

Vibrational behavior of matrix-isolated tetrahedral ions and HDO molecules in inorganic salts – sulfates, selenates, chromates and formates

Delyana Marinova Manasieva

*Institute of General and Inorganic Chemistry – Bulgarian Academy of Sciences
1113 Sofia "Acad. Georgi Bonchev" str. bld.11; e-mail: d.manasieva@gmail.com*

The crystal matrix infrared spectroscopy provides important information about the local potential at the lattice site and the chemical nature of the ligand environment in the lattice. When foreign ions are doped in host lattices at low concentration (less than 7–10 %) the correlation field splitting, the dispersion of phonon curves (due to the interactions between identical oscillators) and LO/TO splitting effects (due to the long-range forces of electrostatic origin) are neglected. Thus, the vibrational spectra of the guest ions are essentially determined by the site symmetry, which is assumed to be the same as that of the respective host ions (substitutionally mixed crystals). The values of $\Delta\nu_3$ and $\Delta\nu_4$ (site-group splitting) and $\Delta\nu_{\max}$ (the differences between the highest and the lowest wavenumbered components of the stretching and bending modes, respectively) are used as an adequate measure for the extent of energetic distortion of matrix-isolated entities.

There are several variants of crystal matrix infrared spectroscopy: isotope dilution technique, i.e. substitution of an atom by 5–10 % of a heavier or lighter isotope; solid solution spectroscopy, i.e. studying matrix isolated molecules or ions on lattice sites of a crystalline matrix and double matrix spectroscopy, i.e. two or more different matrix isolated entities in a matrix come into contact with another forming complexes.

The main idea of our work is to study the possibility to use the crystal matrix infrared spectroscopy as a tool to monitor admixtures in minerals. The foreign ions are either isomorphously (isodimorphously) included in the minerals or they exist as distinct phases. The latter display vibrational spectra similar to those of the respective neat compounds. Our spectroscopic experiments aim at analyzing the vibrational behaviour of tetrahedral ions in synthetic minerals of the type MeXO_4 (Me = Ca, Sr, Ba, Pb; X = S, Se, Cr) as well as that of $\text{X}'\text{O}_4^{2-}$ ions (X' = S, Se, Cr) guest ions matrix-isolated in the above compounds. Additionally, compounds with kröhnkite-type octahedral-tetrahedral chains, $\text{K}_2\text{Me}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Me = Mg, Co, Ni, Zn, Cd), containing SO_4^{2-} guest ions are synthesized and their vibrational spectra are discussed with respect to the energetic distortions of the host and guest anions. The influence of different crystal-chemical and chemical factors on the spectral picture of the tetrahedral ions and the strength of the hydrogen bonds formed in the chromate structures are analyzed. Additionally, the cation distribution at the two crystallographic sites in the isomorphous series $\text{Mg}_x\text{Zn}_{1-x}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}_x\text{Mn}_{1-x}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ has been studied using both the double matrix infrared spectroscopy and the single-crystal X-ray diffraction.

Main results and conclusions

The analysis of the infrared spectra of the neat compounds MeXO_4 ($\text{Me} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$; $\text{X} = \text{S}, \text{Se}, \text{Cr}$) and of those of the $\text{X}'\text{O}_4^{2-}$ ions ($\text{X}' = \text{S}, \text{Se}, \text{Cr}$) matrix-isolated in the above salts in the regions of the normal vibrations of the tetrahedral ions reveals:

- The matrix-isolated $\text{X}'\text{O}_4^{2-}$ ions exhibit three bands corresponding to the ν_3 modes and one band corresponding to the ν_1 modes in agreement with the site group analysis. In some cases the $\text{X}'\text{O}_4^{2-}$ guest ions in the bending mode region display a higher local symmetry than the “rigorous” crystallographic one (effective spectroscopic symmetry);

- The matrix-isolated $\text{X}'\text{O}_4$ -tetrahedra display stronger distortions with respect to the $\text{X}'\text{-O}$ bond lengths as compared to those of the O-X'-O bond angles as deduced from the number and the positions of the corresponding infrared bands and the values of $\Delta\nu_3$ and $\Delta\nu_4$.

- When smaller ions are replaced by larger ones the mean frequencies of the asymmetric stretching and bending modes of the guest ions are shifted to higher frequencies as compared to those of the same ions in the neat compounds due to the larger repulsion potential at the lattice site in the host compound and *vice versa*.

- The values of $\Delta\nu_3$ for the SO_4^{2-} guest ions matrix-isolated in selenate and chromate matrices are smaller than those of the same ions in the respective neat sulfates. However, the values of $\Delta\nu_3$ for the CrO_4^{2-} and SeO_4^{2-} guest ions in sulfate matrices are either smaller or larger as compared to those of the same ions in the neat chromates and selenates and to the different strength of the electrostatic fields.

The crystal structures of four double chromates with kröhnkite-type octahedral-tetrahedral chains $\text{K}_2\text{Me}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{Me} = \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$) were determined from single-crystal and powder X-ray diffraction data. $\text{K}_2\text{Me}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{Me} = \text{Co}, \text{Ni}, \text{Cd}$) crystallize in triclinic space group $P\bar{1}$ (“type A”), while $\text{K}_2\text{Zn}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ (monoclinic space group $C2/c$) represents a new structure type, designated “type H”, with closest relationships to the triclinic “type A” compounds.

The infrared spectroscopic experiments of the neat double chromates as well as those of the SO_4^{2-} ions included in the chromate matrices show:

- The strengths of the hydrogen bonds in $\text{K}_2\text{Me}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{Me} = \text{Mg}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$) are discussed in terms of the respective $\text{O}_w \cdots \text{O}$ bond distances, the Me -water interactions (*synergetic effect*), the proton acceptor capability of the chromate oxygen atoms as deduced from Brown’s bond valence sum of the oxygen atoms. The spectroscopic experiments reveal that hydrogen bonds of medium strength are formed in the chromates. The hydrogen bond strengths decrease in the order $\text{Cd} > \text{Zn} > \text{Ni} > \text{Co}$ in agreement with the decreasing covalency of the respective Me-OH_2 bonds in the same order, i.e. decreasing acidity of the water molecules. The infrared band positions corresponding to the water librations confirm the claim that the hydrogen bonds in $\text{K}_2\text{Cd}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ are stronger than those formed in $\text{K}_2\text{Mg}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ on one hand, and on the other – the hydrogen bonds in $\text{K}_2\text{Ni}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ are stronger than those in $\text{K}_2\text{Co}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$.

- The extend of energetic distortion of the CrO_4^{2-} ions depends on the $\text{Me}^{2+}\text{-OCrO}_3$ bond strength (as deduced from Brown's bond valence), the electronic configurations of the Me^{2+} ions and the hydrogen bond strengths.

- The extend of energetic distortion of the SO_4^{2-} guest ions matrix-isolated in the chromate matrices is affected by both the degree of covalency of the respective $\text{Me}^{2+}\text{-OSO}_3$ bonds and the electronic configurations of the Me^{2+} ions. For example, the energetic distortion of SO_4^{2-} ions included in the chromate lattices decreases in the order $\text{Zn} > \text{Cd} > \text{Mg}$ as a result of the decreasing covalency of the respective $\text{Me}^{2+}\text{-O}$ bonds in the same order. Furthermore, the values of Δv_3 and Δv_{max} are larger when the metal ions have $\text{CFSE} \neq 0$ (crystal field stabilization energy, Co^{2+} , Ni^{2+}). These cations are more resistant to angular deformations of the MeO_6 octahedra (i.e. changes in the O-Me-O bond angles), thus facilitating the extent of distortion of the matrix-isolated SO_4^{2-} ions as compared to those having $\text{CFSE} = 0$ (Mg^{2+} , Zn^{2+} and Cd^{2+}).

- The comparison of the infrared spectra of the compounds with kröhnkite-type chains $\text{K}_2\text{Me}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{Me}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{Me} = \text{Mg}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$), containing matrix-isolated SO_4^{2-} ions evidences that the guest ions included in the selenate matrices are remarkably much distorted than in the chromate ones owing to a stronger static field caused by the smaller Na^+ ions as compared to that caused by the larger K^+ ions. The smaller unit-cell volumes of the selenate host compounds, i.e. the higher repulsion potential at the lattice sites at which the guest ions are situated additionally favor the extent of energetic distortion of the sulfate guest ions in the selenate matrices.

A variant of double matrix infrared spectroscopy (matrix-isolated HDO molecules and different amounts of metal ions) has been applied in order to deduce the cation distribution at the two available different metal sites (hexaformate-coordinated $\text{Me}(1)$ sites and mixed-coordinated $\text{Me}(2)$ sites) in $\text{Mg}_x\text{Zn}_{1-x}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}_x\text{Mn}_{1-x}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ ($1 > x > 0$) mixed crystals. A hypothesis has been made that when Mg^{2+} ions are included in the structures of $\text{Zn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ they will occupy preferentially the $\text{Me}(2)$ sites due to their strong affinity to water molecules. The spectroscopic investigations as well as the single-crystal X-ray diffraction data confirm our assumption.

The infrared spectroscopic studies of synthetic minerals of type MeXO_4 ($\text{Me} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$; $\text{X} = \text{S}, \text{Se}, \text{Cr}$), containing matrix-isolated $\text{X}'\text{O}_4^{2-}$ ions ($\text{X}' = \text{S}, \text{Se}, \text{Cr}$), and also of SO_4^{2-} ions in the structure of compounds containing kröhnkite-type infinite octahedral-tetrahedral chains $\text{K}_2\text{Me}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{Me} = \text{Mg}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$), shows that the matrix infrared spectroscopy can successfully be applied as an express method for determination of the type of inclusions in minerals. Ions included in host salt on base of isomorphically, respectively isodimorphically replacement, show spectrum significantly different from that of the salt, which forms a guest-ion with cations, identical to those of the host salt. One of the advantages of the spectroscopic method is its sensitivity to the concentration of ions involved.