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THE DETERMINATION OF CATION CO-ORDINATION IN GLASSES BY INFRA-RED SPECTROSCOPY

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1. Introduction

It is well known that the cation-oxygen vibrational frequencies of a co-ordinated group AO_n depend on the co-ordination number n of the cation, and several authors have applied this relation to the determination of cation co-ordination in glasses. However, these studies have generally been restricted to the so-called glass-forming cations (B, Si, Ge) [1, 2, 3], and much less attention has been paid to the intermediate oxides and to the network-modifiers. Moreover, some fundamental aspects of the spectroscopic problem have been neglected so far, and this may lead in some instances to misinterpretation of the results. It is the purpose of this paper 1) to discuss the spectroscopic aspects of the problem, and 2) to give some applications of the spectroscopic method to the case of intermediate oxides.

2. The spectroscopic aspects of the problem

2.1. THE CONCEPT OF "SEPARATE" OR "INDEPENDENT" VIBRATIONS

At first sight, the idea of considering the infra-red spectrum of a solid $A_xB_yO_z$ as the result of the vibrations of AO_p and BO_r co-ordinated groups is somewhat puzzling for the spectroscopist. A given oxygen atom is generally bonded to both A and B atoms, and thus there must be some interaction between the vibrations of the AO_p and BO_r co-ordinated groups. Strictly speaking, the vibrations are those of the whole unit cell; but in most cases, a rigorous treatment is unthinkable because of the mathematical complexity of such a treatment.

If, however, vibrational interactions between AO_p and BO_r co-ordinated groups are negligible or weak, it is possible to assign the bands to either AO_p or BO_r groups, which are thus considered as vibrating independently.

This concept of "separate" or "independent" vibrations has been put forward and discussed by the author a few years ago [4]; it has now been tested in a number of cases and found fundamentally correct when the vibrational frequencies of the AO_p and BO_r groups are very different [5, 6]. Things are less simple when some of the vibrational frequencies have similar values: in some cases, the concept of separate vibrations is still valid; but in others, severe vibrational interactions have been observed, thus preventing the assignment of the bands to a definite co-ordinated group.

2.2. FACTORS INFLUENCING THE VIBRATIONAL FREQUENCIES OF A CO-ORDINATED GROUP AO_n , TO WHICH THE CONCEPT OF SEPARATE VIBRATIONS MAY BE APPLIED

These factors are as follows:

- 1) The chemical nature and the valency state of the cation A,
- 2) The value of the co-ordination number n ,
- 3) The "isolated" or "condensed" state of the co-ordinated groups.

2.2.1. The first of these factors, namely the chemical nature and the valency state of the cation A, does not need lengthy comments. It will just be remembered that the highly ionic bonds given by cations such as Na^+ or K^+ have no specific infrared frequencies and thus cannot be studied by infrared spectroscopy.

2.2.2. The influence of the co-ordination number n has been first observed with typical network formers such as boron and germanium [1, 2, 3], and with a few intermediate elements such as aluminum [7] and titanium [8, 9], the vibrational frequencies being higher for the smaller co-ordination numbers. Later on, the investigation of this effect has been extended to a fairly large number of cations (such as Fe^{III} , Ga, Mg, Zn, Co, Ni, Fe^{II} , Li [5, 6]); quite similar results were obtained, and it is highly probable that this variation of the vibrational frequencies with the co-ordination number is a general phenomenon.

A detailed discussion of the physical principles involved is out of place here; but this effect may be simply summarized as follows: *the smaller the co-ordination number, the shorter the bond length and hence the higher the vibrational frequencies.*

2.2.3. The relation between vibrational frequencies and co-ordination number is only an approximate one, first because there is always a more or

less important influence of the neighbouring groups (in other words, the concept of "separate" vibrations is always an approximation), and also because of an additional effect, namely the "isolated" or "condensed" state of the co-ordinated groups under consideration.

This effect is well known in silicates (in *ortho*-silicates, with "isolated" SiO_4 tetrahedra, the strongest bands are generally observed near 900–950 cm^{-1} ; in *poly*-silicates, with "condensed" SiO_4 tetrahedra, this absorption is extended to much higher frequencies, 1100 cm^{-1} or more); but curiously enough, this shift has been ignored or neglected by most authors in the case of other cations.

The values collected in table 1 show the importance of this effect, and its possible incidence on the determination of cation co-ordination by infra-red

TABLE I
Characteristic frequency ranges of some co-ordinated groups*

Cation X	Absorption range in cm^{-1}			
	XO_4 tetrahedra		XO_6 octahedra	
	Condensed	Isolated	Condensed	Isolated
Ge	900–700	850–680	700–550	~500(?)
Ti ^{IV}		800–690	650–500	<500(?)
Al	900–700	800–650	650–500	530–400
Ga	750–600	700–570	600–500	~450–400
Fe ^{III}	750–550	650–550	550–400	450–300
Zn	600–400	500–450	~300(?)	
Mg		600–500	480–350	
Li	600–400	500–400	<300(?)	

* The wave number or repetency λ^{-1} is called "frequency" here, as is the rule in spectroscopy, but not in general ISO terminology.

spectroscopy. The extension towards higher frequencies observed with "condensed" groups is particularly important for six-fold (octahedral) co-ordination and, for certain cations at least, there is some overlapping of the absorption ranges of "isolated" tetrahedra and "condensed" octahedra. It is quite clear that uncautious use of such data may lead to serious errors; this really happened a few years ago in the case of germanium [18].

2.3. OCCURRENCE AND DETERMINATION OF CHARACTERISTIC FREQUENCY RANGES

The question now arises to know whether a reasonably narrow frequency range may be assigned to a given co-ordinated group AO_n , since the proper

vibrational frequencies of the group may be more or less perturbed by the above-mentioned factors (essentially the frequency shift in "condensed" groups, and/or the occurrence of vibrational interactions with other groups).

Experimental studies on a number of crystalline compounds with widely different structures give an essentially positive answer [6]. Except for some cases of severe vibrational interactions, the frequencies of a given co-ordinated group are generally observed in a determined spectral range, which is not too broad and may be considered as typical for the group under consideration. Moreover, the data collected in table 1 show that the characteristic range for four-fold and six-fold co-ordination of a given cation seldom overlap: this is an essential condition for the applicability of these data to the determination of co-ordination numbers.

A further word should be added about what is meant by "characteristic frequency range". It is well known that the vibrations of any polyatomic group may be roughly divided into "stretching" and "bending" vibrations. The bending vibrations are characterized by much lower frequencies (frequently outside the spectral range accessible to most commercial instruments), and generally lower intensities than the stretching vibrations; consequently, their usefulness is much reduced.

The characteristic frequency ranges used in table 1 are thus related to the stretching vibrations only.

The determination of the characteristic frequency ranges is in fact a problem of band assignment. This problem, and appropriate experimental methods for its solution have been discussed elsewhere [4, 6]. These experimental methods may be summarized as follows:

- 1) Use of isotopic shifts. This method, the most rigorous one, is necessarily restricted to light cations such as lithium and boron.

- 2) Study of compounds of such a structure that the co-ordinated group under investigation is the single group which contributes to the IR spectrum.

- 3) Systematic use of the method of isomorphic substitution [4]. If two compounds $A_xB_yO_z$ and $A_xC_yO_z$ give a complete series of solid solutions, the infra-red study of these solid solutions may lead to a fairly detailed assignment of the bands, as far as the concept of separate vibrations may be applied.

2.4. APPLICATION TO VITREOUS SYSTEMS

The experimental determination of the characteristic frequency ranges is carried out on crystalline compounds of known structure. The transferability

of these data to vitreous systems is generally granted as a fact, but this transferability should now be briefly discussed.

It is true that the characteristic frequencies apply to co-ordinated groups in widely different crystalline structures, and thus, it seems quite obvious to extend them to glassy systems.

It should be remembered, however, that the characteristic frequencies are valid only in the absence of important vibrational couplings. This may be checked with crystalline compounds, as vibrational couplings bring out important perturbations in the spectra [6, 10]; but unfortunately, this kind of checking cannot be extended to glassy structures and consequently, some assignments cannot be done with full certitude.

The broadness of the infra-red bands of glassy substances may also prevent reliable assignments, particularly if two or more bands are superimposed in the same spectral region and blended into an ill-defined absorption.

For these reasons, assignments must be made particularly cautiously and they should rely not merely upon a simple comparison of observed infra-red bands with the characteristic frequency ranges, but also upon a careful discussion of the spectra of parent or similar glasses.

3. Some experimental results and their interpretation

3.1. ALUMINA-SILICA GLASSES

The infra-red frequencies of AlO_4 tetrahedra and AlO_6 octahedra have been recently investigated and discussed by several authors, but with quite conflicting conclusions.

The ranges ~ 1200 , 1000 or $900\text{--}700\text{ cm}^{-1}$ have been in turn assigned to AlO_4 tetrahedra; data on AlO_6 octahedra are fairly scarce, but the proposed characteristic frequencies range from ~ 750 to 400 cm^{-1} .

These discrepancies most probably come from the fact that most authors have neglected some of the complications mentioned in § 2 of this paper: they have sometimes assigned to Al-O vibrations absorption bands which are clearly related to mixed vibrations of complex groups (for example Si-O-Al vibrations); and in other cases, they did not make any difference between the frequencies of "isolated" or "condensed" groups.

The author has investigated a series of aluminates and aluminum oxides (so as to eliminate the possibility of mixed Si-O-Al vibrations) and aluminum silicates of the garnet type. The results are collected in table 2. Clearly, the characteristic frequency range of AlO_4 tetrahedra does not extend beyond

TABLE 2

Stretching frequencies of Al-O bonds in various compounds

Compound	AlO ₄ tetrahedra		AlO ₆ octahedra	
	Condensed	Isolated	Condensed	Isolated
LiAl ₅ O ₈		800-650		
5Al ₂ O ₃ ·3Y ₂ O ₃		800-700		
β-Al ₂ O ₃	850-700			
LiAlO ₂	850-800			
CaAl ₂ O ₄	870-750			
Ca ₂ Al ₂ (OH) ₆				~ 525
Ca ₂ Al ₂ Si ₂ O ₁₂				500-400
α-Al ₂ O ₃			650-600	

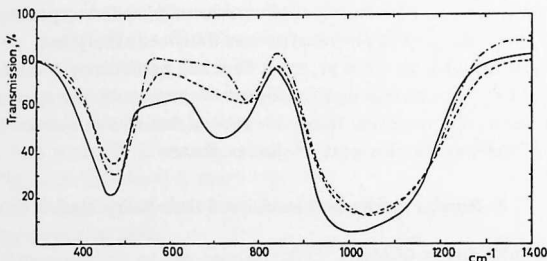


Fig. 1. Infra-red spectra of alumina-silica glasses.

Curve-----Reference glass (No. 1, free from alumina);
 Curve---Glass No. 2 (9,4 % by weight of alumina);
 Curve——Glass No. 3 (25,2 % of alumina).

900 cm^{-1} , and the suggested figures of 1000 or 1200 cm^{-1} correspond to mixed Si-O-Al frequencies.

Fig. 1 shows the infra-red spectrum of a conventional $\text{Na}_2\text{O-CaO-SiO}_2$ glass, and the spectrum of two silicate glasses with increasing amounts of alumina*. Apart from a slight shift in the position of the strong SiO_4 band near 1050 cm^{-1} , the only significant change in the spectrum is the growing of a moderately strong band near 800-700 cm^{-1} . This band has already been observed by different authors in the infra-red spectra of alumino-silicate glasses, and it is generally assigned to AlO_4 tetrahedra [11, 12]. This assignment is in agreement with the characteristic ranges given in table 2, and

* The compositions are collected in table 3. They are given in wt% for complex glasses. Molar compositions have been used for the simple ones.

TABLE 3
Composition of the glasses investigated

No. 1. Na ₂ O: 13,86; CaO: 14,76; SiO ₂ : 70,49 (Reference glass)*
<i>Alumina-silica glasses</i>
No. 2. Na ₂ O: 13,5; CaO: 6,8; MgO: 3,3; Al ₂ O ₃ : 9,4; SiO ₂ : 66,4*
No. 3. Na ₂ O: 15,3; Al ₂ O ₃ : 25,2; SiO ₂ : 59,5 (= NaAlSi ₂ O ₆)*
<i>Magnesia-silica glass</i>
No. 4. Na ₂ O: 14,00; CaO: 0,54; MgO: 14,05; SiO ₂ : 70,30*
<i>Zinc-silica glasses</i>
No. 5. Na ₂ O+CaO: 30; ZnO: —; SiO ₂ : 70 (Reference glass)*
No. 6. Na ₂ O+CaO: 30; ZnO: 8; SiO ₂ : 62 *
No. 7. Na ₂ O+CaO: 30; ZnO: 22; SiO ₂ : 48 *
<i>Titania-silica glasses</i>
No. 8. Na ₂ O: 1; TiO ₂ : 1; SiO ₂ : 3 **
No. 9. Na ₂ O: 2; TiO ₂ : 3; SiO ₂ : 5 **
No. 10. Na ₂ O: 1; TiO ₂ : 2; SiO ₂ : 1 **
No. 11. BaO : 1; TiO ₂ : 1; SiO ₂ : 2 **
<i>Lithium glasses</i>
No. 12. Li ₂ O: 1; B ₂ O ₃ : 1 **
No. 13. Li ₂ O: 1; SiO ₂ : 1 **
No. 14. Li ₂ O: 1; SiO ₂ : 2 **
No. 15. K ₂ O: 10,02; PbO: 35,13; SiO ₂ : 53,80 *

* Composition in weight (%).

** Composition in moles.

with other experimental data obtained by quite different methods such as molar refractivity [12] or X-ray fluorescence [13].

It is much harder to detect six-fold co-ordination of aluminum by infrared spectroscopy, at least in the glasses investigated here. As most of the aluminum is engaged in AlO₄ tetrahedra, the few (if any) AlO₆ octahedra may be considered as "isolated" and thus should absorb near 500 cm⁻¹, where their own absorption is likely to be masked by the strong SiO₄ band centered near 475 cm⁻¹. The comparative spectra of fig. 1 shows only minor, non-significant differences in this region: this suggests that AlO₆ octahedra are either missing, or in fairly low concentration, in agreement with the conclusions drawn from molar refractivity [12] and X-ray fluorescence data [13].

The possibility of five-fold co-ordination of aluminum will not be discussed here, because of the lack of experimental data. This co-ordination

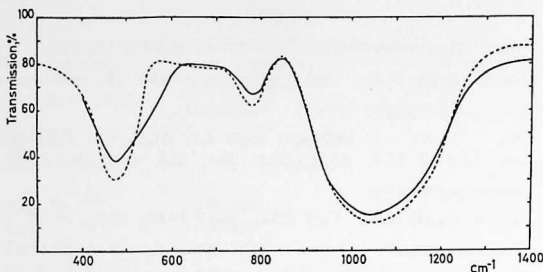


Fig. 2. Infrared spectrum of a magnesia-silica glass.
 Curve-----Reference glass (No. 1);
 Curve——Glass No. 4 (14,05 % by weight of magnesia).

has been found in some aluminum compounds and its occurrence in glassy structures is possible, but no characteristic infra-red data are available.

The aluminum glasses investigated here show a weak, ill-defined absorption near 600 cm^{-1} , for which no definite assignment can be put forward: this absorption can be related either to AlO_5 groups, or to Si-O-Al mixed vibrations.

3.2. MAGNESIA-SILICA GLASSES

Apart from results obtained in this laboratory and summarized in table 1, no data on the characteristic infra-red frequencies of MgO_4 or MgO_6 groups have been published so far. The spectrum of a $\text{Na}_2\text{O-MgO-SiO}_2$ glass is essentially characterized by a rather diffuse absorption in the $600\text{--}550\text{ cm}^{-1}$ region, but no significant change in the SiO_4 bands. The diffuse absorption is thus closely related to the presence of magnesium and, by comparison with the frequency ranges reported in table 1, suggests the presence of MgO_4 tetrahedra.

3.3. ZINC-SILICA GLASSES

Zinc has a marked preference for four-fold co-ordination in its crystalline compounds, and this behaviour is expected to be preserved in glassy structures. The case of silicate glasses is, however, quite unfavourable because ZnO_4 tetrahedra absorb mainly in the $500\text{--}540\text{ cm}^{-1}$ region (table 1), which is obscured by a strong SiO_4 band.

Comparative spectra of fig. 3 show a downward shift of the strong SiO_4

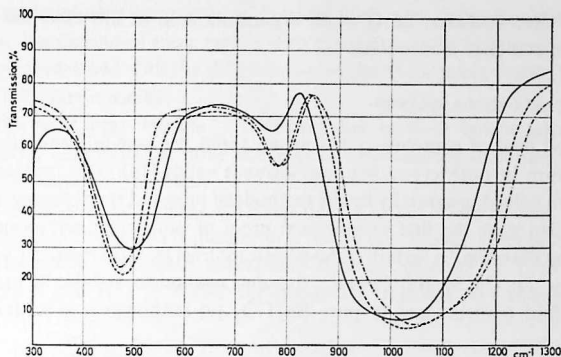


Fig. 3. Infrared spectra of zinc-silica glasses.

Curve-----Reference glass (No. 5, free from ZnO);

Curves——and——: glasses No. 6 and 7 (8 and 22 % by weight of ZnO respectively).

TABLE 4

No.	Glass	Frequency (cm^{-1}) of the SiO_4 bending vibration
	<i>Silica</i>	475
1	$\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{SiO}_2$	475
15	$\text{K}_2\text{O} \cdot \text{PbO} \cdot \text{SiO}_2$	475
11	$\text{BaO} \cdot \text{TiO}_2 \cdot 2 \text{SiO}_2$	470
4	$\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$	475
	<i>Pyrex</i>	475
2	$\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	475
7	$\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{ZnO} \cdot \text{SiO}_2$	500

band near 1050 cm^{-1} with increasing ZnO content, but an upward shift of the 475 cm^{-1} band.

If the SiO_4 high frequency band is known to be fairly sensitive to the amount and chemical nature of additional cations, this does not apply to the 475 cm^{-1} band, the position of which has been found to be fairly constant in a number of silicate glasses of widely different compositions. Now, this band is shifted to 500 cm^{-1} in the glass with high ZnO content and, in view of its nearly constant position in a variety of glasses (table 4), this shift would possibly suggest the presence of a superimposed second band related to ZnO_4 tetrahedra, an hypothesis which is also in accordance with the progressive broadening of the band when the ZnO content increases.

These are, however, fairly weak arguments and, in this case, the spectroscopic evidence is inconclusive.

3.4. TITANIA-SILICA GLASSES

A good deal of controversy has arisen about the four-fold co-ordination of titanium in both crystalline and vitreous solids [14]. This problem has now been solved, essentially by the methods of infra-red spectroscopy. Infra-red spectra gave the first unequivocal proof of isomorphic replacement of silicon by titanium, in certain *ortho*-silicates at least [8, 9] (garnets and X_2SiO_4 with $X = Zn, Ca, Sr, Ba$); later on, the same method proved that all titanium is four-fold co-ordinated in pure Ba_2TiO_4 [9] (although it is six-fold co-

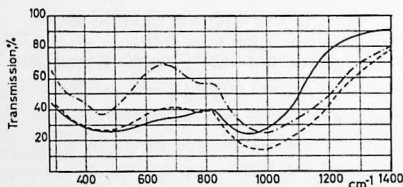


Fig. 4. Infrared spectra of titania-silica glasses.

Curve - - - - - Glass No. 8, of molar composition $Na_2O.TiO_2.3 SiO_2$;
 Curve - · - · - Glass No. 9, of molar composition $2 Na_2O.3 TiO_2.5 SiO_2$;
 Curve ——— Glass No. 10, of molar composition $Na_2O.2 TiO_2.SiO_2$.

ordinated in Sr_2TiO_4) and this quite unexpected result was confirmed simultaneously and independently by a detailed X-ray study of monocrystals [15].

Infra-red studies of titanium glasses have been generally restricted to compositions with fairly low titanium content, and to the near or medium infra-red region [16]. Results given by glasses with high titanium content will be presented here.

Figure 4 shows the spectra of $Na_2-SiO_2-TiO_2$ glasses, with a TiO_2 amount varying from 20 to 50 moles %.

These glasses have a broad absorption extending from 800 to 300 cm^{-1} , the intensity of which increases with the TiO_2 content. The sample with a very high TiO_2 content (50 moles %) gives a spectrum essentially characterized by the following features:

1) An extremely diffuse absorption extending from 850 cm^{-1} down to 300 cm^{-1} ;

2) One band only (near 940 cm^{-1}) has a fairly well defined contour.

Now, comparison of these results with the well-known frequencies of the SiO_4 tetrahedra and with the data relative to the Ti-O bonds (table 1) leads to the following remarks:

1) The band near 940 cm^{-1} is clearly due to Si-O bonds (stretching frequency); this numerical value points to an *ortho*-silicate structure, i.e. the SiO_4 tetrahedra are "isolated".

The other band commonly observed near 475 cm^{-1} in silicate glasses (SiO_4 bending frequency) is merged in a nearly continuous absorption.

2) The nearly continuous absorption must be assigned to Ti-O bonds (and possibly to Ti-O-Si mixed vibrations). Its extension to frequencies as

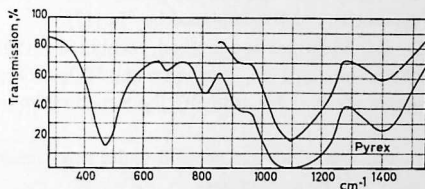


Fig. 5. Infrared spectrum of a Pyrex commercial glass.

high as 800 cm^{-1} suggests that a certain amount of titanium is four-fold co-ordinated; its nearly continuous character is accounted for if one imagines that all the possible co-ordinations of titanium (4, 5 and 6) are present in such a glass.

The infra-red data also allow some conclusions to be drawn about the degree of order or disorder present in such glasses. The *ortho*-silicate structure indicated by the 940 cm^{-1} value for the SiO_4 stretching frequency would not be realized if the SiO_4 tetrahedra were concentrated in distinct micelles. This leads to the conclusion that the two glass-forming units, namely SiO_4 and TiO_4 tetrahedra, are more or less uniformly distributed in the glassy structure. This is supported by the extreme diffuseness of the spectrum, which suggests a highly disordered structure.

This type of glassy network is quite different from glasses such as borosilicates, where the two glass-forming oxides are concentrated in distinct micelles. This results in a well-defined infra-red spectrum with relatively narrow bands (fig. 5).

3.5. LITHIUM BORATE AND SILICATE GLASSES

Because of its low atomic number, lithium is not easily detected by the conventional X-ray methods, and the study of its structural role in glasses is difficult.

Infra-red bands related to LiO_4 tetrahedra have been recently identified in the spectra of simple crystalline lithium compounds [6, 17]. These bands are generally located in the $550\text{--}400\text{ cm}^{-1}$ range, whereas LiO_6 octahedra do not absorb in this region (no bands related to LiO_6 octahedra have been observed so far; they are most probably located below 300 cm^{-1} , the low frequency limit of our actual infra-red equipment). On the other hand, Li-O infra-red bands are easily identified by a frequency shift of $20\text{--}30\text{ cm}^{-1}$ when natural lithium (essentially ^7Li) is replaced by ^6Li [17].

This unquestionable identification method, combined with the differences in spectroscopic behaviour of LiO_4 tetrahedra and LiO_6 octahedra, provides a new and attractive method for studying the structural role of lithium in glasses.

The possibilities of this technique are still under investigation, and a few positive results only will be quoted here.

Figure 6 shows the infra-red spectra of crystalline (high-temperature form) and glassy LiBO_2 . The $^6\text{Li}\text{--}^7\text{Li}$ isotopic shift is quite evident in the spectrum of crystalline LiBO_2 , where all the low frequency bands are displaced by an amount of $17\text{--}28\text{ cm}^{-1}$ (table 5); this is a clear-cut proof of four-fold co-ordination of lithium.

The evidence is perhaps not so striking for glassy LiBO_2 , because of the broadness of the bands; nevertheless, the $^6\text{Li}\text{--}^7\text{Li}$ isotopic shift is easily detected in the low frequency band near 460 cm^{-1} , thus proving that lithium has at least predominantly retained its four-fold co-ordination in the glassy network.

This case may be considered as a most favourable one, because of the high lithium content, and of the absence of B-O bands in the low frequency region.

Lithium silicate glasses are much less favourable from this point of view because possible LiO_4 bands may be masked by the strong SiO_4 band located near $500\text{--}450\text{ cm}^{-1}$. Nevertheless, the $^6\text{Li}\text{--}^7\text{Li}$ isotopic shift appears clearly in the infra-red spectrum of glassy Li_2SiO_3 (fig. 7); this effect is much attenuated, but still detectable, in the spectrum of glassy $\text{Li}_2\text{Si}_2\text{O}_5$ (fig. 8).

The isotopic shift is by itself a sufficient proof for the occurrence of a LiO_4

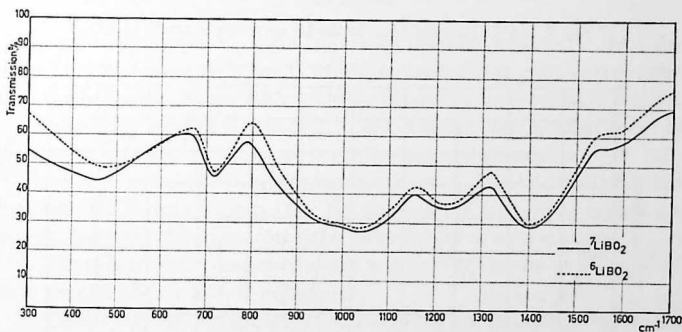
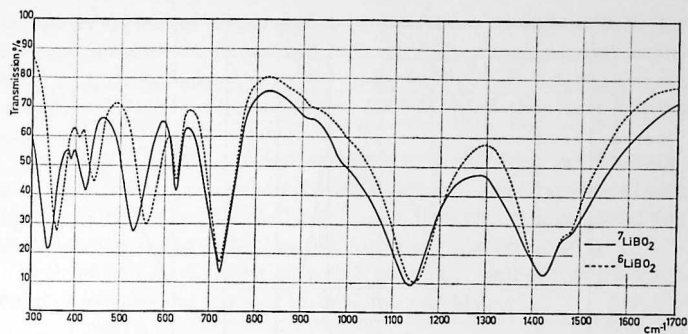


Fig. 6 (a). ${}^6\text{Li}$ - ${}^7\text{Li}$ isotopic effect in the spectrum of crystalline LiBO_2 ;
 (b). the same effect in the spectrum of glassy LiBO_2 .

TABLE 5

${}^6\text{Li}$ - ${}^7\text{Li}$ isotope effect on the low frequency bands of crystalline and glassy LiBO_2

Crystal			Glass		
${}^6\text{LiBO}_2$	${}^7\text{LiBO}_2$	$\Delta\nu$	${}^6\text{LiBO}_2$	${}^7\text{LiBO}_2$	$\Delta\nu$
725	725	0	~722	~720	(-2)
633	632	(-1)			
564	536	-28			
445	422	-23	~480	~460	~-20
408	391	-17			
358	340	-18			

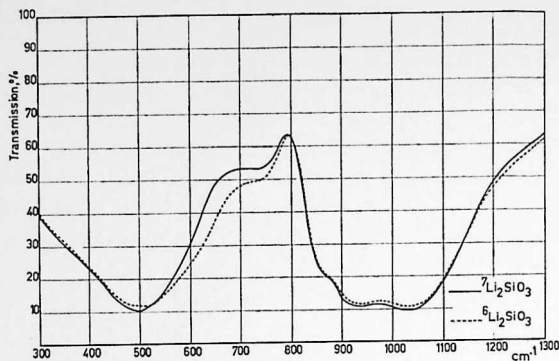


Fig. 7. ${}^6\text{Li}$ - ${}^7\text{Li}$ isotopic effect in the IR spectrum of glassy Li_2SiO_3

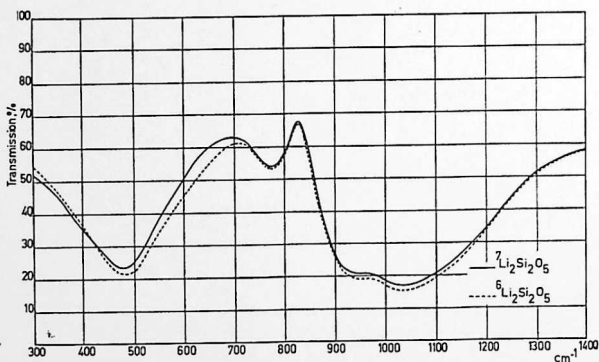


Fig. 8. ${}^6\text{Li}$ - ${}^7\text{Li}$ isotopic effect in the IR spectrum of glassy $\text{Li}_2\text{Si}_2\text{O}_5$

band; it is worth mentioning, however, that two further features point to the superposition of two bands near 500 cm^{-1} : the high intensity of the band, and its broadness.

It has been observed in a fairly large number of silicate glasses that the band related to the SiO_4 stretching frequency (near 1000–1100 cm^{-1}) is always more intense than the band corresponding to the SiO_4 bending frequency (this is in fact a well-known and quite general phenomenon). In

the case of the lithium silicate glasses discussed here, it will be noticed that the peak intensities of the 500 and 1000 cm^{-1} absorption are very nearly equal for Li_2SiO_3 , and not very different for $\text{Li}_2\text{Si}_2\text{O}_5$. This suggests that a second band (LiO_4) is superimposed on the SiO_4 band, thus increasing the total intensity of the absorption.

The shape of the band under consideration is also fairly characteristic: these bands have a half-width of about 200–250 cm^{-1} , to be compared with 50–100 cm^{-1} for a number of silicate glasses. Here also, it is suggested that the broadening is due to the superposition of two components.

Thus, we have good experimental evidence that at least part of lithium is four-fold co-ordinated in glassy Li_2SiO_3 and $\text{Li}_2\text{Si}_2\text{O}_5$.

4. Conclusions

The infra-red spectra of glasses containing elements such as Al, Mg, Zn, Ti or Li exhibit absorption bands which, in most of the cases investigated here, can be assigned with confidence to the tetrahedrally co-ordinated cation.

Infra-red spectroscopy is thus able to give a direct, unequivocal proof of the structural role of these cations in the investigated glasses.

The picture is, however, rather incomplete, as six-fold co-ordination has been detected in one case only (Ti). The detection of six-fold co-ordination by infra-red absorption spectroscopy is not easy for several reasons:

- 1) The characteristic frequency range is generally not so well delimited as in the case of four-fold co-ordination;
- 2) These vibrations are generally located in the low frequency region, the experimental study of which is difficult;
- 3) The bonds corresponding to six-fold co-ordination have a fairly ionic character with, as a consequence, much less characteristic frequencies.

Besides the difficulties inherent to the study of the groups with high co-ordination numbers, the application of infra-red spectroscopy to structural studies of glasses suffers from more general drawbacks such as:

- 1) Lack of sensitivity, essentially due to the broadness of the bands;
- 2) Difficulties in the correct assignment of the bands; in some cases, it is quite impossible to choose between several interpretations;
- 3) Impossibility to study the structural role of the most characteristic network modifiers such as Na or K;
- 4) Complete lack of data on the heavy cations such as Pb or Ba.

Among these problems, some are a consequence of the physical principles

involved in the method, so that the situation cannot be seriously improved: these are for example the lack of sensitivity and the impossibility of studying Na or K; but some other difficulties will be at least partially overcome by further systematic studies: this is certainly true for several problems of interpretation, and for the detection and study of six-fold co-ordination.

5. Experimental

Glasses were prepared by fusion in Pt crucibles of the appropriate amounts of component oxides or carbonates. Reagents of analytical purity were used for those glasses, the compositions of which correspond to definite crystalline compounds.

Infra-red spectra were registered with a double-beam Unicam SP 100 spectrometer equipped with NaCl and KBr prisms ($2000\text{--}400\text{ cm}^{-1}$); the low frequency range ($400\text{--}300\text{ cm}^{-1}$) has been scanned with a Perkin-Elmer 112 (single beam, double pass) spectrometer equipped with a CsBr prism.

The KBr disc method was used for all samples; Nujol mulls were also used as a check in the case of lithium compounds and glasses.

Some of the glasses have been prepared at the "Institut National du Verre" under the direction of Drs. P. Gilard and P. Migeotte; their kind collaboration has been of great help in the preparative part of this work. The author gratefully acknowledges the financial support given by the "Fonds National de la Recherche Scientifique".

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Discussion

STEVENS: Are there any examples for Al^{3+} in fourfold coordination in *crystals* and if so, what infrared absorption bands must be assigned to this configuration?

TARTE: Four-fold co-ordination of aluminum in crystals is rather common: this co-ordination is found in some varieties of alumina (β , γ , δ ...), in a number of aluminates such as $CaAl_2O_4$ (silica-like structure), $LiAl_5O_8$ (spinel), $Y_3Al_5O_{12}$ (garnet), and in alumino-silicates (melilites, feldspaths, etc...).

Despite the diversity in chemical composition and crystal structure of these compounds, the IR absorption bands related to AlO_4 tetrahedra are always found in the $900-650\text{ cm}^{-1}$ region; some difficulties, however, may arise with alumino-silicates, because of the possible occurrence of mixed Al-O-Si vibrations.

MACKENZIE: If you have no prior knowledge from crystal absorption, can you assign the absorption bands in glass to any particular coordination from theoretical consideration?

TARTE: I am not able to discuss this point in detail, as I have no experience in this particular field. During the discussion, Dr. Egelstaff kindly pointed out that some vibrational frequencies can be deduced from lattice vibration theory.

I think, however, that realistic theoretical calculations are possible in very simple cases only. On the other hand, it is always possible to find appropriate crystalline compounds for experimental studies, which not only allow a safe determination of the absorption ranges, but also may bring the worker's attention on unexpected difficulties such as vibrational interactions. These are the reasons for which experimental determinations have been preferred so far.

GEFFCKEN: You have only plotted the transmission values. But you are in a frequency region where the refractive index shows anomalous dispersion with steep increase in a narrow region. This might influence the transmission. Are you sure your results are not affected by it?

TARTE: It is true that the transmission pattern is able to be affected by anomalous dispersion and reflection effects. However, with the type of substances investigated here, and when both transmission and reflection data were available, it has been found that the position of the transmission and reflection peaks were very similar.

This is the important point here, as the assignment to a given co-ordination number does not rely on precise frequency measurements, but on the comparison with a frequency range.