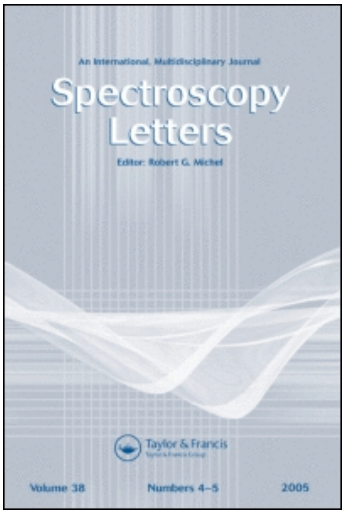

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Vibrational Spectra of Ag_2CrO_4

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VIBRATIONAL SPECTRA OF Ag_2CrO_4

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It has been shown[1] recently that Ag_2CrO_4 has a crystal structure which is unique among simple anhydrous chromates studied to date. Like the chromates of potassium[2], rubidium[3], and cesium[4], it may be assigned to the space group Pnma - D_{2h}^{16} with four formula units per unit cell and chromium atoms on C_s sites. However, unlike the alkali-metal chromates, the cations are equally divided between sites of C_s and C_i symmetries. Furthermore, metal-oxygen distances in Ag_2CrO_4 range from 2.34 to 2.62Å, as contrasted with 2.7 to about 3.2Å in K_2CrO_4, and point to a greater degree of convalent bonding between cations and anions.[1] The present infrared and Raman data have been obtained with an interest in determining the spectral manifestations of this unique structure.

Silver chromate was obtained by mixing solutions of sodium chromate and silver nitrate in the stoichometric amounts. The precipitate was collected by filtration, washed with distilled water, and dried for several hours at 140°C. The resulting product was very dark brown, appearing to be almost black. Attempts to prepare single crystals by slow diffusion in silica gel, similar to the method used by Hackert and Jacobson[1], yielded crystals which were too small for oriented single-crystal Raman studies.

The survey infrared spectrum of Ag_2CrO_4 has been published by Campbell[5], although no specific frequencies were reported. Consequently infrared spectra have been obtainted as part of the present study. Spectra were

obtained in the region 250-1200 cm^{-1} from Nujol mull samples on CsI plates with a Perkin-Elmer 225 spectraphotometer. These spectra are essentially the same as the published spectrum[5], except that certain weak bands appearing in Campbell's spectrum in the region 400-600 cm^{-1}, and which can not be attributed to Ag_2CrO_4, are not found in the spectra reported here.

Initial attempts to obtain the Raman spectrum of Ag_2CrO_4 with a 90 mw He/Ne laser (6328Å) were unsuccessful, probably due to the low laser power levels and absorption by the sample. Rapid sample decomposition occurred with the more powerful Kr-6471Å excitation. Sample rotation at 3000 rpm, in the manner of Kiefer and Bernstein[6], proved to be a successful technique for obtaining the Raman spectrum with 6471Å excitation at a power level of 200 mw, measured at the sample. The data reported here were obtained with a Cary 82 triple monochromator at constant spectral band widths of 1.5 to 3.0 cm^{-1}. Attempts to use Ar-5145Å excitation with sample rotation gave spectra with broad spurious bands, probably arising from fluorescence.

The factor group selection rules which form the basis for interpreting the spectra, are summarized in Table 1.

In keeping with the centrosymmetric space group, mutual exclusion of infrared and Raman frequencies is predicted. As with the crystal structures, the selection rules for Ag_2CrO_4 and the alkali-metal chromates of D_{2h} symmetry[7] are similar but not identical.

TABLE 1

Type of Mode	Number Active	
	Infrared	Raman
ν_1	2	2
ν_2	3	4
ν_3	5	6
ν_4	5	6
rotatory	4	6
translatory	16	12

A typical survey Raman spectrum of Ag_2CrO_4 is shown in Figure 1. Table 2 lists infrared and Raman frequencies gleaned from more carefully obtained spectra. In the absence of single crystal data, the assignments of the spectra must be regarded as tentative.

Evidence for appreciable cation-anion covalent bonding can be seen in the vibrational spectra of Ag_2CrO_4. The frequencies of the stretching modes (ν_1 and ν_3) are 20-40 cm^{-1} lower than those of the alkali-metal chromates[7]. The typically clean separation between ν_1 and ν_3, in the order $\nu_1 < \nu_3$, appears to be lost in Ag_2CrO_4; and a strong Raman band at 777 cm^{-1}, below the very strong ν_1 component, appears to be due to ν_3. It is

TABLE 2

Vibrational Frequencies of Ag_2CrO_4[a]

Raman, cm^{-1}	Infrared, cm^{-1}	Assignment
ca. 1630 w		$2\nu_1$, $2\nu_3$, $\nu_1+\nu_3$
876 vw (sh)		
856 vw (sh)	860 s	ν_3
849 w (sh)	826 s	
812 vs	798 s	ν_1
777 s		ν_3
375 w	398 vw	ν_4
355 vw	376 w	ν_2
339 w	360 w	
115 vw	b	
50 m		lattice
40 w		
28 w		

a. Abbreviations: v-very, w-weak, s-strong, sh- shoulder.

b. No data below 250 cm^{-1}.

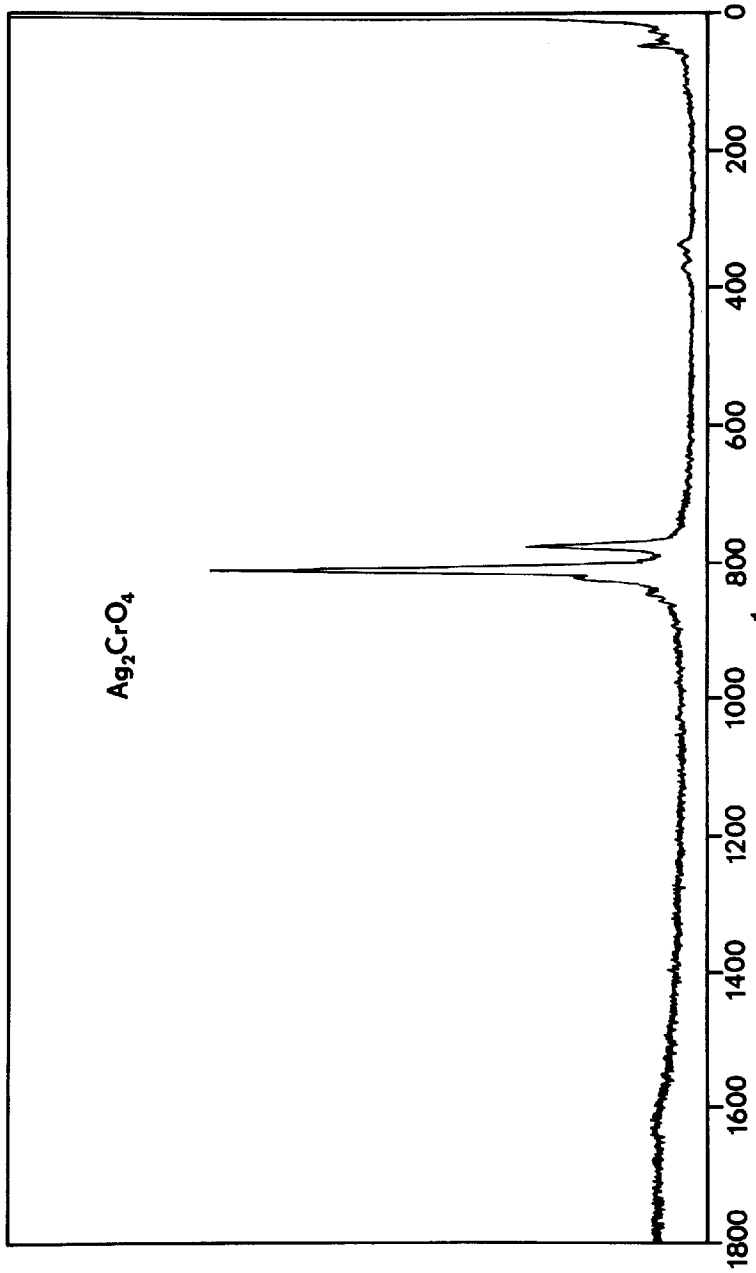

Figure 1. Raman spectrum of Ag_2CrO_4 obtained with sample rotation and 6471Å excitation.

noteworthy that $PbCrO_4$ also displays ν_3 components of both higher and lower frequencies than the strong ν_1 mode[8].

By contrast, the bending modes of Ag_2CrO_4 have comparable frequencies to those found for the alkali-metal chromates; although the separation between ν_2 and ν_4 components is less distinct for the silver compound.

Unlike typically ionic compounds, the separation between factor group components of the same free-ion origin is slight. Consequently many accidental degeneracies occur, and the number of bands observed is considerably less than the number allowed. Comparison of the infrared and Raman frequencies indicates mutual exclusion, in agreement with the selection rules, and there can be little doubt that the crystal structure of Ag_2CrO_4 is centrosymmetric. The disparity between gerade and ungerade modes is generally small for ionic compounds. The atypically large differences between infrared and Raman frequencies for Ag_2CrO_4 appear to arise from directional Ag-O covalent bonding.

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