4123.9′	24242′	
				L	4122.70	24249.1	3nd
				L	4120.5	24262	2d
24278′	24280′			L	4118.7	24273	3d
					4116.5′	24286′	
	24298′	24290	5d	L	4115.6	24291	6d
24316′	24319′				4114.8′	24296′	
				L	4112.6	24309	4d
	24336′	24331	4d	L	4108.5′	24333′	5d "2'
					4107.9′	24337′	
				L	4105.5	24351	3d
				L	4103.9	24365	1d
				L	4099.8	24385	1d
				L	4096.6	24404	1d
				L	4093.8	24420	0
				L	4091.3	24435	0
24459′				L	4088.6	24452	0
	24469′	24463.2	8nd	H	4086.15	24466.0	5nd
		24478′		?	4084.55	24475.7	1vs
	24483′		9d	H	4082.6	24487	8d
	24498′	24495′		H?	4080.85c	24497.9c	6nd
	24507′	24504′		H?	4079.5	24506	8d
24513′				H?	4078.65	24511.0	8nd
			8bd	H?	4077.55	24517.6	8nd
	24521′			H?	4076.70	24522.8	8nd
		24535′		L	4075.8′	24528′	9d
24540′	24535′				4074.2′	24538′	
		24541′	9d	H	4073.6′	24541′	
	24546′	24557′					10b
	24559′	24566c	8d	L			
↓↓	↓24565′	24574c	8d	L	4067.1′	24581′	

TABLE I. (*Continued*).

R. T.	E. T.	N. T.	Int.	Type	H. T.		Int.
$\tilde{\nu}$ (cm^{-1})	$\tilde{\nu}$ (cm^{-1})	$\tilde{\nu}$ (cm^{-1})			λ (A)	$\tilde{\nu}$ (cm^{-1})	
††24593′	†24579′	24588.9	8nd	L	4065.85c	24588.2c	9nd
	24588			L	4065.05c	24593.1c	9nd
				L	4056.8′	24643′	2d
					4054.2′	24659′	
				L	4051.8′	24674′	2d
					4048.8′	24692′	
24715′				L	4044.5′	24718′	4vd
					4041.5′	24740′	
				L	4038.1′	24757′	3vd
	24775′				4034.8′	24777′	
		24783′			4032.7′	24790′	
				L	4029.9	24807	4d
			9db	L	4027.2c	24824c	10d
	24958′	24953′			4006.3′	24953′	
				L	4004.3	24966	7vd
	25007′	25008	6vd	L	3997.8	25007	7vd
	25028′	25051	5bd	L	3989.6′	25058′	
25038′	25040′		6d	L	3987.4′	25072′	7d
	25061′	25079			3985.5′	25084′	
	25076′	25093	8d	L	3984.5′	25090′	9d
	25099′				3982.7′	25102′	
	25115′	25118	8d	L	3981.2′	25111′	9d
	25127′				3978.9′	25126′	
			8d	L	3978.2′	25130′	9d
	25137′	25139			3976.1′	25143′	
	25150′			L	3974.6	25153	8d
	25179′	25165	2vd	L	3971.6	25171	2d
	25195′	25188	4vd	L	3968.50	25191.2	8nd
	25215′	25221c	8d	L	3965.1′	25213′	9d
	25234′				3961.1′	25238′	
25251′				L	3958.0	25258	6d
		25265′			3957.1′	25264′	
				L	3956.25	25269.4	2nd
				L	3954.3	25282	4d
		25336	2d	H	Faintly evident		
		25373	3d	L	3939.75	25375.1	6nd
				L	3935.3	25404	3d
		25425	4d	L	3932.7	25421	6d
				L	3930.2	25437	6d
25484′	25488′	25480′	8d	H	3922.2	25489	6d
	25502′	25498′					
25512′		25505′	8d	H	3919.80	25504.4	4nd
25527′	25538	25524′		H	3917.8	25517	6d
	25546′	25534	7d	H	3914.3′	25540′	
25573′	25559′	25549	9d	HL			9vd
		25564	7d	HL	3908.8′	25576′	
				L	3906.7	25590	9d
25613′	25614′			L	3904.4	25605	8d
	25625′	25619	9d	L	3902.7′	25616′	
	25633′			L	3900.7′	25629′	10d
	25645′	25638c	9d	L	3900.0′	25634′	10vd
25661′					3897.9′	25648′	
				L	3896.55	25656.6	6nd
25694′	25695	25669	4d	L	3893.50	25676.5	4nd
		25693	4d	L	3891.15	25692.0	4nd
					3889.3′	25704′	
25721′	25723			L	3888.5	25710	8d
	25733′	25719	9d	L	3886.3	25724	10d
25755′	25744′	25737	9d	L	3883.9	25740	10d
					3882.8′	25747′	
		25758.7	5nd	L	3880.80	25760.5	9nd
		25776.2	5nd	L	3878.65	25774.8	8nd
				L	3877.45	25783.0	8nd
		25809	3d	L	3873.0	25812	6d
		25845′	0	L	3867.9′	25846′	2d
		25864′			3865.1′	25865′	
	25882′	25881′	0	L	3860.4′	25897′	2d
	25904′	25909′			3857.2′	25919′	
				L	3840.2′	26033′	2vd
					3834.1′	26074′	
26324′	26327	26321.1	2s	H			
	26362	26352.1	1s	H			
26388′				L	3787.65	26394.1	3nd
26509′				L	3771.9	26505	2d
		26549	8d	H	3766.4	26543	6d
	26558			H	3764.6	26556	6d
	26570′	26565′		L	3762.7′	26569′	8nd "2"
					3761.30c	26579.2c	
				L	3758.8	26597	9db
	26631′			L	3755.4	26621	9db "2"
	26641′		9db	L	3753.0′	26638′	10db
	26676′				3747.7′	26675′	
	26687′			L	3746.4′	26685′	9d "2"
					3744.1′	26701′	
	26712′	26714′		L	3742.8	26710	3d
	26729′	26723′	9db	L	3741.6′	26719′	9db
	26750′	26751′			3737.1′	26751′	
	26815′	26812	7d	H			
	26838′	26833	8d	L	3725.5	26834	8d
	26859	26857	8d	L	3722.8	26854	8d
	26892	26888	6d	H?	3718.5	26885	4d
				H?	3716.6	26899	6d
	26928	26926	8d	L	3713.8	26919	8d
				L	3712.0	26932	9d
26982′				L	3710.4	26944	7d
		26962	4d	L	3706.9	26969	7d
		26994	3d	L	3702.7	27000	6d
			4d	L	3698.4′	27031′	6d
		27042			3695.6′	27052′	
27260′	27268′	27273	7d	H			
	27288′	27302	8d	H	3662.5	27296	6d
	27297′			H	3661.1	27306	6d
27325′	27317′			H	3659.5	27319	6d
			8d	L	3657.5′	27334′	9d
	27344	27340			3655.9′	27346′	
		27359	8d	L	3654.7′	27354′	9d
	27363				3652.9′	27368′	
27421′	27457′	27453′					
	27488′	27481′	9d	H	3638.2	27478	8d
	27499′	27492′	8db	L	3636.3′	27493′	
	27524′	27512′					
	27541′	27584′	8db	L			8wb
	27571′	27617′					
	27591′	27637′	8db	L			
	27621′	27662′			3600.0′	27770′	
	27634′	27809′		L	3597.9	27786	6d
	27663′		8db	L	3593.2	27822	6db
27739′	27810′	27862′		L	3589.2	27854	8db
27837′	27866′	27886′		L	3583.8c	27896c	8d
	27879′		8db	L	3581.25	27915.3	5s
27924′	27919′	27926′		L	3579.75c	27927.0c	5s
					3573.6′	27975′	
		28055	2d	H			
	28067	28087	6d	H	3560.2	28080	4d
				H	3558.5	28094	4d
	28094	28125	9d	L	3554.50c	28125.2c	9s
				L	3553.85c	28130.6c	9s
	28130	28159	9d	L	3550.50′	28156.9′	9se
					3549.00′	28168.8′	
28153′	28163	28178	3d	H			
28197′	28184	28207	5d	H	3544.6	28204	4d
				H	3542.8	28218	4d
		28244	8d	L	3538.9	28249	8d
	28250	28283	8d	L	3534.0	28288	8d
28287′	28289			L	3513.7	28452	0
28303′				L	3511.5	28470	0
		28640	5d	H	3490.9	28638	4d
	28643			H	3489.35	28650.5	4vs
28657′		28673	6d	L	3486.6	28673	6d
	28673			L	3485.05	28686.0	4vs
28692′				L	3483.35	28699.8	4vs
28761′		28782	5d	H	3473.3	28783	3d
	28788	28812	5d	L	3469.5	28814	5d
28811′	28817	28845	5d	L	3465.2	28850	5d
28842′	28841′						

behavior. Tables II and III give examples of the constant intervals found. The lower levels of the diagram and tables account for all of the important lines of the multiplets considered and for most of the high-temperature lines in other parts of the spectrum. The complexity of the other multiplets seems to be the chief factor hindering attainment of complete agreement.

TABLE II. *Prominent "low-temperature" lines and their "high-temperature" satellites (78°K).*

L.-t. line	Satellite *A*	$\Delta\tilde{\nu}_A$	Satellite *B*	$\Delta\tilde{\nu}_B$
17847	17809	38	17783	64
17871	17832	39		
18857	18817	40	18790	67
18878	18839	39	18810	68
19987	19949	38	19920	67
20009	19970	39		
20110	20072	38	20044	66
20382	20342	40	20315	67
21509	21472	37	21442	67
21641	21600	41		
22043.0	22003	40	21975	68
22144	22104	40	22076	68
22185			22117	68
22708	22669	39	22642	66
23898.8	23859	40	23830	69
24588.9	24549	40		
26926	26888	38		
27340	27302	38	27273	67
28125	28087	38	28055	70
28244	28207	37	28178	66

The lines at nitrogen temperatures are somewhat more diffuse for the bromate than for the chloride. This probably results from the fact that the lines already have started to split apart. At hydrogen temperature the splitting is so pronounced that at first sight the spectrum seems to present an entirely different appearance. All of the levels evidently have split into two components. This splitting amounts to from 5 to 15 cm^{-1} for the lower levels and is somewhat less for the extreme upper ones. Of the two components resulting from each of the lower levels the one with higher energy appears not to be single (uncertain for the 67–82 pair). It is probably double and may be still more complex. Of particular interest is the fact that after the levels have split all the lines resulting therefrom cannot be referred to common upper levels, except in cases where it is obvious that the low temperature lines in question are complex and are not completely resolved. As a result, the levels 0, 45, and 67 seem to be associated with one set of excited levels and 0, 37 and 82 with another.[5] Only a few lines arising from the excited lower level at 82 cm^{-1} are observed, since the lines are very faint because of the low population in this state at 20°K. Because of this low intensity the above rule has not as much confirmation for this level as might be desired, though the behavior described is certainly true of the 37 and 45 levels.

It is not at all certain just what causes this splitting of the levels, though in any case the effect is probably brought about by a slight change in the crystal structure. The symmetry of the field about the Sm^{+++} ion may become less at the lower temperatures, causing the levels to be less degenerate. On the other hand, the selection rules mentioned above suggest that in the crystalline change some of the samarium ions in the unit cell have become different from the others (with respect to field), and that in a mole of ions in the crystal one has a fraction of a mole of one type of Sm^{+++} and the remainder of another kind.[6]

Any crystalline change that might bring about this effect is small, however, as appears from the fact that the bromate crystals show no pronounced tendency to crack when they are suddenly cooled, nor do they undergo crystal transitions during prolonged exposures at low temperatures.

There is some evidence that other lower levels exist. New lines make their appearance at liquid ethylene temperature, though they are quite diffuse and faint. The probabilities of transitions from such levels seem to be small and only a few of them appear. Thicker absorbing layers tend to bring these lines out more strongly, but in any case they are hard to measure accurately (see dotted level and band of Fig. 3). The most

---

[5] It will be noticed that the method employed here cannot determine whether the basic level, 0, is or is not split at low temperatures. The diagram, Fig. 3, is based upon the assumption that it is not. If the low-temperature doublets were all of the same separation, one might conclude that the high upper levels are not split and that the basic one has divided this much. However, according to our measurements such cannot be the case, even if there is some splitting in the normal level. This ground state probably does split similarly to the next higher one, though it does so in smaller amount.

[6] The ions in a crystal of $\mathrm{SmCl_3 \cdot 6H_2O}$ must all have the same energy states, since no such selection rules have been found for that salt.

TABLE III. *Prominent "low-temperature" lines and their "high-temperature" satellites (20°K).*

L.-t. line	A_{I}	$\Delta\tilde{\nu}_{A_{\text{I}}}$	A_{II}	$\Delta\tilde{\nu}_{A_{\text{II}}}$	B_{II}	$\Delta\tilde{\nu}_{B_{\text{II}}}$	B_{I}	$\Delta\tilde{\nu}_{B_{\text{I}}}$
17844.9 (I)	17808.3	36.6						
17847.4 (II)			17802.5	44.9	17780	67		
17875.6 (I, II)	17839.3	36.3	17830	46				
17939 (II)			17894	45				
17949 (I)	17912	37					17867	82
18857.2 (II)			18812	45				
18859.6 (I)	18823.1	36.5						
18878 (II)			18832.9	45				
18882.9 (I)	18846.3	36.5						
19985.6 (I, II)	19949.7	35.9	19941	45	19919	67	19904	82
20007.7 (I, II)	19973.2	34.5	19962	46				
20032.9 (I)	19996.2	36.7						
20108 (II)			20063	45				
20117 (I)	20080	37						
20339 (I, II)	20304.7	34	20293	46	20270	69		
20385.9 (I)	20348.9	37.0						
20485 (I, II)	20448	37	20440	45				
20679 (I, II)	20644	35	20636	43				
21511 (?)			21465	46	21445	66		
22040.7 (IIa)			21998	43 } 44.5	21977	64 } 65.5		
22044.0 (IIb)			21998	46 }	21977	67 }		
22048.5 (I)	22011	38					21965	84—
22145 (I, II)	22112	33	22100	45				
22187 (I, II)					22120	67		
22489.3 (I, II)	22453	36	22445	44	22425	64		
22503.5 (I, II)	22467	37	22459	45				
23013 (I, II)			22968	45	22945	68	22931	82
23901.4 (II)			23857.2	44.2				
23904.5 (I)	23867.6	36.9						
24533 (I, II)	24497.9	35	24487	46	24466.0	67		
26579.2 (I, II)	26543	36						
28125.2 (II)			28080	45				
28130.6 (I)	28094	37						
28249 (I, II)	28218	31	28204	45				

The Roman numerals refer to the two components formed at 20° from single lines at 78°.

definite cases of such lines are those at 23,660 to 23,783 (see Table I). Judging from these bands the levels would be separated from the basic one by about 100 to 230 cm^{-1}, probably existing as two doublets with centers at 140 and 220 cm^{-1}.

CONCLUSIONS

The absorption spectra of $Sm(BrO_3)_3 \cdot 9H_2O$ crystals are composed of lines that originate in transitions from a basic state and other low ones to excited levels which are grouped in multiplets. These multiplets probably arise from excited levels that are split apart in the electric field of the crystal. The over-all splitting of these high levels is somewhat less than in the monoclinic chloride.

The separations of the lower levels are also less than in the chloride, being chiefly from 39 to 68 cm^{-1} as compared with 145 to 217 cm^{-1} in the chloride, though greater intervals probably also occur in both. The existence of more than three such levels in the samarium salts makes the assumption of more than one low-lying electronic state, as advocated by one of us,[7] highly probable.[8]

---

[7] Spedding, J. Am. Chem. Soc. **54**, 2593 (1932).

[8] The basic level of Sm^{+++} as predicted by Hund is a $^6H_{5/2}$ and should yield only $J+\frac{1}{2}$ or 3 levels in an electric field.

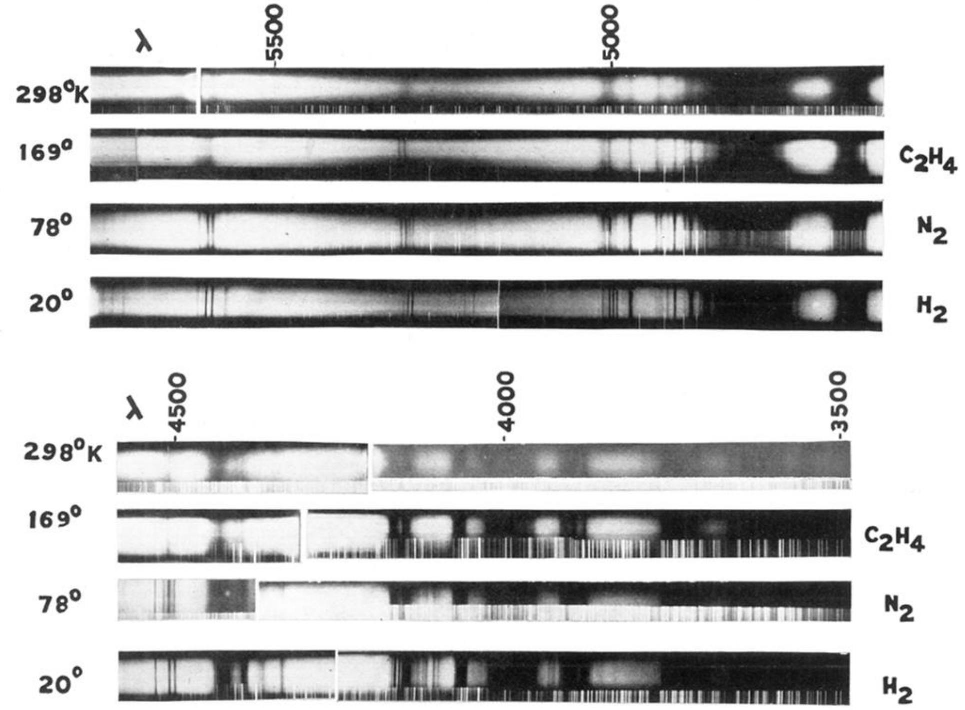

FIG. 1. Conglomerate absorption of $Sm(BrO_3)_3 \cdot 9H_2O$. The substances at whose boiling points the spectra were photographed are indicated on the right, the corresponding temperatures on the left. The three conspicuously simple multiplets on the long wave-length end are considered in more detail in Figs. 2 and 3.

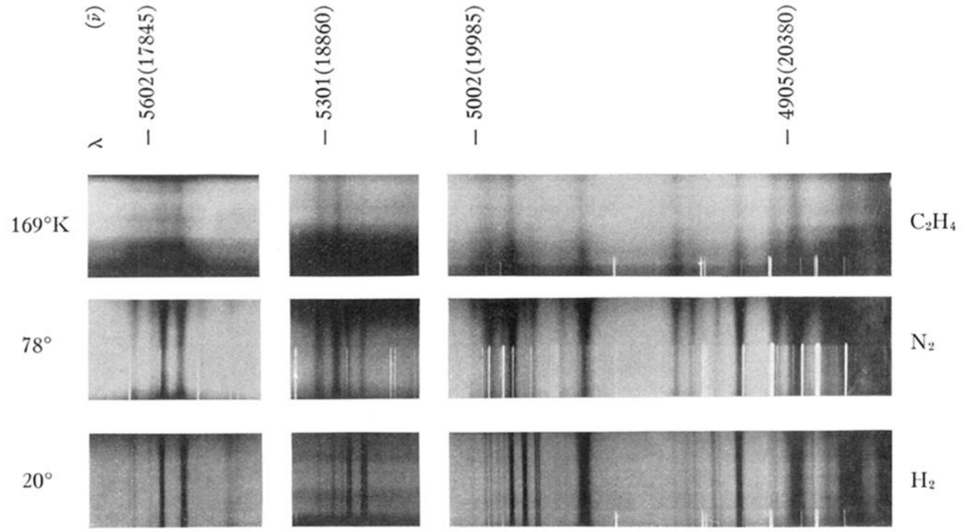

FIG. 2. Selected multiplets of $Sm(BrO_3)_3 \cdot 9H_2O$ absorption. Several of the multiplets of simplest structure are shown here magnified. The temperatures are given on the left, these being the boiling points of the substances on the right. Above are quoted wave-lengths and wave numbers for purposes of orientation with respect to the other figures and tables.