

## SHORT COMMUNICATIONS

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### The Raman spectrum of crocoite

CROCOITE, monoclinic  $\text{PbCrO}_4$ , is used as a pigment and has therefore been the subject of numerous optical studies. The Raman spectrum, however, does not seem to have been recorded.

The crystal structure of crocoite was described independently in 1964 by Naray Szabo and Argay and by Quareni and De Pieri. A three-dimensional refinement was published in 1965 by the latter authors. The space group is  $P2_1/n (C_{2h}^6)$  with  $Z = 4$ . In aqueous solution the chromate ion has  $T_d$  symmetry. All the allowed vibrations ( $1A_1 + 1E + 2T_2$ ) are Raman active but only the  $T_2$  symmetry species are infra-red active. In the structure of crocoite the chromium ion is in a position of  $C_1$  symmetry surrounded by four oxygens in distorted tetrahedral configuration. In the crystal therefore, all the degeneracies are removed and the resulting 9A vibrational modes are all Raman and infra-red active. Cr-O distances in crocoite are unusually small (average 1.65 Å) indicating a substantial amount of multiple-bonding character in the chromate ion. This leads to strong Raman interactions.

The  $\text{CrO}_4^{2-}$  ion absorbs strongly in the blue and violet region over the range 24 000–28 000  $\text{cm}^{-1}$  (Campbell, 1965) but transmits in the red. The present spectrum was obtained from a powdered specimen of natural crocoite from Tasmania (probably Dundas area) (U.Q. M2052) using a Perkin-Elmer LRI spectrometer with exciting red He-Ne laser radiation (8 milliwatts;  $\lambda$  6328 Å). Under low resolution the spectrum appears simpler than expected due to near coincidences of several of the lines. This was anticipated because in solution the symmetric  $\nu_1(A_1)$  and asymmetric  $\nu_3(T_2)$  stretching vibrations of  $\text{CrO}_4^{2-}$  are at 847 and 884  $\text{cm}^{-1}$  and the deformation modes  $\nu_2(E)$  and  $\nu_4(T_2)$  are at 348 and 368  $\text{cm}^{-1}$  respectively (Stammreich, 1958). With removal of degeneracies by the lowering of site symmetry, a maximum of four bands should appear in the 850  $\text{cm}^{-1}$  region and five bands in the 350  $\text{cm}^{-1}$  region. The actual spectrum (fig. 1) agrees well with that predicted except that only three bands are observed in the high-frequency region, the fourth band not being observed due to low intensity or accidental coincidence. The weaker bands below 300  $\text{cm}^{-1}$  can be assigned to Pb-O or lattice vibrations. The frequencies observed are (Raman frequencies for  $\text{CrO}_4^{2-}$  in solution, Stammreich, 1958, in parentheses): 838  $\text{cm}^{-1}$  ( $\nu_1$  847); 853, 825, ( $\nu_3$  884); 400, 377, 359, 336, 326 ( $\nu_4$  368,  $\nu_2$  348); Pb-O or lattice modes, 184, 135, 36.

The well-defined simple Raman spectrum makes an interesting comparison with the equivalent complex infra-red spectrum (Campbell, 1965; Duval and Lecomte,

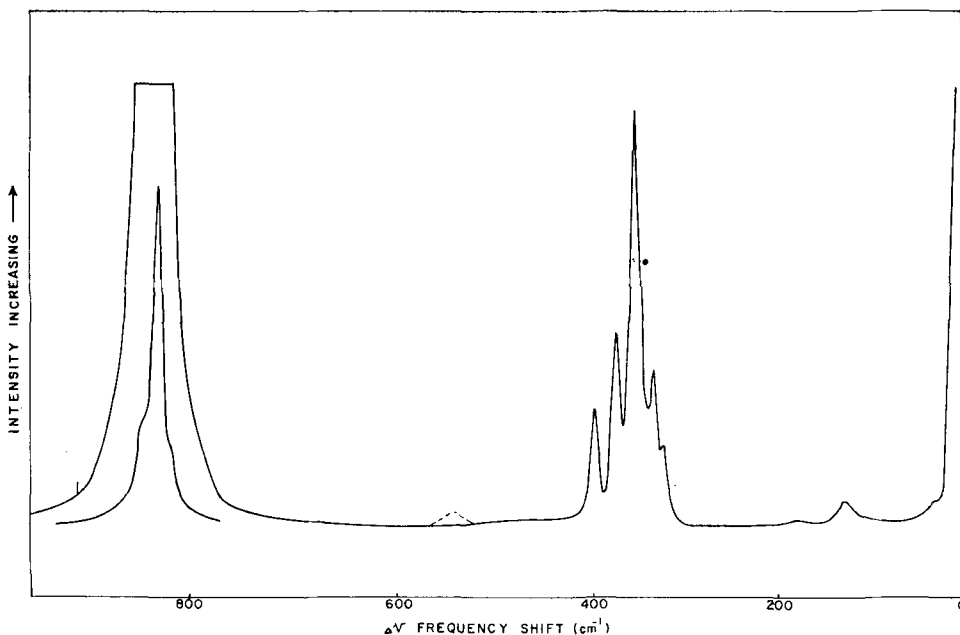


FIG. 1. Raman spectrum of crocoite. Spectral slit widths: upper spectrum ( $5 \text{ cm}^{-1}$ ), lower spectrum ( $2 \text{ cm}^{-1}$ ). Spurious laser peak dotted.

1954; Moenke, 1960). Reasons for this difference have been discussed by Griffith (1969) in a survey of the Raman spectra of several minerals. With a more intense laser source it should be possible to observe the factor-group splittings due to the presence of four  $\text{PbCrO}_4$  'molecules' in the unit cell.

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