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Abstract

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Electronic Absorption Spectrum of Crystals of Certain Dichromates at Low Temperatures

Interpretation of the Spectra

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As shown in previous works ([1],[2]), in all the dichromates studied—sodium, ammonium, tetramethylammonium, and potassium—at the long-wavelength edge of absorption at 20.4° K a group of bands appears. The absorption spectrum begins with sharp, narrow, and intense bands, between which there are weak but also relatively sharp ones; as one moves into the short-wavelength part of the spectrum, the bands broaden and sink into the increasing continuous spectrum. The position of the most long-wavelength band in the spectra of different dichromates changes little. In sodium and tetramethylammonium dichromates the frequencies of this band coincide; in ammonium dichromate the most long-wavelength band is shifted by 100 cm^{-1} toward higher frequencies, and in potassium dichromate by 520 cm^{-1} toward lower frequencies. This indicates that the electronic transitions in dichromates depend only weakly on intermolecular interaction. The similarity of the spectra of different dichromates suggests that these spectra have the same origin, determined by the molecular ion Cr_2O_7. If this is so, then the differences in the spectra of dichromates are due to a slight perturbation of the Cr_2O_7 ion by different cations and by the crystal field. This assertion is also supported by the fact that, in aqueous solutions, the spectra of different dichromates are close to one another.

In addition to works devoted to the spectra of mono- and dichromates, there are data ([3]) on the spectra of other chromium compounds at low temperatures. In chromium alum, in some complex chromium salts, in chromphosphors, and in Cr_2O_3, discrete spectra are observed in the region 14,000-16,000 cm^{-1} and often also in the region 19,000-23,000 cm^{-1}, which are interpreted as transitions in the chromium 3d shell; moreover, it is asserted that transitions occur in the trivalent chromium ion Cr^{3+}. Some bands in complex chromium compounds are interpreted as transitions between components of the splitting of the ground level Cr^{3+} ^4F.

Tel’ tov ([2]) gives a similar interpretation for potassium dichromate as well, namely, that in both CrO_4 and Cr_2O_7 the line absorption is determined by transitions in the well-screened 3d shell of the central chromium ion. The narrow

Fig. 1 and Fig. 2 diagrams

Figure 1: Fig. 1 and Fig. 2 diagrams

and sharp bands of the spectrum obtained are treated by him as purely electronic transitions in the chromium ion, split as a consequence of the asymmetry of the crystal field and the complex form of the Cr_2O_7 radical.

Such an interpretation of the spectra of mono- and dichromates is not sufficiently convincing. Since all the electrons of the 3d shell participate in the valence bonds of chromium, it makes no sense to speak of a well-screened 3d shell of chromium. One can speak only of a continuity relation of the electronic terms of CrO_4 and Cr_2O_7 with the terms of the chromium 3d shell. If, however, the absorption is associated with electronic transitions in the central chromium, then such a hexavalent chromium ion (with a noble-gas shell) can have transitions only in the far ultraviolet and should not absorb in the region of 19,000 cm^{-1}.

Therefore, speaking of electronic transitions in dichromates, in our opinion, one should have in mind electronic transitions in the molecular ion Cr_2O_7 as a whole, and not in some shell of chromium. These transitions combine both with vibrations of the molecular ion Cr_2O_7 and with vibrations of the crystal lattice.

We ascribe the narrow sharp bands in the long-wavelength part of the dichromate spectrum to purely electronic transitions; the intense, relatively

Fig. 1. Projections of Cr_2O_7 ions onto the *ac* plane in an ammonium dichromate crystal. Black circles denote chromium; white circles denote oxygen, which forms two distorted tetrahedra around chromium atoms with a common vertex (O_4). In one of the Cr_2O_7 ions the oxygen atoms have been renumbered.

Fig. 2. The Cr_2O_7 ion on the basis of paper (4). Cr—Cr = 3.2 Å, Cr—O_1 = 1.55 Å, Cr—O_2 = 1.57 Å, Cr—O_3 = 1.78 Å, Cr—O_4 = 1.91 Å.

broad bands in the short-wavelength part of the spectrum—to electron-vibrational bands of the molecular ion Cr_2O_7. The weak, but for the most part sharp, satellites located between the intense bands, and the continuous background increasing toward the ultraviolet region, are apparently connected mainly with vibrations of the crystal lattice.

It would, of course, be desirable to compare the vibrational frequencies that appear under the interpretation of the dichromate spectra proposed above with data obtained by other methods for studying molecular vibrations. Unfortunately, the vibrational frequencies of dichromate molecules in the region of interest to us (up to 400 cm^{-1}) have not been experimentally investigated either in the infrared spectrum or in the Raman scattering spectrum.

A theoretical calculation of the vibrational frequencies of dichromates, in addition to cumbersome computations, requires exact knowledge both of the force constants and of the geometrical configuration of the molecules, which, unfortunately, is far from completely known. X-ray diffraction data on the structure of the Cr_2O_7 ion are known only for ammonium dichromate. In Fig. 1, on the basis of the numbers given in paper ([4]), projections of Cr_2O_7 ions onto the *ac* plane of an ammonium dichromate crystal are shown (the radii of the circles have been chosen only for convenience of the drawing). In Fig. 2 a diagram of the arrangement of atoms in the Cr_2O_7 ion is given, based on the numbers of paper ([4]). It may be thought that this ion has an analogous structure in other dichromates as well, i.e., that Cr_2O_7 consists of two deformed oxygen tetrahedra with one common oxygen atom, and with chromium at the center of each tetrahedron.

Let us estimate the minimum vibrational frequency ν_{min} of the isolated Cr_2O_7 ion. Obviously, the lowest frequency will be possessed by deformation vibrations associated with the angle formed by the longest valence bonds, at the ends of which are the heaviest atoms (or groups of atoms). In the case of Cr_2O_7 such a valence angle is the angle Cr—O—Cr (the distance Cr—O is equal to 1.9 Å) ([4]). In estimating ν_{min} for the force constant we shall use the value obtained for the valence angle H—O—H in H_2O ([5]). We shall assume that the other three oxygen atoms are rigidly bound to chromium. As a result we obtain for ν_{min} a value of about 100 cm^{-1}. As is evident from the analysis of dichromate spectra, in them repeatedly

sequences with a similar period (50 cm^{-1}) occur. This estimate, moreover, shows that all vibrational frequencies substantially smaller than ν_{min} should be assigned to lattice vibrations.

The frequency of deformation vibrations associated with the valence angle O —Cr—O can be roughly estimated from calculations of such vibrations for a tetrahedron; in this case ν is about 300 cm^{-1}.

Thus, the repeatedly occurring period in the spectra, $\nu \simeq 262^{-1}$ cm, may be associated with deformation vibrations of O—Cr—O.

Unfortunately, the absence of the necessary data on the vibrational frequencies and the structure of bichromate molecules does not permit a more detailed interpretation of the vibronic spectra.

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CITED LITERATURE

1. I. W. Obreimov, W. J. de Hass, Comm. phys. Lab. Univ. Leiden, No. 191a (1928).

2. J. Teltow, Zs. phys. Chem., (B), **43**, H. 5, 375 (1939).

3. Landolt-Börnstein, *Zahlenwerte und Funktionen aus Physik, Chemie*, 1, T. 2, Berlin, 1955, pp. 906–910.

4. A. Byström, K. A. Wilhelm, Acta Chem. Scand., **5**, 1003 (1951).

5. G. Herzberg, *Vibrational and Rotational Spectra of Polyatomic Molecules*, Moscow, 1949.

Note: Figure translations are in progress. See original paper for figures.