

Contribution from the Christopher Ingold Laboratories,
University College London, London WC1H 0AJ, United Kingdom

Raman, Resonance Raman, and Infrared Spectroscopic Study of Silver(I) Chromate

ROBIN J. H. CLARK* and TREVOR J. DINES

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The resonance Raman spectrum of silver(I) chromate has been recorded over a wide range (363.8–799.3 nm) of excitation wavelengths in order to probe the nature of the broad electronic transition of the complex centered around 450 nm responsible for the red color. Under resonance conditions, the $\nu_1(a_1)$ band of silver chromate is greatly enhanced, but no overtone progressions involving ν_1 are observed. This behavior contrasts in key respects with that of alkali metal salts of the chromate ion; the latter are yellow, with the lowest charge-transfer band at ca. 360 nm, and, under resonance conditions, not only is the $\nu_1(a_1)$ band greatly enhanced but long intense overtone progressions in ν_1 are obvious. Moreover, the excitation profile of the ν_1 band of silver chromate does not maximize at the resonance electronic band maximum, as it does for alkali metal salts of the chromate ion, but at 14 650 cm^{-1} , over 5000 cm^{-1} below the absorption maximum of the resonant electronic band. Reasons for this behavior of the silver salt of the chromate ion are discussed in relation to the X-ray crystal structure of the salt, which implies significant, though small, deviations of the chromate ion from tetrahedral geometry and, more importantly, significant Ag–O and possibly Ag–Ag interactions. Both the infrared and the Raman spectra of the ion imply the presence of substantial site and factor group effects.

Introduction

The "anomalous" red color of silver(I) chromate, $\text{Ag}_2[\text{CrO}_4]$ (in common with the unusual colors of many other salts of post transition metals), is a well-known but poorly understood phenomenon. Most chromate salts, especially those of the group 1A and 2A metals, are yellow due to an absorption band at around 360 nm (27 800 cm^{-1}) arising from the lowest allowed ligand-to-metal charge-transfer transition, ${}^1T_2 \leftarrow {}^1A_1$ ($t_1^5 e^1 \leftarrow t_1^6$). However, in $\text{Ag}_2[\text{CrO}_4]$ there is an intense absorption centered on 450 nm,^{1,2} which is responsible for the red color. The explanations put forward for the appearance of this absorption band and possible assignments for it may be summarized as follows: (1) transfer of an Ag^+ 4d electron to the lowest unoccupied e orbitals of the $[\text{CrO}_4]^{2-}$ ion (an interionic transition);¹ (2) a shift of the ${}^1T_2 \leftarrow {}^1A_1$ transition of the $[\text{CrO}_4]^{2-}$ ion to lower energy, due to a "second-order Davydov interaction" between the 1T_2 excited state of the $[\text{CrO}_4]^{2-}$ ion and an excited state of the Ag^+ ion resulting from intraionic transitions of the $5s \leftarrow 4d$ or $5p \leftarrow 4d$ sorts;² (3) induction of allowed character to the ${}^1T_1 \leftarrow {}^1A_1$ ($t_1^5 e \leftarrow t_1^6$) transition (which is very weak, at $\sim 22\,500\text{ cm}^{-1}$, for $\text{K}_2[\text{CrO}_4]$) due to the lowering of symmetry of the $[\text{CrO}_4]^{2-}$ ion in the $\text{Ag}_2[\text{CrO}_4]$ lattice.³

Robbins and Day² recorded the absorption spectrum of $\text{Ag}_2[\text{CrO}_4]$, doped into a single crystal of $\text{Ag}_2[\text{SO}_4]$, at 4.2 K. At this temperature, the 450-nm band displays vibronic structure, the average separation between the components being ca. 750 cm^{-1} . This wavenumber is similar to that found for the ${}^1T_2 \leftarrow {}^1A_1$ absorption band of alkali metal chromates, and because the Franck–Condon factors are also similar, the authors plausibly concluded that the 450-nm band arises from the ${}^1T_2 \leftarrow {}^1A_1$ transition, red shifted in the silver salt, rather than from a transition of the $[\text{CrO}_4]^{2-}(e) \leftarrow \text{Ag}(4d)$ type, which would involve breaking the 4d shell and therefore presumably lie at higher energy. The third possibility, that the 450-nm band is due to the ${}^1T_1 \leftarrow {}^1A_1$ transition,³ needs careful consideration in that the $[\text{CrO}_4]^{2-}$ has been shown, by an X-ray crystallographic study,⁴ to suffer significant (though small) distortions from tetrahedral geometry in $\text{Ag}_2[\text{CrO}_4]$. The similarity between the Franck–Condon factors and vibrational intervals for the 450-nm band of chromate ion doped in $\text{Ag}_2[\text{SO}_4]$ and for the 360-nm, ${}^1T_2 \leftarrow {}^1A_1$, band of alkali metal chromate salts might then be explained in terms of the fact that the 1T_1 and 1T_2 states both derive from the same

excited configuration of the $[\text{CrO}_4]^{2-}$ ion. However, this interpretation seems improbable, since it seems unlikely that relatively small site and factor group effects could induce such great intensity into a band that is forbidden in T_d symmetry and because it would require that the ${}^1T_2 \leftarrow {}^1A_1$ band should still be present at 360 nm in the spectrum of $\text{Ag}_2[\text{CrO}_4]$, a situation that appears not to be the case.

Although we favor the interpretation of Robbins and Day² concerning the assignment of the 450-nm band, it seemed appropriate to perform a resonance Raman study of $\text{Ag}_2[\text{CrO}_4]$, since the technique of resonance Raman spectroscopy has become important as an aid to making electronic band assignments. The Raman spectrum of $\text{Ag}_2[\text{CrO}_4]$ has not been previously reported, presumably on account of problems arising from photodecomposition of the sample. By use of a rotating-sample device we have successfully obtained Raman spectra of $\text{Ag}_2[\text{CrO}_4]$ using laser excitation in the range 363.8–799.3 nm. Additionally, we have measured the infrared spectrum, which previously had only received cursory examination.⁵

Experimental Details

$\text{Ag}_2[\text{CrO}_4]$ was prepared metathetically by reaction of $\text{Ag}[\text{NO}_3]$ and $\text{K}_2[\text{CrO}_4]$ in aqueous solutions and dried in vacuo. For Raman measurements, solid samples were dispersed in $\text{Na}_2[\text{SO}_4]$ and rotated at ca. 1000 rpm to minimize decomposition. Attempts to record the resonance Raman spectra of $[\text{CrO}_4]^{2-}$ doped into $\text{Ag}_2[\text{SO}_4]$ were unsuccessful, owing to the rapid photodecomposition of the sample in the laser beam. Low-temperature (ca. 14 K) Raman measurements were obtained from $\text{Ag}_2[\text{CrO}_4]$ dispersed in a pressed disk of $\text{Na}_2[\text{SO}_4]$ by using an Air Products Displex cryostat in association with a Leybold-Heraeus turbomolecular pump. For minimization of decomposition, a cylindrical lens was employed to produce a line focus of the laser beam on the sample.

Raman spectra were recorded with Spex 1401 and 14018 (Ramalog 6) double monochromators, in conjunction with Coherent Radiation Models CR3 and CR12 argon ion and CR500K krypton ion lasers. Detection of the scattered radiation was by standard photon-counting techniques employing RCA C31034 photomultipliers. Wavenumber measurements were calibrated by reference to the emission spectrum of neon, and band intensities were corrected for the spectral response of the spectrometers.

Infrared spectra were obtained from Nujol mulls with use of a Perkin-Elmer 225 infrared spectrometer. Diffuse-reflectance spectra of $\text{Ag}_2[\text{CrO}_4]$ dispersed in $\text{Mg}[\text{CO}_3]$ were recorded with a Pye-Unicam SP800 spectrophotometer.

Infrared and Raman Spectra. The Raman and infrared spectra of $\text{Ag}_2[\text{CrO}_4]$ are shown in Figures 1 and 2 and the band wavenumber measurements and assignments in Table

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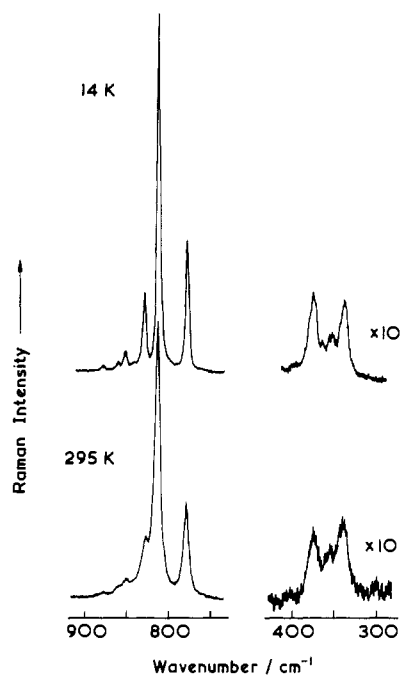


Figure 1. Raman spectrum of $\text{Ag}_2[\text{CrO}_4]$ recorded with 647.1-nm excitation, at 295 K and 14 K, with power at the sample ca. 100 mW, spectral slit width 2 cm^{-1} , scan speed $25 \text{ cm}^{-1} \text{ min}^{-1}$, and time constant 1 s.

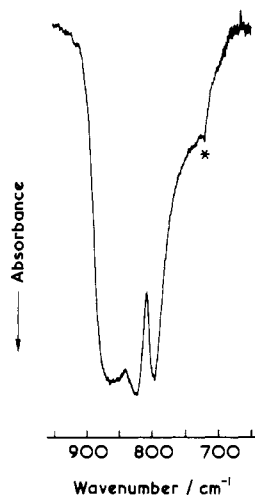


Figure 2. Infrared spectrum of $\text{Ag}_2[\text{CrO}_4]$ in the region $700\text{--}900 \text{ cm}^{-1}$ (asterisk denotes a Nujol band).

I. In the Raman spectrum, bands attributable to all four of the fundamentals of the free $[\text{CrO}_4]^{2-}$ ion are observed. The infrared spectrum, by contrast, only displays bands in the $\nu(\text{Cr-O})$ region. The observation of multiple components for each of the fundamentals is due to the presence of both site group and factor group perturbations. $\text{Ag}_2[\text{CrO}_4]$ crystallizes in the space group $Pnma$ (D_{2h}^{16}) with four formula units per unit cell, the $[\text{CrO}_4]^{2-}$ ions occupying sites of C_s symmetry. Table II shows the correlation diagram and factor group selection rules for $\text{Ag}_2[\text{CrO}_4]$. From this table it is evident that the splitting of the $[\text{CrO}_4]^{2-}$ internal modes is as follows: (1) The totally symmetric stretching mode $\nu_1(a_1)$ gives rise to four bands, of which two are Raman active and two are infrared active. (2) The symmetric deformation mode $\nu_2(e)$ gives rise to eight bands, of which four are Raman active, three are infrared active, and one is inactive. (3) The asymmetric stretching mode $\nu_3(t_2)$ and the asymmetric deformation mode $\nu_4(t_2)$ each give rise to twelve bands, of which six are Raman active, five are infrared active, and one is inactive.

Table I. Details of the Infrared and Raman Spectra of $\text{Ag}_2[\text{CrO}_4]$

assignt	wavenumber/ cm^{-1}		
	IR	Raman	
		295 K	14 K
ν_2, ν_4		339 ± 1	339 ± 1
		355 ± 2	354 ± 2
		375 ± 1	364 ± 2
		776.9 ± 1	376 ± 1
ν_1	797 ± 1		777.0 ± 0.5
		812.3 ± 0.5	812.0 ± 0.5
ν_3		826 ± 1	828.2 ± 0.5
		849 ± 2	842 ± 1
	858 ± 2		851 ± 1
		859 ± 2	860 ± 1
		878 ± 2	878 ± 1

Table II. Correlation Diagram and Selection Rules for the Internal Modes of the $[\text{CrO}_4]^{2-}$ Ion in the $\text{Ag}_2[\text{CrO}_4]$ Lattice

free ion	site ^a	cryst	activity
T_d	C_s	D_{2h}	
$\nu_1 A_1$	A' }	A_g	} Raman
		B_{2g}	
		B_{1u}	} IR
		B_{3u}	
$\nu_2 E$	A' }	A_g	} Raman
		B_{2g}	
		B_{1u}	} IR
	B_{3u}		
	A'' }	B_{1g}	
		B_{3g}	
A_u		inactive	
$\nu_3, \nu_4 T_2$	2A' }	B_{2u}	IR
		$2A_g$	} Raman
		$2B_{2g}$	
		$2B_{1u}$	} IR
	$2B_{3u}$		
	A'' }	B_{1g}	} Raman
		B_{3g}	
		A_u	inactive
B_{2u}		IR	

^a The σ_{xz} correlation is appropriate because it is the xz plane in the D_{2h} factor group that corresponds to the mirror plane of the C_s site group.

The number of infrared- and Raman-active bands observed, especially in the OCrO bending region, is many fewer than is predicted, probably because some of the splittings are too small to be resolved and also because some component bands are too weak to be detected. In the infrared spectrum no bands attributable to the deformation modes $\nu_2(e)$ and $\nu_4(t_2)$ were observed. Such bands were reported by Campbell⁵ to be seen in the infrared spectrum of silver(I) chromate, although no band wavenumber measurements were given. Their observations may be due to the fact that their spectra were obtained from samples held in KBr disks, a procedure that may result in exchange of cations. We have shown that grinding of $\text{Ag}_2[\text{CrO}_4]$ in KBr produces a yellow coloration that is considered to be due to the formation of $\text{K}_2[\text{CrO}_4]$; this conclusion is supported by the appearance of bands in the infrared and Raman spectra attributable to this salt. It was for this reason that we obtained our infrared spectra from Nujol mulls and the Raman spectra from samples dispersed in $\text{Na}_2[\text{SO}_4]$, in which media no cation exchange occurs.

In an endeavor to improve the resolution of the infrared and Raman spectra, they were also recorded from samples held at 14 K. This resulted in the observation of an additional component of ν_3 and an additional band in the OCrO deformation region in the Raman spectrum, but no additional features were observed in the infrared spectrum. The Raman

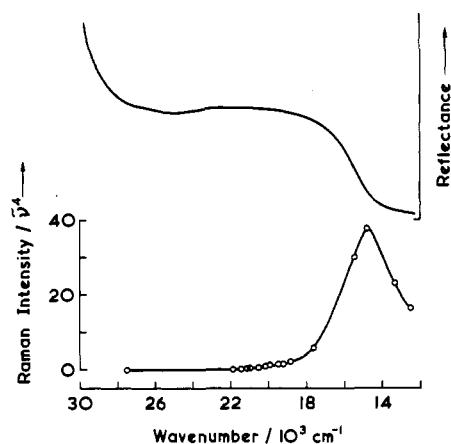


Figure 3. Diffuse-reflectance spectrum of $\text{Ag}_2[\text{CrO}_4]$ and Raman excitation profile for the bands assigned to ν_1 .

band wavenumbers and relative intensities measured at 14 K are, within experimental error, identical with those obtained at ambient temperature. Such an observation is strong evidence for the absence of any structural phase transitions occurring upon cooling of the sample to 14 K. It also suggests that the lattice does not contract significantly upon cooling, since this would cause the Raman bands to shift to higher wavenumbers.

The likely importance of solid-state effects on the spectroscopic properties of silver(I) chromate is evident from the insolubility of the salt in polar solvents and from the known structural details thereon. The chromate ion itself deviates significantly, but not markedly, from tetrahedral geometry;⁴ thus, the Cr–O bond lengths range from 1.63 to 1.69 Å and the OCrO bond angles from 106.1 to 111.6°. Of much greater importance, spectroscopically, is likely to be the more covalent nature of the Ag–O (than alkali metal-to-oxygen) bonds, as evidenced by their shortness (down to 2.35 Å) and directionality. Although no bands attributable to Ag–O stretching modes could be detected in either the infrared or Raman spectra of $\text{Ag}_2[\text{CrO}_4]$, nevertheless the virtual “bridging” nature of the $\text{Ag}\cdots\text{O}-\text{Cr}$ linking has the consequence of a 4–6% lowering of the Cr–O stretching (though virtually none of the bending) mode wavenumbers as compared to their values for the free $[\text{CrO}_4]^{2-}$ ion: viz., for free $[\text{CrO}_4]^{2-}$, ν_1 and ν_3 are 846 and 890 cm^{-1} , respectively, whereas for $\text{Ag}_2[\text{CrO}_4]$, the average values of the factor group components of ν_1 and ν_3 are 795 and 853 cm^{-1} , respectively. Moreover, the silver ions themselves can be considered to lie in chains and are only 3.51 Å apart (cf. 3.3 Å in the $\text{Ag}_2[\text{SO}_4]$ structure),⁶ and thus the formation of an exciton band localized on the silver ions is possible.

Resonance Raman Spectra and Excitation Profiles. By using the ν_1 band of $\text{Na}_2[\text{SO}_4]$ as an internal intensity standard, we have constructed an excitation profile for the ν_1 band of $\text{Ag}_2[\text{CrO}_4]$, using laser excitation ranging from 799.3 to 363.8 nm, and the resulting plot is shown in Figure 3, together with the diffuse-reflectance spectrum. The intensity measurements were obtained for both components of ν_1 , but it was found that, for each exciting line, the ratio of the intensities of the two was the same, the 812- cm^{-1} component being 3 times more intense than the 777- cm^{-1} one.

Excitation within the contour of the 360-nm band of $\text{K}_2[\text{CrO}_4]$ ^{7,8} (and also of the analogous 530-nm band of $\text{K}[\text{MnO}_4]$)^{9,10} leads to enormous enhancement of the intensity

of the $\nu_1(a_1)$ band, the excitation profile of which peaks at the resonance band maximum, and to the development of long overtone progressions in ν_1 . This is as expected for a band whose intensity is controlled by the Franck–Condon (*A*-term) scattering mechanism.¹¹ However, the excitation profile of the ν_1 band of $\text{Ag}_2[\text{CrO}_4]$ differs substantially from that of alkali metal salts thereof, and no overtones of ν_1 are detected. Instead, we observe maximum Raman intensity for the ν_1 band with 676.4-nm excitation and a rapid decrease in its intensity at both shorter and longer wavelengths. It was initially thought that this was a result of photodecomposition of the sample for excitation within the contour of the 450-nm band. However, we were able to rule this out by using a bracketing procedure for the intensity measurements; i.e., for each exciting line the intensities of the ν_1 bands of $\text{Ag}_2[\text{CrO}_4]$ and $\text{Na}_2[\text{SO}_4]$ were measured alternately several times. Also we established that the intensities obtained with the red excitation lines (647.1–799.3 nm) were not altered after several hours' exposure to shorter wavelength laser excitation. A quantitative intensity measurement, obtained with use of a sample containing known proportions of $\text{Ag}_2[\text{CrO}_4]$ and $\text{Na}_2[\text{SO}_4]$, showed that for 647.1-nm excitation the 812- cm^{-1} component of ν_1 of $\text{Ag}_2[\text{CrO}_4]$ is 1300 times more intense than ν_1 of $\text{Na}_2[\text{SO}_4]$. This is strong evidence for resonance enhancement in the red region of the spectrum.

General Discussion. The lack of overtones of ν_1 of $\text{Ag}_2[\text{CrO}_4]$ at resonance is striking, in view of the long progressions (to $10\nu_1$) and the high $I(2\nu_1)/I(\nu_1)$ ratio (0.67) observed under these conditions for $\text{K}_2[\text{CrO}_4]$.^{7,8} Such long progressions are a consequence of a substantial (~ 0.1 -Å) change in CrO bond length on excitation from the ground to the resonance excited state. The lack of such progressions in the resonance Raman spectrum of $\text{Ag}_2[\text{CrO}_4]$ could be interpreted to imply that the structural change on excitation in this case is very small ($\ll 0.1$ Å). This could occur if either (a) the resonance electronic transition were not in this case the ${}^1T_2 \leftarrow {}^1A_1$ ($t_1^5 e^1 \leftarrow t_1^6$) transition but (for example) one involving the cation only or (b) the distinct three-dimensional nature of the bonding, and in particular the significant Ag–O covalent bonding, operates to restrict any structural changes on excitation. We discount (a) for the reasons outlined by Day² and note, apropos of (b), that it is not unusual for resonance Raman spectra of large molecules (even under conditions favoring *A*-term scattering) to lack overtones, by virtue of the structural changes on excitation being very small along any one coordinate, viz., the situation for ruthenium red and brown.¹² Yet this interpretation cannot be correct, since a Franck–Condon progression in ν_1 is observed in the electronic absorption spectrum of $[\text{CrO}_4]^{2-}$ doped into $\text{Ag}_2[\text{SO}_4]$ at 4.2 K. The relative intensities of the members of this progression, and the vibrational intervals, are very similar to those observed in $\text{K}_2[\text{CrO}_4]$, indicating that the Cr–O bond lengths do, in fact, increase by ca. 0.1 Å upon excitation to the lowest-energy 1T_2 state of $\text{Ag}_2[\text{CrO}_4]$.

It is possible that the lack of observation of an overtone progression involving ν_1 in the resonance Raman spectrum may be due to significantly larger bandwidths for the overtones than for the fundamental. This would be the case if vibrational relaxation from the $\nu_1 \geq 2$ levels of the ground state were much faster than from $\nu_1 = 1$. Resonance Raman studies of transition-metal oxo- and thioanions (see, for example, refs 13 and 14) have demonstrated that the bandwidths of the members

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of overtone progressions are dependent on the nature of the cation. It is found that overtone progressions in ν_1 bands of complex anions are sharper and better resolved for salts containing large cations such as $[\text{Bu}_4\text{N}]^+$ or $[\text{Ph}_4\text{P}]^+$ than for small ones such as K^+ or $[\text{NH}_4]^+$ and also better resolved for complex anions isomorphously diluted into a host lattice. These results are believed to indicate that short distances between adjacent anions, and therefore strong interactions, favor fast vibrational relaxation and consequently large bandwidths. Although the unit cell dimensions for $\text{Ag}_2[\text{CrO}_4]$ are similar to those for $\text{K}_2[\text{CrO}_4]$, the factor group perturbations of the vibrational spectra of the former are indicative of strong interactions between neighboring $[\text{CrO}_4]^{2-}$ ions. It is thus likely that such interactions could promote faster vibrational energy transfer from the $\nu_1 \geq 2$ levels of the ground state of $\text{Ag}_2[\text{CrO}_4]$ than from those of $\text{K}_2[\text{CrO}_4]$, leading to the absence of an overtone progression for the former.

The unusual nature of the ν_1 band excitation profile of $\text{Ag}_2[\text{CrO}_4]$ in the sense that it maximizes over 5000 cm^{-1} to the low-frequency side of the resonant band maximum could have three possible explanations.

(1) The decrease in ν_1 band intensity at wavelengths shorter than 676.4 nm could result from an interference between contributions to the Raman intensity arising from the 450-nm band and from ones lying at higher energies. This effect has been observed at resonance with ligand field bands.^{15,16} However, the transition moments of the resonant bands were much lower in these cases than that apparent for the 450-nm band of $\text{Ag}_2[\text{CrO}_4]$, and the extent of Raman band intensity loss in the vicinity of the resonant transition was much less than that reported on here. Hence this possibility is discounted.

(2) The behavior of the ν_1 band could be a consequence of a surface-enhancement effect operating most effectively in the 700-nm region. Indeed, there is a close similarity between the ν_1 band excitation profile of $\text{Ag}_2[\text{CrO}_4]$ and those observed for bands of pyridine and related molecules adsorbed onto silver surfaces; such bands all maximize in intensity in the $720\text{--}780\text{-nm}$ region.¹⁷ However, the similarity of excitation

profiles is probably coincidental, since the silver chromate and the silver surfaces seem to be too disparate in nature for a common explanation to be operative (there are, in any case, at least four entirely different "explanations" of surface-enhanced Raman spectroscopy).¹⁷

(3) The behavior of the excitation profile of ν_1 is closely similar to that of the $\text{X-Pt}^{\text{IV}}\text{-X}$ chain-stretching mode of a large number of linear-chain halogen-bridged mixed-valence complexes of platinum.¹⁸ In these cases, the resonant transition is the $\text{Pt}^{\text{IV}} \leftarrow \text{Pt}^{\text{II}}$ intervalence transition, which is highly anisotropic and best discussed in terms of one-electron band structures determined from the tight-binding scheme based upon the extended Hückel method.¹⁹ Robbins and Day² have already suggested that the red shift of the ${}^1\text{T}_2 \leftarrow {}^1\text{A}_1$ ($t_1^5 e^1 \leftarrow t_1^6$) transition in $\text{Ag}_2[\text{CrO}_4]$ is a consequence of a "second-order Davydov effect", viz., a mixing between two nondegenerate intramolecule transitions through the crystal potential, lowering the transition energy of the one and raising that of the other. They identified the higher energy transition with an intraionic excitation of the silver ion chains and the lower transition with the 450-nm band, viz., the intramolecular ${}^1\text{T}_2 \leftarrow {}^1\text{A}_1$ transition of the $[\text{CrO}_4]^{2-}$ ion. The dispersion of the exciton band localized on the silver ions would show semiconductor properties and considerable anisotropy and, in consequence, the ${}^1\text{T}_2 \leftarrow {}^1\text{A}_1$ transition of the $[\text{CrO}_4]^{2-}$ ion (insofar as it is coupled to the former via $\text{Ag}\cdots\text{O}$ covalent bonding) would likewise. The ${}^1\text{T}_2 \leftarrow {}^1\text{A}_1$ transition thus acquires significant anisotropy and semiconductor character, and hence the excitation profile of the ν_1 band of $\text{Ag}_2[\text{CrO}_4]$ peaks to the red side of the resonant transition, presumably at a wavenumber that coincides with that of the imaginary part of the dielectric constant (ϵ''), which is also the gap frequency (ω_g) of a semiconductor.²⁰⁻²² This last possibility is the one we favor; we propose to extend such Raman intensity studies to other deeply colored silver(I) salts and also to salts of other post transition metals, especially those of mercury and thallium.

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