

Use of medium-weight isotopes in infrared spectroscopy of inorganic solids: A new method of vibrational assignments

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Abstract—Isotopic shifts related to medium-weight cations (Mg, Ca, Ni, Zn, Cr, Ge) have been observed in the vibrational spectrum of inorganic solids. It is possible, by this technique, to evidence the simultaneous participation of several cations to a given vibrational frequency. These data may be of great help in solving the difficult problem of vibrational assignments. The possibilities and limitations of the method are briefly outlined.

INTRODUCTION

THE correct and complete interpretation of the vibrational spectrum of an inorganic solid is often a difficult problem if two or more cations are present in the compound investigated.

If this compound is a salt, the occurrence of a well individualized complex anion leads to the well-known separation of the normal modes into the so-called internal and external vibrations. But there always remains the possibility of vibrational interactions between internal and external vibrations which belong to the same class of symmetry. Moreover, if the salt is constituted of a fairly light, polyvalent, cation associated with a heavy complex anion, some of the external frequencies may be as high as (or even higher than) the low-lying internal frequencies (corresponding to the bending motions of the complex anion). This quite unfavourable situation may lead to erroneous or meaningless interpretations.

On the other hand, if compounds of the double-oxide type are dealt with, the usefulness of the concept of internal and external vibrations is considerably reduced. Some at least of the vibrations are not related to a particular cation-oxygen bond (or to a given co-ordinated group), but to complex motions involving the displacement of two (or more) different cations.

Very few cases of this type have been handled. Success was met only for very simple and symmetrical structures (such as BaTiO_3), whereas uncompatible and conflicting assignments were recently published for such compounds as the rare earth garnets [1-3].

Now, it should be pointed out that these assignment problems cannot be solved by theoretical considerations only: a group theoretical treatment leads to the classification and numbering of the vibrations into symmetry classes, and a normal co-ordinate analysis will give information about the displacements of the atoms.

[1] J. P. HURRELL, S. P. S. PORTO, I. F. CHANG, S. S. MITRA and R. P. BAUMAN, *Phys. Rev.* **173**, 851 (1968).

[2] J. A. KONINGSTEIN and O. SONNICH MORTENSEN, *J. Mol. Spectry* **27**, 343 (1968).

[3] N. T. McDEVITT, *J. Opt. Soc. Am.* **59**, 1240 (1969).

But none of these methods will lead to an unequivocal correlation between the normal modes of vibration and the observed frequencies. In some instances, these correlations may be evident but, apart from the frequencies of some characteristic complex anions, such simple cases are rarely met with when handling the vibrational spectrum of inorganic solids. To solve this assignment problem, we must know to what extent one or several given cations are involved in the frequency under consideration; and this in turn will be found by modifying the cations and looking at the corresponding modifications in the spectrum.

The modification of the cation may be obtained by replacing the cation, either by one of its isotopes (isotopic replacement) or by a different cation which, however, does not change the crystal structure (isomorphic replacement). The possibilities and limitations of the method of isomorphic substitution have been investigated by the authors for several families of compounds [4-6]. Although successful results have been obtained in a number of cases, the interpretation of the experimental data is not always evident, since the isomorphic replacement of a cation by another involves a *simultaneous* change of *four* parameters which are able to modify the vibrational frequencies, namely the cationic mass, the cation-oxygen distance and bonding force, and the unit cell dimensions.

From the theoretical point of view, the isotopic replacement is much more favourable, since one parameter only, the cationic mass, is modified. Its use, however, has been restricted so far to light cations such as lithium [7]. The method has never been applied to medium- or heavy-weight cations, for 2 reasons at least: (1) The trivial, but important problem of availability of such stable isotopic species; (2) The rather small frequency shifts which are to be expected for isotopic cations, the mass ratio of which is not very different from unity (1.10 in the most favourable case).

Nevertheless, we found it worthwhile to investigate the possibilities of this technique. This paper is devoted to a general survey of the present results. More detailed and systematic studies on selected families of compounds will be reported in due time.

EXPERIMENTAL

The spectra have been recorded with a Beckman IR-12 spectrophotometer in the 1500-200 cm^{-1} region, a CAMECA SI 36 spectrometer in the 200-50 cm^{-1} region, KI and polythene discs being used in turn.

Since the isotopic shifts are generally small, the precision and the reproducibility of frequency measurements are of prime importance. The reproducibility has been determined on a solid compound, MgRh_2O_4 , which gives a very sharp band near 250 cm^{-1} . This band was scanned ten times, the recording conditions being those already selected for the isotopic spectra (low scanning speed and frequency scale expansion); the band position was found to be reproducible to better than $\pm 0.2 \text{ cm}^{-1}$. It is evident that, in most cases, the precision of the frequency measurements is limited by, and depends on, the intrinsic broadness of the bands.

[4] P. TARTE, *Mém. Acad. Roy. Belges* **35**, 4a and 4b (1965).

[5] P. TARTE, *Spectrochim. Acta* **18**, 467 (1962); **19**, 25 (1963).

[6] J. PREUDHOMME, Doctorate Thesis, University of Liège (1970).

[7] P. TARTE, *Spectrochim. Acta* **20**, 238 (1964); **21**, 313 (1965).

Table 1. Isotopic purity data*

Element	Isotopic composition (%)		Element	Isotopic composition (%)	
Ca(Natural)	⁴⁰ Ca	96.96	⁶⁴ Zn	⁶⁴ Zn	99.66
	⁴² Ca	0.64		⁶⁴ Zn	0.8
	⁴⁴ Ca	2.06		⁶⁸ Zn	98.5
⁴⁴ Ca	⁴⁰ Ca	5.22	⁷⁰ Ge	⁷⁰ Ge	91.38
	⁴⁴ Ca	94.0		⁷² Ge	3.73
				⁷³ Ge	1.01
⁵⁰ Cr	⁵⁰ Cr	90.40	⁷⁶ Ge	⁷⁴ Ge	2.70
	⁵² Cr	8.59		⁷⁶ Ge	1.18
	⁵³ Cr	0.83		⁷⁰ Ge	7.69
	⁵⁴ Cr	0.18		⁷² Ge	6.65
⁵⁴ Cr	⁵² Cr	6.96	⁷³ Ge	1.69	
	⁵³ Cr	2.18	⁷⁴ Ge	10.68	
	⁵⁴ Cr	90.60	⁷⁶ Ge	73.89	
⁵⁸ Ni	⁵⁸ Ni	99.89			
⁶² Ni	⁶⁰ Ni	0.51			
	⁶² Ni	99.02			

* We have neglected the isotopic species whose abundance is less than 0.5%.

The compounds have been synthesized by conventional solid state reaction techniques. The stable isotopes have been purchased from the Oak Ridge National Laboratory. The relevant isotopic purity data are collected in Table 1.

RESULTS AND INTERPRETATIONS

As stated previously, the compounds discussed in this paper correspond to a selection among the present results, each of them being representative of a particular type of structure. Some of them have already been investigated by the method of isomorphic substitution [4].

Ni₂GeO₄

The structure is of the spinel type, with a normal distribution of the cations (tetrahedral co-ordination of Ge; octahedral co-ordination of Ni). Apart from a weak band at 766 cm⁻¹, the spectrum exhibits the 4 bands expected for a spinel structure [8]. Since these 4 fundamentals belong to the same class of symmetry, they may interact one with another, and their assignment to a definite cation-oxygen vibration will be true only as far as the vibrational interactions are weak. Indeed, the occurrence of vibrational interactions was deduced, at least for one of these vibrations, from an extensive study by the method of isomorphic substitutions [9]. But it appears from Table 2 that much more detailed information may be gained from the isotopic frequencies.

It is clear from these data that one band only, namely ν_1 , is practically free from vibrational interactions, and may be described as the antisymmetric stretching of the GeO₄ tetrahedra.

[8] W. B. WHITE and B. A. DE ANGELIS, *Spectrochim. Acta* **23A**, 985 (1967).

[9] P. TARTE, *Spectrochim. Acta* **19**, 49 (1963).

Table 2. Isotopic frequencies of Ni₂GeO₄

	Ni ₂ ⁷⁰ GeO ₄	Ni ₂ ⁷⁶ GeO ₄	Δν	⁵⁸ Ni ₂ GeO ₄	⁶² Ni ₂ GeO ₄	Δν
ν ₁	694	688	-6	692	692	0
ν ₂	456	451	-5	455	453	-2
ν ₃	336	334	-2	337	330.5	-6.5
ν ₄	201	199.5	-1.5	201	196.5	-4.5

ν₂ is a mixed vibration with, however, a predominant influence of the Ge—O bond, and could be assigned, as a rough approximation, to a bending motion of the GeO₄ tetrahedra.

On the contrary, ν₃ and ν₄ are also mixed vibrations, but with a predominant influence of the Ni—O bonds.

Table 3 gives a brief comparison of the assignments deduced from the isomorphic and the isotopic replacements. The agreement is good, but the isotopic technique is

Table 3

Vibrational mode	Assignment deduced from	
	isomorphic replacement	isotopic replacement
ν ₁	GeO ₄ stretching	GeO ₄ stretching
ν ₂	Essentially, but not purely GeO ₄ bending	Essentially GeO ₄ bending, but with some non negligible contribution from Ni—O bonds
ν ₃ and ν ₄	Vibrations of the lattice of NiO ₆ octahedra	Mixed vibrations, predominantly Ni—O, but with some contribution from the Ge—O bonds

considerably more sensitive and more reliable since it gives a clear-cut proof of the simultaneous participation of 2 cations to 3 (out of a total of 4) vibrational modes.

CaMoO₄

A detailed assignment of the infrared spectrum of CaMoO₄ has been proposed [10, 11] on both the group-theoretical analysis of the scheelite structure, and an experimental study of the reflection spectrum of oriented monocrystals [12]. But, as stated by the authors themselves, the choice between the translatory and the rotatory modes of the E_u type is somewhat arbitrary, since important vibrational interactions between these modes are quite possible. The observed ⁴⁰Ca—⁴⁴Ca isotopic shifts are collected in Table 4, together with the previous and the new assignments.

It is quite evident that, first, the assignments of the external 237 and 153 cm⁻¹ frequencies should be inverted; and second, the weak, although significant isotopic shift of the internal 329 and 284 cm⁻¹ modes reveals the occurrence of non-negligible interactions between the internal and the external modes.

[10] S. P. S. PORTO and J. F. SCOTT, *Phys. Rev.* **157**, 716 (1967).

[11] J. F. SCOTT, *J. Chem. Phys.* **48**, 874 (1968).

[12] A. S. BARKER, JR., *Phys. Rev.* **135A**, 742 (1964).

Table 4

$^{40}\text{CaMoO}_4$	$^{44}\text{CaMoO}_4$	$\Delta\nu$	Previous	Assignments	
					New
432	432	0	ν_2	ν_2	
329	326	-3	ν_4	Essentially ν_4 but vibrational interactions with a translation mode	
284	282	-2	ν_4	Essentially ν_4 , but vibrational interactions with a translation mode	
237	224	-13	Rotation	Translation	
200	192	-8	Translation	Translation	
153	153	0	Translation	Rotation	

Here again, the study of isotopic species leads to unequivocal assignments, and points to vibrational interactions which could not be detected by another technique.

Zn_2GeO_4

This compound has a phenacite structure (space group $R\bar{3}$, 6 molecules in the rhombohedral unit cell, tetrahedral coordination of all cations). From the vibrational point of view, this is a rather complicated case, and no vibrational analysis by the group theory has been published so far.

The following interpretations had already been deduced from the study of $\text{Zn}_2(\text{Si, Ge})\text{O}_4$ solid solutions [5] (which did not include the low-frequency region below 300 cm^{-1}): Bands of the $800\text{--}700\text{ cm}^{-1}$ region: stretching vibrations of GeO_4 tetrahedra. Bands of the $600\text{--}500\text{ cm}^{-1}$ region: stretching vibrations of the ZnO_4 tetrahedra. Bands of the 300 cm^{-1} region: bending vibrations of GeO_4 tetrahedra.

It appears from the isotopic frequencies collected in Table 5 that these assignments are essentially correct. However, a careful discussion of these data leads to the following comments: (1) For the bands of the $800\text{--}700\text{ cm}^{-1}$ region, the occurrence of a significant $^{70}\text{Ge}\text{--}^{76}\text{Ge}$ isotopic shift, and the lack of $^{64}\text{Zn}\text{--}^{68}\text{Zn}$ shift may be considered as a good combined evidence for their assignment to stretching vibrations of the GeO_4 tetrahedra.

The observed shifts, however, are systematically and significantly lower than those already noticed for Ni_2GeO_4 . On the other hand, the bands under discussion are not very sharp, and the estimated error on frequency measurements is about ± 0.5 or $\pm 1\text{ cm}^{-1}$. As a consequence, the possibility of small $^{64}\text{Zn}\text{--}^{68}\text{Zn}$ isotopic effects cannot be excluded, since these small frequency shifts will fall within the experimental error.

In conclusion, the group of the high-frequency bands must be assigned to stretching vibrations of the GeO_4 tetrahedra, but the possibility of weak vibrational interactions with the ZnO_4 tetrahedra is not excluded. (2) The same comments may be applied, mutatis mutandis, to the group of medium-frequency bands in the $600\text{--}500\text{ cm}^{-1}$ region. They must originate essentially from ZnO_4 vibrations; but here again, the bands are not sharp enough to allow the detection of small $^{70}\text{Ge}\text{--}^{76}\text{Ge}$ isotopic

Table 5. Isotopic frequencies of Zn_2GeO_4

$\text{Zn}_2^{70}\text{GeO}_4$	$\text{Zn}_2^{76}\text{GeO}_4$	$\Delta\nu$	$^{64}\text{Zn}_2\text{GeO}_4$	$^{68}\text{Zn}_2\text{GeO}_4$	$\Delta\nu$
800	797	-3	798	798	0
774	771	-3	772	772	0
(746)	(744)	(-2)	(748)	(746)	(-2)*
574	574	0	574	573.5	-0.5
556	556	0	558	556	-2
538	538	0	541	537.5	-3.5
498	497	-1	498	496	-2
327.5	324	-3.5	326.5	325	-1.5
313	311	-2	312	310.5	-1.5
293	289	-4	292	289	-3
256	255	-1	258	253	-5
232.5	231	-1.5	234	229.5	-4.5
214.5	214	-0.5	216	211.5	-4.5
196	195	-1	198.5	192	-6.5
150.5	149.5	-1	151	148	-3
140.5	139	-1.5	140.5	137.5	-3

* This band is broad and asymmetric, and the observed shifts are not significant.

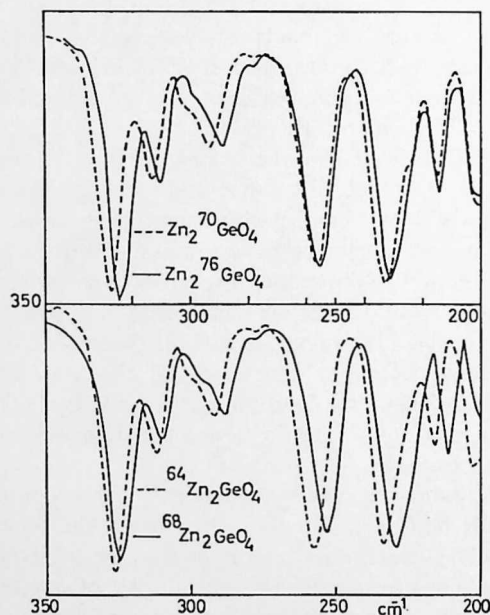


Fig. 1. Infrared spectrum of the isotopic species of Zn_2GeO_4 in the low frequency region.

shifts which would imply weak vibrational interactions. (3) Finally, all the low frequency bands are shifted by both Zn and Ge isotopic replacements and thus must be assigned to complex vibrations (This part of the spectrum is represented in Fig. 1; the 1200-300 cm^{-1} region has already been represented in Ref. [5]).

But there is a predominant influence of germanium on the 2 bands near 325 and

310 cm^{-1} (which thus could be approximately assigned to bending vibrations of the GeO_4 tetrahedra), and a predominant influence of zinc on all the low-frequency bands below 260 cm^{-1} . Here again, the general results and assignments are in agreement with those deduced from isomorphic substitution (Table 6).

Table 6

Group of bands (cm^{-1})	Ge—Si isomorphic replacement	Assignment deduced from isotopic replacement
800–700	GeO_4 stretching	GeO_4 stretching
600–500	ZnO_4 stretching	ZnO_4 stretching
330–300	GeO_4 bending	Essentially Ge—O, but contribution from Zn—O
260–140	Not investigated	Mixed vibrations, with Zn—O predominant contribution

α - CaSiO_3

In this type of structure, the SiO_4 tetrahedra are linked by common oxygen atoms so as to form Si_3O_9 rings. The same structure is found in SrSiO_3 and in the low-temperature form of BaSiO_3 [13]. Thus, we can make a comparative study of both isomorphic (Ca, Sr, Ba) and isotopic (^{40}Ca – ^{44}Ca) species (Table 7, Figs. 2 and 3). As

Table 7

$^{40}\text{CaSiO}_3$	$^{44}\text{CaSiO}_3$	$\Delta\nu$	SrSiO_3	BaSiO_3
1090	1090	0	1068	1040
1074	1074	0		
990	990	0	975	955
942	942	0	928	910
923	923	0	915	900
718	718	0	707	693
565	565	0	550	532
434	434	0	436	438
			326	323
310	310	0	293	288
300	293	–7	250	223
250	245	–5	192	162
218	212	–6		
186	180	–6	142	112
170	164	–6		

expected, no ^{40}Ca – ^{44}Ca isotopic shift is observed, and the spectrum of the 3 Ca, Sr and Ba compounds is nearly the same, in the 1100–400 cm^{-1} region. All these bands must be assigned to vibrations of the Si_3O_9 ring. They exhibit a more or less important downward shift when the ionic radius of the cation increases, but this is a well-known effect.

All the low-frequency bands (300–150 cm^{-1}) of CaSiO_3 are shifted by the ^{40}Ca – ^{44}Ca

[13] H. FUNK, *Z. Anorg. Allgem. Chem.* **296**, 46 (1958).

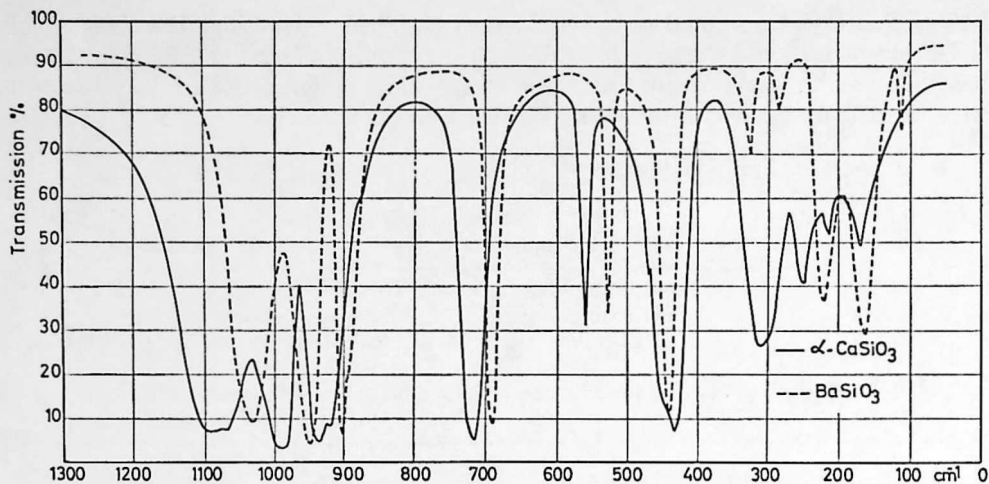


Fig. 2. Infrared spectrum of CaSiO_3 and of the low-temperature form of BaSiO_3 .

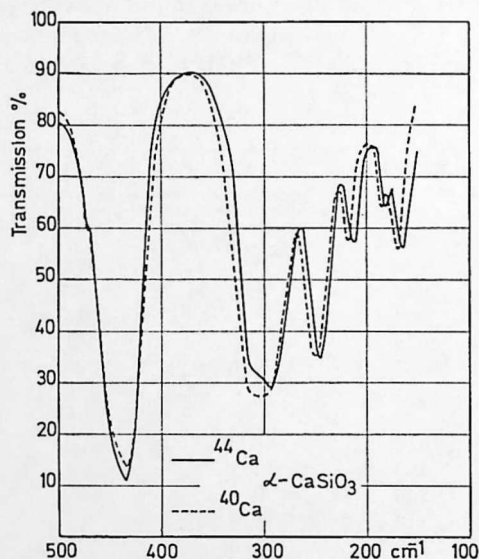


Fig. 3. ^{40}Ca - ^{44}Ca isotopic shifts in the spectrum of CaSiO_3 .

isotopic replacement, but the isotopic behaviour of the 300 cm^{-1} band is not clear since this band is fairly broad (Fig. 3).

This behaviour, however, may be explained by the occurrence of 2 bands: one, near 310 cm^{-1} , which is *not* displaced (the corresponding band is observed at 326 or 293 cm^{-1} in the spectrum of SrSiO_3); and the other, which is displaced from about 300 to 293 cm^{-1} ; for this second, mass-sensitive component, the corresponding bands are observed at much lower frequencies for SrSiO_3 (250 cm^{-1}) and BaSiO_3 (223 cm^{-1}).

For these bands, a plot of the frequency vs. the square root of the cationic mass reveals a rather regular, although not linear, relationship (Fig. 4). This is true also for the bands observed at 250, 192 and 162 cm^{-1} in Ca, Sr and BaSiO_3 ; but no evident correlation has been found for the lowest frequency bands (Fig. 4).

Strictly speaking, the compounds under discussion are not true salts; but the combined evidence from both isotopic and isomorphous replacement reveals a salt-like vibrational behaviour, with well-separated internal vibrations of the Si_3O_9 ring, and external, mass-sensitive, vibrations of the cation against the Si_3O_9 anion.

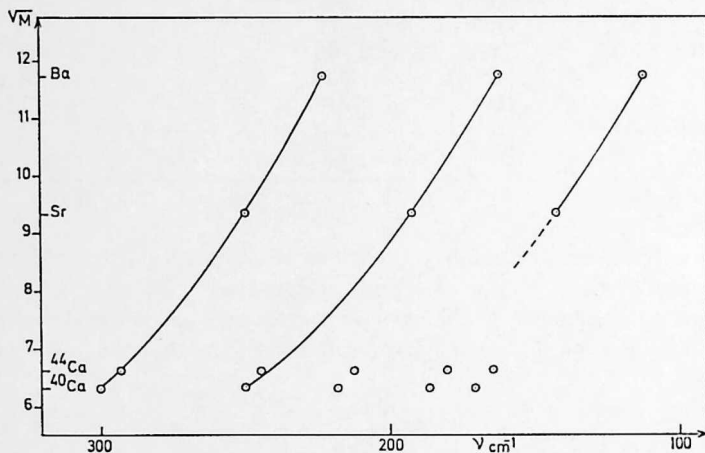


Fig. 4. Relationship between the square root of the cationic mass, and the low frequencies of $^{40}\text{CaSiO}_3$, $^{44}\text{CaSiO}_3$, SrSiO_3 and BaSiO_3 .

$\text{Ca}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$

This compound has the garnet structure. Despite the overall cubic symmetry, the structure is fairly complicated, and the number of infrared active fundamentals is rather high [1]. On the other hand, a systematic investigation of the garnet germanates and of their solid solutions lead to the general conclusion that the approximation of independent vibrations is a rather rough one for these compounds [4]. Some assignments were nevertheless proposed and are compared with the observed ^{50}Cr - ^{54}Cr isotopic shifts (Table 8). It is clear that, apart from the group of high-frequency bands which are insensitive to the mass of chromium and should be assigned to the stretching vibrations of the GeO_4 groups, practically all of the remaining bands are more or less displaced and thus are related to some extent to chromium-oxygen vibrations. Since it is unthinkable to assign all these bands to vibrations of the CrO_6 octahedra it is highly probable that most, and possibly all, of these bands are related to mixed vibrations. A study of the ^{40}Ca - ^{44}Ca and of the ^{70}Ge - ^{76}Ge isotopic shifts will be necessary to clear up this point, and also to bring the definite proof that the high-frequency bands are essentially related to GeO_4 vibrations.

Nevertheless, the actual isotopic results sufficiently demonstrate that the correlation between the assignments deduced from either the isomorphous or the isotopic replacement is not satisfactory (Table 8): in such complicated cases, the method of isomorphous substitution is unable to lead to a realistic interpretation of the spectrum.

Table 8. $\text{Ca}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$

Approximate assignments deduced from isomorphous substitution	^{50}Cr - ^{54}Cr isotopic frequencies			Correlation
	^{50}Cr	^{54}Cr	$\Delta\nu$	
GeO_4 stretching	744	743.5	(-0.5)	Good
	713	713	0	
	682	682	0	
	506	502	-4	
GeO_4 bending	487.5	482.5	-5	Bad
	420	417	-3	
Mixed vibration?	384	380	-4	Bad
CrO_6	336	335	-1	
Not investigated	310	310	0	
	292.5	288	-4.5	
	232	230	-2	

Simple oxides

We shall finally report preliminary results on the vibrational behaviour of simple oxides, since some of these results are quite unexpected.

GeO_2 (*quartz-type structure*). Nearly all the bands are shifted by 5-10 cm^{-1} (Table 9) and thus involve significant displacements of the Ge atom. A more detailed

Table 9

$^{70}\text{GeO}_2$	$^{76}\text{GeO}_2$	$\Delta\nu$
962	960	-2
885	877	-8
592	584	-8
559	551	-8
523	516	-7
345	339	-6
265?	262	-3?
258	251	-7
215	212	-3

interpretation depends on the feasibility of a realistic evaluation of the atomic displacements. However, the purely qualitative aspect of the results presented here is not without interest, in view of the results given by the investigation of Cr_2O_3 .

Cr_2O_3 . The spectrum of this compound exhibit 5 out of the 6 infrared active fundamentals predicted from group theoretical considerations [14] (Fig. 5). But, quite unexpectedly, a significant ^{50}Cr - ^{54}Cr shift is observed for one band only (Table 10). It is true that the possibility of small shifts cannot be excluded for the 2 high-frequency bands in view of their broadness. But we now have good reasons to believe that the mass effect on these frequencies should be small or even negligible, this conclusion being strongly suggested by the parallel study of the structurally related oxides Al_2O_3 and Rh_2O_3 .

[14] A. S. BARKER, JR., *Phys. Rev.* **132**, 1474 (1963).

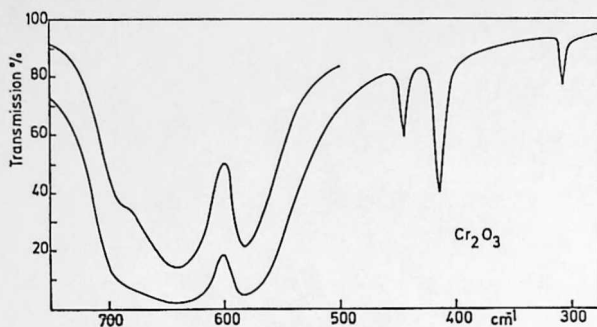
Fig. 5. Infrared spectrum of Cr_2O_3 .

Table 10

$^{50}\text{Cr}_2\text{O}_3$	$^{54}\text{Cr}_2\text{O}_3$	$\Delta\nu$	Rh_2O_3	Al_2O_3
643 vs	643	0	655 vs	642 vs
583 vs	583	0	612 vs	602 vs
444.5 w	444.5	0		488 w
414.5 w	415	(+0.5)	462 w	456 s
312 w	302	-10	232 vw	384 w

The observed frequencies for these oxides are collected in Table 10. It would be premature to propose a detailed, band-to-band correlation for the 3 spectra; but this correlation is nearly evident for the 2 very strong, high-frequency bands.

The observed frequencies are nearly the same for these oxides (and in fact, the values are slightly higher for Rh_2O_3). Very often, the vibrational frequencies depend on both the atomic masses and the cation-anion restoring force; the resulting frequency, however, is an overall effect and, in some instances, a higher restoring force may counteract the influence of a heavier mass; this may explain the apparent lack of a mass effect. However, for the rhodium and aluminum oxides, the Rh/Al mass ratio is so high (3.81), that a significant mass effect could not be compensated for by a higher Rh—O restoring force acting in the opposite direction. Thus, it should be concluded that, in this type of structure, the high-frequency vibrations are practically independent of the mass of the cation; this conclusion is in perfect agreement with the lack of any significant isotopic effect.

It is worth while to mention that similar behaviour has already been observed for LiCrO_2 and LiRhO_2 [15], and has now been found for a series of isomorphous chromium and rhodium compounds; these results will be reported and discussed in a forthcoming paper. On the contrary, the low-frequency band is strongly mass-sensitive; here again, the results deduced from the study of either isotopic or isomorphous species are consistent, leading to a smooth relationship between the vibrational frequency and the square root of the mass of the cation (Fig. 6).

Now, if we compare these results with the preceding ones on GeO_2 , we find a fairly different vibrational behaviour for GeO_2 (a lattice of condensed tetrahedra),

[15] P. TARTE and J. PREUDHOMME *Spectrochim. Acta*, **26A**, 747 (1970).

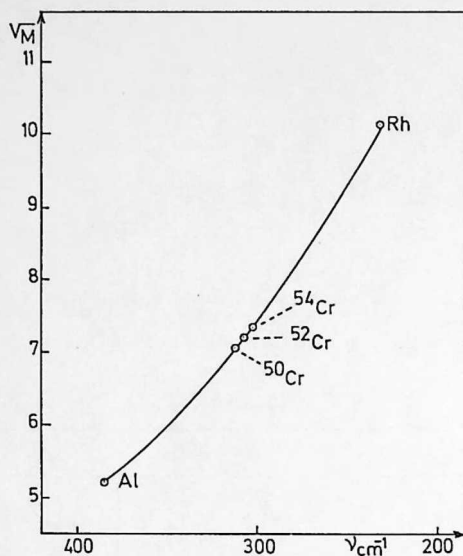


Fig. 6. Relationship between the square root of the cationic mass and the frequency of the low-frequency band of Al_2O_3 , the isotopic species of Cr_2O_3 and Rh_2O_3 .

or for Cr_2O_3 (a lattice of condensed octahedra). It should be pointed out that the lack of a cationic mass effect on the high-frequency bands has also been observed for other compounds with a lattice of condensed octahedra [6]. Nevertheless, further work is needed to know to what extent these experimental data may be generalized to various lattices of tetrahedral or octahedral groups.

DISCUSSION

Since the use of medium-weight isotopes in vibrational spectroscopy is quite new, we just want to point to the most evident advantages and limitations of this method, as they are suggested by the actual results.

(1) Isotopic species of medium-weight cations exhibit measurable frequency shifts in the vibrational spectrum of inorganic solids, and this type of information may be of great help in solving assignment problems.

(2) The most trivial limitation of the method is the availability of the necessary isotopic species. Some important elements such as aluminum have one stable isotope only. In other cases, several stable isotopes exist, but their natural abundance may be so small that, practically, they are not available. Likewise, the mass ratio between the available isotopes should be sufficiently different from unity (1.05–1.10). Since the isotopic shifts are generally small, the possibility of significant measurements is restricted to sharp bands.

(3) If the necessary conditions (favourable isotopic mass ratio; sharpness of the bands) are fulfilled, the technique of isotopic replacement is able to give a clear-cut proof of the simultaneous participation of several cations to a given vibrational frequency: in most cases, it is much more sensitive to the occurrence of mixed vibrations than the method of isomorphic substitutions.

(4) The possibilities of isotopic replacement of the cation are of course restricted to those vibrations which involve a displacement of the cation. This eliminates the study of highly symmetrical vibrations. But, quite unexpectedly, we also failed to find a measurable mass effect for some vibrations of a lattice of condensed octahedra. A detailed explanation is still to be found for this peculiar vibrational behaviour. But, whatever the interpretation, this type of result must be carefully evaluated and discussed, since it may lead to erroneous interpretations. The possibility of errors will be greatly reduced if a parallel study by the method of isomorphic substitution is also carried out.

In conclusion, the study of both isotopic and isomorphic compounds is useful in interpreting the vibrational spectrum of inorganic solids. The method of isotopic replacement is more simple in its basic principles, and is more sensitive to complex vibrations, than the method of isomorphic replacement. It has, however, a number of practical and theoretical limitations, and the interpretation of its results is not always evident.

Much work, both theoretical and experimental, is still needed before a detailed and realistic comparison of the 2 methods can be made. But their complementary nature is nearly evident, and will probably be confirmed by further studies which are actually carried out in this laboratory.

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