

The use of infrared spectra for the determination of minerals

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Any physical or chemical method of analysis can be used for substance identification. With respect to minerals, the method of infrared spectroscopy is notable for its quickness and accuracy, requiring only a small quantity of material.

The great range of IR wavelengths which can be recorded on modern apparatus (from 400 to 4000 cm^{-1}) makes it possible to distinguish quite surely one mineral from the other, because in practice in no case do we encounter minerals with completely identical absorption spectra (Farmer, 1974; Moenke, 1962-1966; Nakamoto, 1970; Nyquist and Kagel, 1971).

For the successful use of IR-spectroscopy in mineral diagnostics, it is necessary to take into account the main factors which affect the position of fundamental and characteristic absorption bands in the IR spectra of minerals. During the two recent decades many important and fundamental works were devoted to this question (Lippincott *et al.*, 1958; Dacheville and Roy, 1959; Milkey, 1960; Tarte, 1962; White and Roy, 1964; Povarennykh, 1970). As was shown earlier (Povarennykh, 1970), these factors are primarily those which determine the relative strength of chemical bonds between adjacent atoms.

These factors are as follows: V_k and V_a —valencies of cation and anion, CN—coordination number of cation; d —interatomic distance cation-anion; M —the reduced mass of cation, equal to the sum of atomic weights of a given cation and of all anions that coordinate it; k —coefficient of relative bond strength, which varies from 1 to 2 according to the degree of covalency of the bond.

Interaction of all the above-mentioned factors may be summarized in the main formula, which allows the calculation of relative bond strength σ between the adjacent atoms in the structure of a crystal:

$$\sigma = \frac{k(V_k \cdot V_a)}{\text{CN} \cdot d \cdot \sqrt{M}} \quad (1)$$

Between the value of σ and the frequency of valency vibration ν_3 of the polyhedron XO_n (Povarennykh, 1970) there is a ratio: $\nu_{\text{val}} = A\sigma \text{ cm}^{-1}$ (2)

where A is a proportionality coefficient that depends (with constant anion valency) on the cation valency. Since the repulsion between the X and O atoms in the XO_n radical decreases with decrease of the X atom valency, the values of the coefficient A increase gradually in the same direction (Table 1).

For each coordination polyhedron XO_n we get a separate parabolic curve for A as a function of valency of X (Fig. 1).

Some of the factors in equation 1 contribute much more than others to the variation in relative bond strength. The most important are: valency of atoms V_k and V_a , coordination number (CN), and mass of atoms (M). Of lesser importance are interatomic distances (d) and a coefficient of relative bond strength (k), which vary within narrower limits.

Valency of atoms

Since the overwhelming majority of minerals are oxygen and sulphide combinations, the most important contribution to the variation in the strength of interatomic bonds is made by cations, the valency of which ranges from 1 to 6. A unit increase of a cation valency greatly shifts the absorption band ν_3 to higher frequencies (Povarennykh, 1970, Fig. 5). Still greater difference in the positions of absorption bands ν_3 is noticed when we pass from oxygen combinations to halides, when the valency of both atoms is changed, *e.g.* $\text{MgO} \rightarrow \text{NaCl}$ or $\text{KF} \rightarrow \text{CaS}$, *etc.* Naturally, the IR method is a very convenient one for determination in minerals of the real valency of those elements which have variable valency (*e.g.* Ti, V, Mn, Fe, Cu, As, Se, Sn, *etc.*)

Coordination number of atoms

The valency vibration, ν_3 , shifts spasmodically to higher frequency (or stronger bonds) with decreasing coordination number. This shift arises not only from increase in atomic distances, but from the increase of quantum-mechanical interaction (resonating bonds). As the coordination number decreases in the order of 6, 4, 3, 2 this interaction increases in the order 0.75, 0.8, 0.9, 1.0. Of course such a shift is seen more

Table 1. Values of the coefficient A for the different valency and coordination of atoms in polyhedra

Valency of the central atom in polyhedron (cation)	Values of the coefficient A		
	Polyhedrons		
	XO_3	XO_4	XO_6
1	8100	10600	13000
2	5800	7800	9800
3	4200	6000	7600
4	3100	4800	6400
5	2100	3800	5300
6	--	3000	4600

distinctly in the case of coordination number change by high-valent and light atoms (e.g., Si, B, Al, Be, etc.).

Mass of atoms

The increase of atomic mass in the mineral composition leads to decreasing frequency. Naturally, the value of this shift in isostructural minerals is in proportion to the difference between square roots of the total atomic weights. It is very noticeable on comparison of IR spectra of analogous pairs of combinations, especially in the following classes: silicates and germanates, phosphates and arsenates, sulphates and selenates. For each pair, the absorption bands of radicals with the heavier element are shifted to the right by more than 200–300 cm^{-1} (Povarennykh, 1970). Of course, besides the mass of atoms, the value of this shift is also influenced by the increase of interatomic distances.

Obviously, each mineral consists of a set of different cation-anion polyhedra of definite composition, dimensions, and mass, and the strength of an inter-

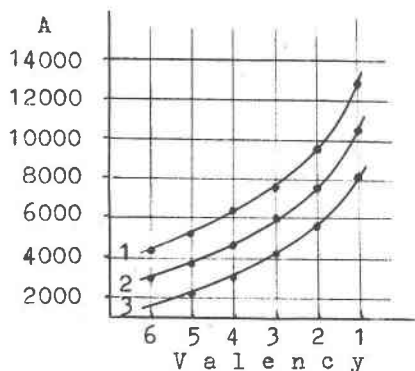


Fig. 1. The regular change of values of the coefficient A for atoms with different valency: (1) XO_6 polyhedra; (2) XO_4 polyhedra; (3) XO_3 polyhedra.

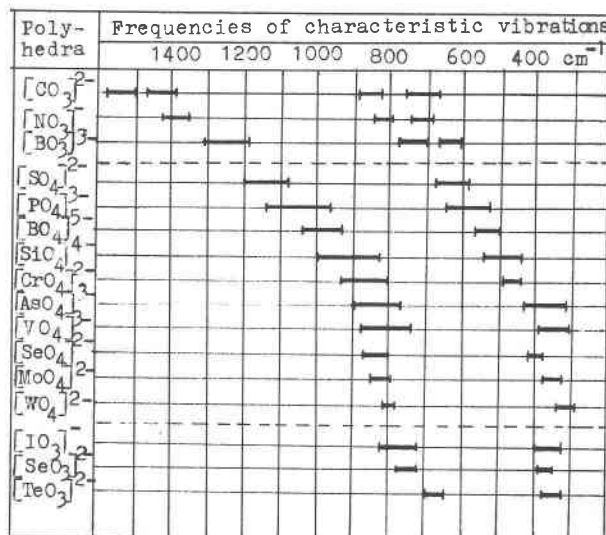


Fig. 2. The limits of frequencies of characteristic vibrations of important "closed" polyhedra in IR spectra of minerals.

atomic bond depends on the interconnection of these polyhedra. Limits to the vibrational frequencies in a given class of minerals depend on the variation of composition, dimensions, and mass of atoms within that class (Tarte, 1962). By substituting in equation (1) the structural data of minerals (Povarennykh, 1972), it is easy to calculate limits of vibrations of the

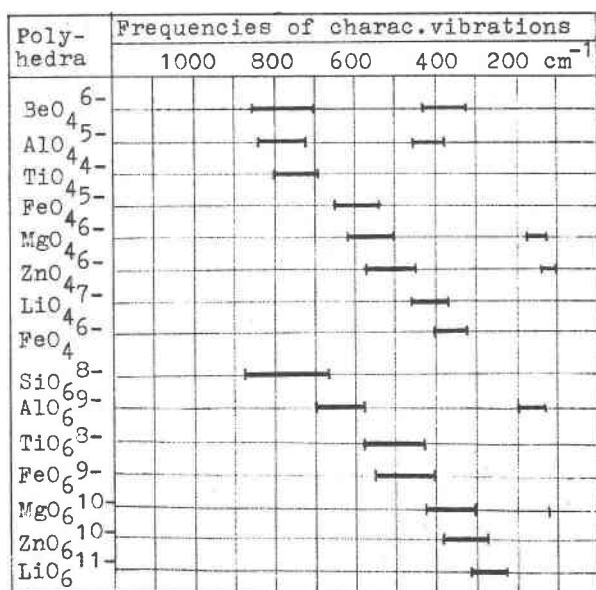


Fig. 3. The limits of frequencies of characteristic vibrations of important "open" polyhedra in IR spectra of minerals.

Table 2. The limits of characteristic vibrations of "closed" and "open" atomic polyhedra in minerals

Classes or radicals	Frequencies of characteristic vibrations		Classes or radicals	Frequencies of characteristic vibrations	
	ν_3	ν_4		ν_3	ν_4
Carbonates	1570-1500 1475-1390	765-675	Beryllates	850-700	400-320
Nitrates	1430-1350	750-695	Aluminates	840-760	460-380
Borates	1315-1190	680-605	Titanates	800-690	?
Sulphates	1200-1080	680-580	Ferriates	660-540	-
Phosphates	1140-960	650-525	Magnesiates	620-500	170-130
Orthoborates	1040-940	570-500	Zincates	570-450	140-100
Silicates	1000-830	540-435	LiO ₇ -	460-370	-
Chromates	930-800	400-360	FeO ₄₆ -	400-320	-
Arsenates	900-760	420-310	SiO ₄₃ -	380-670	?
Vanadates	880-740	390-310	AlO ₆₉ -	700-580	200-140
Selenates	870-800	415-375	TiO ₆₆ -	580-430	-
Molibdates	850-790	375-330	FeO ₆₉ -	560-400	-
Wolframates	815-785	340-295	MgO ₆₁₀ -	420-300	130
Iodates	825-720	400-320	ZnO ₆₁₀ -	370-270	-
Selenites	770-720	390-350	LiO ₆₁₁ -	320-230	-
Tellurites	700-650	375-315			

values of relative bond strength σ in every class. But it is still easier to do it in an experimental way by means of the IR spectra of minerals.

The diagrams show the limits of the maxima of absorption bands of valent ν_3 and deformation ν_4 vibrations for closed (Fig. 2) and open (Fig. 3) com-

binations, that exist in the mineral kingdom (Povarennykh, 1970).

It appears from Figures 2 and 3 and Table 2 that the area of absorption peaks ν_3 and ν_4 for classes of minerals overlap greatly, which is a serious obstacle for the confident use of the IR method alone for the accurate determination of mineral species. As always in such cases, we have to have recourse to additional (microchemical, optical, or X-ray) methods of investigation. It is particularly helpful to know the location of absorption bands of H₂O molecules and OH groups, which are essential parts of most minerals with complex composition.

There is also another method of mineral determination by IR spectra. This is the method of visual comparison of the experimental IR curves to the standard IR spectra of minerals. The most complete atlas, including more than 90 percent of mineral species now known, will be published next year in an individual book by the author of this paper. It is especially convenient for the determination of minerals that belong to mesodesmic combinations—some borates and silicates, which are rather given to polymerization of B triangles and Si tetrahedra, and to formation of dimers, trimers, and infinite chain, sheet, and framework radicals (Povarennykh, 1972). Figure 4 shows absorption bands of some complex borates, silicates and other similar classes of minerals.

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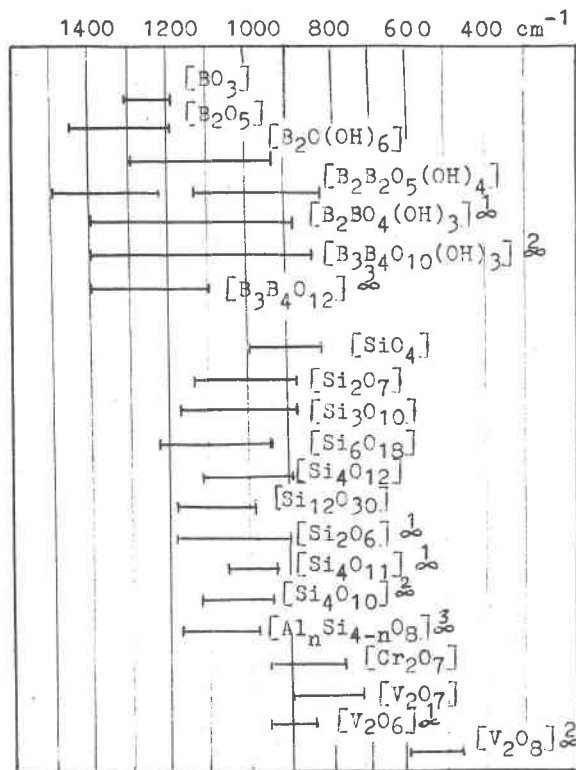


Fig. 4. The frequencies of characteristic vibrations of some important complex radicals of borates, silicates, and others.

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