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Foreign Technology Division
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13. ABSTRACT

Absorption bands of IR spectra of the title compds. were assigned and frequencies of fundamental vibrations of mols. of all elements of the group IIIB were detd. Distances metal oxygen in Al_2O and B_2O were estd.

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	ROLE	WT	ROLE	WT	ROLE	WT
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Indium Oxide						
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IR Absorption Spectrum						
Metal Oxide						

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М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

INFRARED ABSORPTION SPECTRA OF ALUMINUM, GALLIUM AND INDIUM SUBOXIDE VAPORS. SOME REGULARITIES IN FREQUENCIES OF OSCILLATIONS OF SUBOXIDES OF ELEMENTS OF THE III GROUP AND EVALUATION OF MOLECULAR CONSTANTS OF B_2O

A. A. Mal'tsev and V. F. Shevel'kov

Continuing the previously begun investigations of spectra of suboxides of elements of the III group of the periodic system of elements [1, 2], we have more thoroughly studied the infrared absorption spectra of Al_2O, Ga_2O and In_2O molecules.

Spectra were obtained on the [IKS-21] (ИКС-21) spectrometer in the 200-2000 cm^{-1} range. Automatic opening of slits permitted determining the position of maxima of absorption bands much more precisely than on other instruments [1]. Evaporation conditions did not fundamentally differ from those described previously [1]. In the case of gallium and indium suboxides, in a number of experiments an insulated quartz container was used with a multipass device [3], which made it possible to operate under purer conditions and also to run experiments in an oxygen atmosphere.

Infrared absorption spectra, frequencies of oscillations, and internuclear distance of boron, aluminum, gallium, indium, and thallium suboxides.

Molecule	Absorption band cm⁻¹	Reference	Fundamental frequencies of oscillations, cm⁻¹			r_{MO}, Å
			ν_1	ν_2	ν_3	
Al_2O	950 (Very intense) 1440 (Average)	ν_3 $\nu_3 + 2\nu_2$ $(2\nu_1)$	710*	235* 245**	994* 950	1,70**
Ga_2O	770 (Very intense) 1140 (Average)	ν_3 $\nu_3 + 2\nu_2$ $(2\nu_1)$	590**	180**	770	1,83*
In_2O	340 (Average) 500 (Weak) 550 (Weak) 680 (Very intense) 990 (Average)	$2\nu_2$ Impurities ν_3 $\nu_3 + 2\nu_2$ $(2\nu_1)$	520**	150–170**	680	2,02*
Tl_2O	480 Intense 620 (Very intense) 890 (Average)	ν_1 ν_3 $\nu_3 + 2\nu_2$ $(2\nu_1)$	480	130**	620	2,15*
B_2O			1450**	4[illegible]0**	1870**	1,29**

* Reference data [4–6].

** Evaluations of authors of article.

The maxima of measured absorption bands of aluminum, gallium, and indium suboxides are given in the table. Given there are maxima of absorption bands of thallium suboxide [2]. It should be noted that after publication of the results of our investigations [1] work [4] came out, in which were determined all fundamental oscillatory frequencies of aluminum suboxide in a matrix of inert gas at the temperature of liquid helium (see table).

With concurrent examination of the spectra of suboxides of elements of the III group it is possible to distinguish two series of bands that are characteristic for all the compounds investigated. These are the series of the most intense bands (950, 770, 680 and 620 cm^{-1}) and the series of shortwave bands (1440, 1140, 990 and

890 cm^{-1}) of average intensity. There is no doubt that the first should belong to antisymmetrical valence oscillations ν_3, and the second to the overtone or compound oscillation. Combining the fundamental frequencies of the Al_2O molecule [4], it is possible to relate its shortwave band (1440 cm^{-1}) to the oscillations $2\nu_1$ or $\nu_3 + 2\nu_2$, if it is considered that the intensity of "hot" bands connected with difference combination frequencies are narrow enough. An analogous reference should be taken also for the remaining molecules of the series under consideration. Preference cannot be given to $2\nu_1$ or $\nu_3 + 2\nu_2$ solely on the basis of sums of component frequencies, since the precision of measurement of maxima of bands is not more than ±10-20 cm^{-1}.

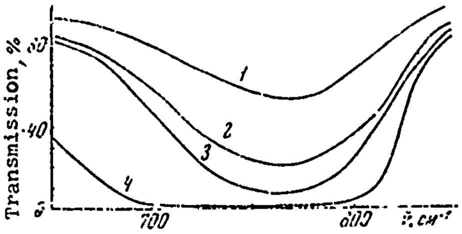
In the present work we could not reproduce a band of about 420 cm^{-1} obtained previously in the absorption of Ga_2O [1]. Inasmuch as the conditions of running experiments in the given work are considerably purer, this band should evidently belong to impurities. As for bands at 340 cm^{-1} in the spectrum of the In_2O molecule, it much rather belongs to overtone $2\nu_2$.

For identity of reference of observable spectra on the example of gallium, indium, and thalluim suboxides, the dependence of intensity of absorption bands upon addition of oxygen additive was studied. It is clear that at high oxygen pressures absorption bands of suboxides must disappear (or be weakened) on account of the formation of oxides. Actually addition of oxygen led to complete disappearance of both absorption bands of vapors over gallium suboxide and bands at 340, 680, and 990 cm^{-1} in the absorption spectrum of vapors over indium suboxide. Therefore, the weak bands at 500 and 550 cm^{-1}, which remain in the spectrum after admission of oxygen, must belong to impurities and not to absorption of In_2O molecules. The effect of oxygen on the spectrum of thallium suboxide vapors is less effective and led only to insignificant weakening of bands [2].

With detailed examination of the obtained spectra attention is attracted by the considerable asymmetry of the bands ν_1 of Ga_2O and In_2O molecules. Given on the figure for example is the absorption spectrum of gallium suboxide in the range 650-850 cm^{-1} at temperatures of 900-1020°C. At high temperatures such "shading" of bands in the direction of lower frequencies can be caused by the following factors: first, formation of R-edging in a rotating structure on account of the difference $B_{001}-B_{000}$; in the second place application of "hot" bands of the type $2\nu_3 - \nu_3$, and third, overlapping of the bands ν_3 and ν_1. Unfortunately the contours of the bands being considered cannot be analyzed into their components without knowing the molecular constants, and therefore an unambiguous interpretation of the asymmetry of bands is impossible.

It was noted above that shortwave bands (1440, 1140, 990, and 890 cm^{-1}) in the absorption spectra of Al_2O, Ga_2O, In_2O, and Tl_2O molecules can belong to oscillations $2\nu_1$ or $\nu_3 + 2\nu_2$. In connection with the fact that the intensity of the band ν_1, which can be a shortwave wing ν_3, is evidently lower than the intensity of the bands being considered, they should be related to component frequency $\nu_3 + 2\nu_2$, since for curved molecules the intensity of the overtone $2\nu_1$ cannot be greater than the intensity of fundamental oscillation ν_1. Such reference permits evaluating the frequency of deformation oscillations ν_2 (see table).

As yet the laws of change of force constants or frequencies of oscillations in series of symmetrical triatomic molecules with replacement of extreme atoms have not been established, and therefore there are no criteria for evaluating the frequencies ν_1 (and ν_2), which are not found experimentally. To at least evaluate the frequencies ν_1 of Ga_2O and In_2O molecules we used a very rough approximation ν_3/ν_1 = constant. The obtained values are given in the table. It is interesting to note that in this case for the whole series of molecules the dependence is observed $\nu_1 + \nu_2 \approx \approx \nu_3$.



Contour of absorption band of gallium suboxide in the range 650-850 cm-1 at temperatures 900 (1), 950 (2), 970 (3), and 1020°C (4).

Reliable proof of the angular structure of suboxides of elements of the III group is the presence in the absorption spectrum of a band of symmetrical valence vibration ν_1. Unfortunately the data of our investigations of the infrared absorption spectra of Al_2O, Ga_2O, and In_2O do not give direct proof of the angular structure of these molecules since the band ν_1 is not clearly marked off. Only in the case of Tl_2O can it be said that the band at 480 cm^{-1}, referred to ν_1, evidences the angular configuration of thallium suboxide. At the same time the absence of visible bands ν_1 in the spectra of heated Al_2O, Ga_2O, and In_2O molecules still does not speak of their linearity and does not refute the data of works [5, 6], according to which Ga_2O, In_2O, and Tl_2O molecules have an angle of about 145°. The picture observed by us is explained, evidently, by the fact that with transition from thallium suboxide to indium suboxide the intensity of the band ν_1 decreases, and moreover at high temperatures it is partially overlapped by an intense and broad band of antisymmetrical oscillation ν_3.

The present interpretation of spectra differs from the original interpretation [1], which was based upon an insufficiently perfected procedure of investigations of vapors of almost involatile compounds and also upon not completely reliable data, which showed that a molecular beam of Al_2O is not deflected in a nonuniform electrical field [7], i.e., an Al_2O molecule is linear.

In order to completely trace the laws in spectra and structure of suboxides of elements of the III group, we tried to obtain the absorption spectrum of vapors of boron suboxide B_2O, which exists in the condensed phase [8]. However, to obtain its spectrum is almost impossible. Therefore, we evaluated frequencies of oscillations of the B_2O molecule (see table), using the fact that the frequency ν_3 of M_2O molecules is very close to the first oscillatory quantum $\Delta G_{1/2}$ of diatomic MO molecules [1], and the fundamental frequencies ν_1, ν_2 and ν_3 are related as discussed above.

Having considered the general regularities in oscillatory frequencies for all suboxides of elements of the III group, it is interesting to trace the regularities also in lengths of bonds in order to evaluate them in such practically important molecules as Al_2O and B_2O. Again based upon the fact that the frequencies ν_3 of suboxides and $\Delta G_{1/2}$ of the corresponding monoxides approximately match, it can be assumed that the lengths of metal-oxygen compounds in these series of molecules vary symbatically, and the geometric configuartion does not vary. Therefore, in our evaluations we used the widely known comparative method [9]. With use of experimental values of MO bonds in gallium, indium [5], and thallium [6] suboxides, which are given in the table, and in the monoxides BO (r_e + 1.20 Å) [10], AlO (r_e + 1.62 Å) [10], GaO (r_0 = = 1.74 Å) [11], and also estimates for the monoxides InO(r_e = = 1.97 Å) and TlO(r_e = 2.07 Å) [12, 13], a graph was plotted of the dependence of $r_{e(MO)}$ upon $r_{(MO)}$ in suboxides and from it by extrapolation the values were obtained of $r_{(MO)}$ for Al_2O and B_2O

molecules given in the table. The found value of r_{AlO} in aluminum suboxide, equal to 1.70 Å, is in satisfactory agreement with the value 1.66 Å, obtained in work [4] through the power constant.

The results given in the summary table can serve as source data for statistical calculation of the thermodynamic functions of the investigated compounds.

Conclusions

The infrared absorption spectra of vapors of aluminum, gallium, and indium suboxides are refined.

Identification was made of absorption bands and values were determined of frequencies of fundamental oscillations of molecules of a whole series of suboxides of elements of the IIIb group.

The internuclear distances of M-O were evaluated in Al_2O and B_2O molecules.

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