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Electronic and vibrational spectra of $\text{Cr}_2\text{O}_7^{2-}$ ions in potassium halide matrices

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Optical and infrared spectra of dichromate ions in KCl, KBr, and KI matrices are reported. Optical spectra of $\text{Cr}_2\text{O}_7^{2-}$ consist of three absorption bands that are attributed to the electronic transitions ${}^1A_1(t_1^6) \rightarrow {}^1T_2(t_1^5 t_2^1)$; ${}^1A_1(t_1^6) \rightarrow E(t_1^5 t_2^1)$ or ${}^1T_2(t_1^5 t_2^1)$; and ${}^1A_1(t_1^6) \rightarrow {}^1T_2(t_1^5 e^1)$ on the basis of molecular orbitals. Fine structure caused by coupled vibration-electronic transitions is observed in the ${}^1A_1(t_1^6) \rightarrow {}^1T_2(t_1^5 e^1)$ band. This fine structure further splits at low temperature (77°K) because of the symmetry lowering of the dichromate ion from T_d to C_{3v} . Infrared spectra show a number of lines. A model that assumes that the dichromate ion enters the lattice by replacing two halide ions with no charge compensating vacancy satisfactorily explains all the experimental results.

INTRODUCTION

In recent years the properties of complex molecular impurities in different crystalline matrices have acquired special interest in solid state research since such investigations yield appreciable information regarding the impurity ions.¹⁻⁶ In the optical spectra of such complex impurities in crystals, one observes electronic transitions within the molecular orbitals of the ions, but more interesting is the fact that superposed on such electronic transitions a fine structure arising due to the vibration levels of the molecule is also observed. In cases where the symmetry of the molecule is changed in the crystal field, corresponding splittings in the degenerate vibrational and electronic levels of the molecule are also observed. Many forbidden transitions make their appearance because certain selection rules⁵ are broken. With a view to study such properties a large ion (Cr_2O_7) has been chosen for the present investigations. The ion has been incorporated in cubic KCl, KBr, and KI matrices. A preliminary report on such investigations has already been published.⁶ In this paper we describe the results of detailed investigations on the system.

Dichromate ion consists of a linear Cr-O-Cr skeleton with each chromium atom having three more oxygen atoms bound to it. The four oxygens around each chromium form a distorted tetrahedron.⁷ The over-all symmetry of the molecule as inferred from infrared and Raman spectra is C_{2v} .^{8,9} The optical spectra of such molecular ions are treated on the basis of molecular orbital theory.^{5,10} The optical absorption spectra of chromate¹ and dichromate (present investigations) ions in aqueous solution are identical in nature. Two bands are observed in each case, which differ slightly in position. X-ray band spectra¹¹ also agree qualitatively for the two ions. Since the optical properties of these ions arise due to charge transfer from ligands to the metal atoms and the effect of metal-metal ligand is too small on the molecular orbitals, one can consider the dichromate ion to consist of two (T_d) chromate ions having a common oxygen for all optical transitions. Therefore the molecular orbital picture as proposed for tetrahedral chromate ions¹² is valid in the present case too. All the electronic transitions henceforth discussed in this communication have

thus been accounted for on the basis of molecular orbitals of the chromate ion. However, in explaining the vibrational spectra, one has to consider the over-all symmetry of the dichromate molecule, which is C_{2v} in the present case.⁷

EXPERIMENTAL

Crystals used in the investigations were grown from melt using Kyropoulos technique. AR grade BDH powders of alkali halides and potassium dichromate were used as the growth materials. Some chemical and EPR experiments⁶ were performed to confirm that the dichromate ions did not decompose during the growth from melt at high temperatures. Optical spectra were recorded using a Cary-14 spectrophotometer. A metal cryostat was used for low temperature optical experiments. X-ray coloration was done on a Philips x-ray unit with molybdenum target operating at 35 kV and 15 mA. Additive coloration was done by heating the crystals in potassium vapors at high temperatures (400–500 °C) in evacuated and sealed glass tubes. Infrared spectra were recorded on Beckman IR-12 and Perkin-Elmer (model 257) units. The absorption due to the host crystal was subtracted from the measurements to get the absorption spectra of the impurity.

RESULTS AND DISCUSSION

Optical spectra

Curve 1 in Fig. 1 shows the optical spectra of aqueous solution of potassium dichromate. Two bands are observed at 38170 and 28170 cm^{-1} , respectively. Figure 2 shows the molecular energy diagram proposed for chromate ion having a T_d symmetry by Ballhausen and Liehr.¹² The two bands observed arise because of transitions from the nonbonding filled t_1 orbital to the antibonding empty t_2 and e orbitals, respectively. In the ground state the t_1 orbitals are completely filled. The f ground state is therefore represented by the total symmetric 1A_1 state. The first excited configuration $t_1^5 e^1$ results in the ${}^1A_1, {}^1E, {}^1T_1, {}^1T_2$ states in order of increasing energy.¹⁰ The only allowed transition is ${}^1A_1 \rightarrow {}^1T_2$ which corresponds to the bands around 28170 cm^{-1} . The next higher excited configuration of the dichromate ion is $t_1^5 t_2^1$ which leads to the states ${}^1A_1, {}^1E, {}^1T_1, {}^1T_2$ in order

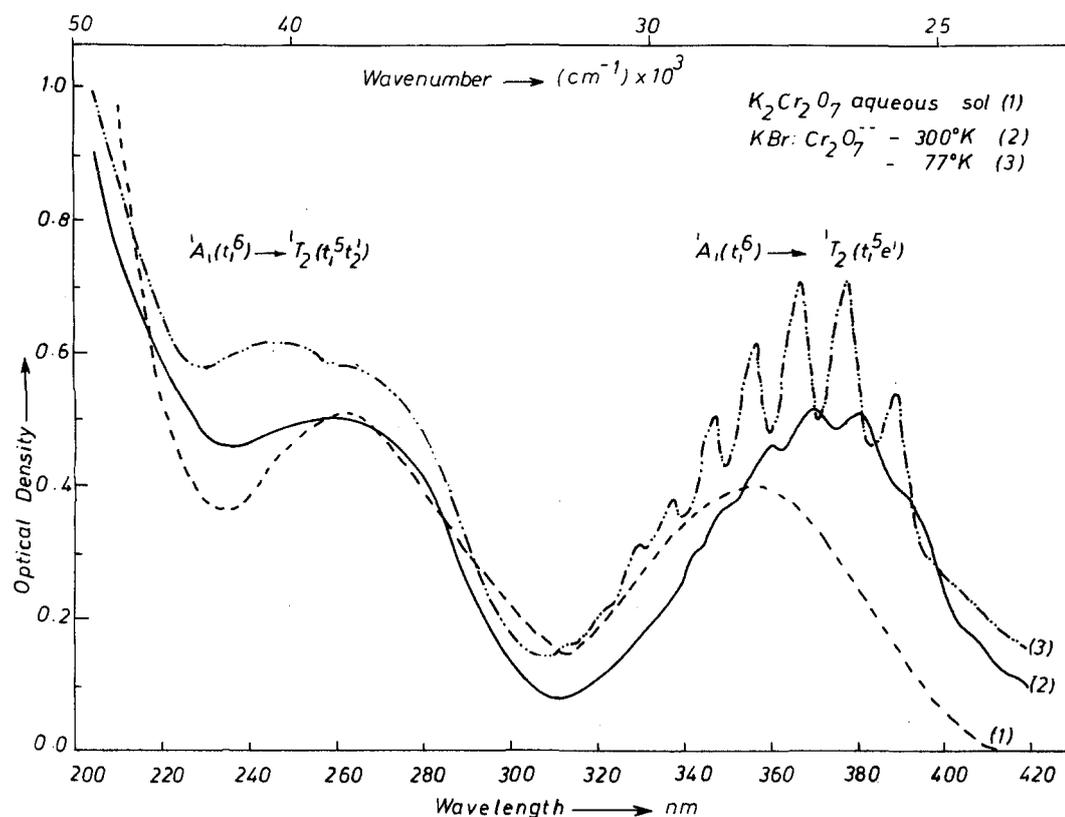


FIG. 1. Optical absorption spectra of $\text{K}_2\text{Cr}_2\text{O}_7$ aqueous solution (curve 1 at 300°K) and $\text{KBr}:\text{Cr}_2\text{O}_7^{2-}$ (curves 2 and 3 at 300 and 700°K, respectively).

of increasing energy. In this case also there is only one allowed transition namely ${}^1A_1 \rightarrow {}^1T_2$, which corresponds to the band around 38170 cm^{-1} .

Curves 2 and 3 in Fig. 1 show the optical spectra of KBr crystals containing dichromate ions at 300 and 77°K, respectively. Two bands around 28000 and 40000 cm^{-1} are observed at 300°K. The visible band shows a fine structure with an average spacing 780 cm^{-1} between

the lines. The ultraviolet band does not show any structure. These two bands are attributed to the allowed transitions ${}^1A_1 \rightarrow {}^1T_2(t_1^5 e^1)$ and ${}^1A_1 \rightarrow {}^1T_2(t_1^5 t_2^1)$, respectively. The fine structure in the visible band is attributed to the coupled vibration-electronic transitions.⁵ Since the transition involved is a nonbonding to antibonding orbital transition, the molecule expands in the excited state and the Condon parabola shifts in position. The minima of the ground state and the excited state para-

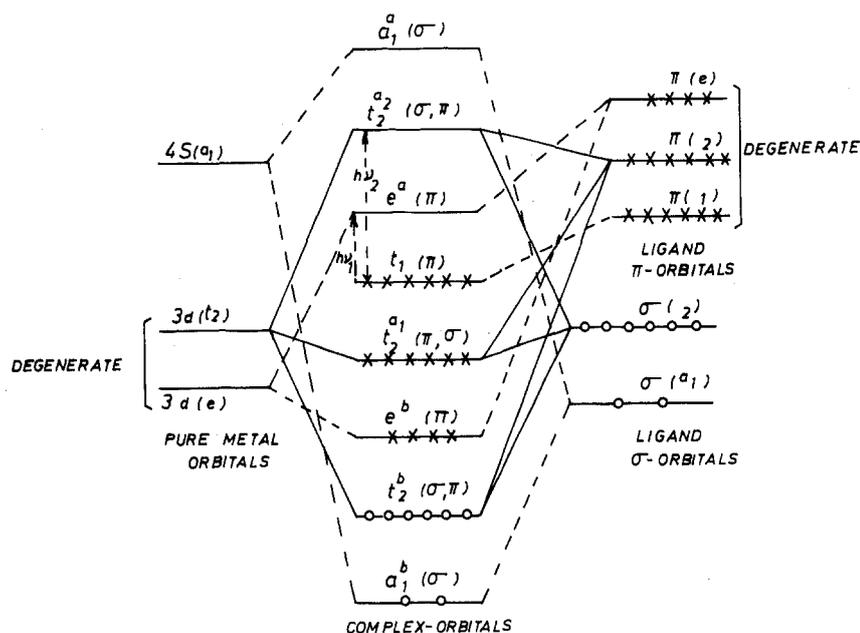


FIG. 2. Molecular energy level scheme for complex chromate ion (T_d symmetry) illustrating both π and σ bondings.

TABLE I. Peak positions of the various transitions of dichromate ion in solution (300 °K) and different matrices at 77 °K.

(Cr_2O_7^-) ⁻ in various matrices	Transition ${}^1A_1 \rightarrow {}^1T_2(t_1^5 e^1)$ (cm^{-1})	Transition ${}^1A_1 \rightarrow {}^1E$ or ${}^1T_1(t_1^5 t_2^1)$ (cm^{-1})	Transition ${}^1A_1 \rightarrow {}^1T_2(t_1^5 t_2^1)$ (cm^{-1})
$\text{K}_2\text{Cr}_2\text{O}_7$ -water Solution	28170	Not observed	38170
KCl	26670	37310	40320
KBr	27030	37040	40000
KI	27400	36360	38460

bola no longer lie at the same position. The selection rule,⁵ that transitions can take place only between two electronic levels which have the same vibrational states, becomes invalid. One observes transitions from the ground state to the various vibrational overtones in the excited state.² The spacing between the two adjacent lines gives the frequency of the total symmetric mode of vibration in the excited state. We notice that the frequency of this mode in the excited state is decreased to 780 from 895 cm^{-1} in the ground state as inferred from infrared measurements (discussed in next section) in $\text{KBr}:\text{Cr}_2\text{O}_7^-$ crystals. At low temperatures (77 °K) another band appears on the low energy side of the band corresponding to the transition ${}^1A_1 \rightarrow {}^1T_2(t_1^5 t_2^1)$. The difference between the two bands is $\sim 3000 \text{ cm}^{-1}$. The two bands can be seen clearly in the curve 3 of Fig. 1. This new band is probably due to one of the forbidden transitions to the levels 1E or 1T_1 lying below 1T_2 level and become allowed partially in the crystal field.³ Similar results are obtained in other crystals also. The position of this forbidden band and the other allowed bands are briefly summarized in Table I.

TABLE II. Peak positions in cm^{-1} of various fine structure lines in the visible band of dichromate ion at 77 °K in different matrices.

KCl	KBr	KI
25477	25740	25850
	25940 ^a	26032 ^a
26281	26523	26621
	26725 ^a	26807 ^a
27064	27313	27406
	27510 ^a	27582 ^a
27855	28084	28166
	28285 ^a	28350 ^a
28719	28856	28906
	29055 ^a	29088 ^a
29499	29626	29654
	29824 ^a	29829 ^a
30303	30416	30419
Average spacing	Average spacing	Average spacing
(804)	(779)	(761)
	(200) ^b	(181) ^b

^aSet of weaker lines.

^bAverage spacing between a weak line and an adjacent intense line on the low energy side.

The fine structure in the band corresponding to the transition ${}^1A_1 \rightarrow {}^1T_2(t_1^5 e^1)$ shows further splitting at lower temperatures. As can be seen from Fig. 1 (curve 3) at 77 °K the fine structure shows an asymmetry and another set of poorly resolved fine structure lines appear on the higher energy side of the original lines. The two adjacent lines are separated from each other by an average spacing $\sim 200 \text{ cm}^{-1}$. If one joins the tips of the two sets of lines separately, two different bands separated by

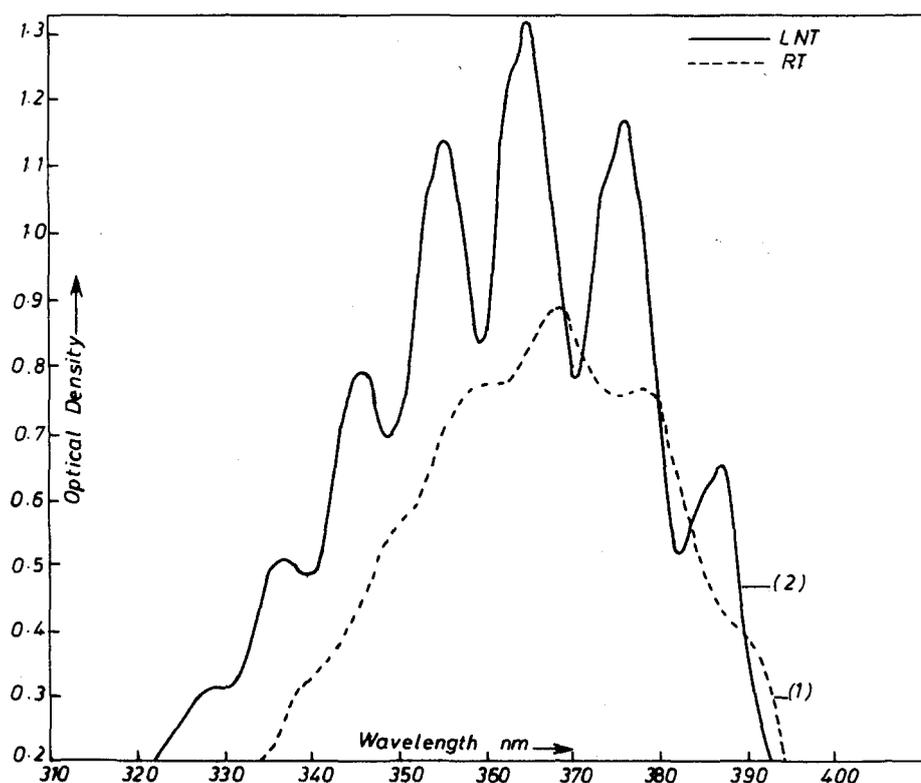


FIG. 3. Optical absorption spectra of $\text{KI}:\text{Cr}_2\text{O}_7^-$ crystals (curve 1 at 300 °K and curve 2 at 77 °K).

TABLE III. Vibrational spectra in cm^{-1} of dichromate ions in various matrices at room temperature. (d) indicates diffused lines, (s) symmetric, and (as) antisymmetric.

$\text{K}_2\text{Cr}_2\text{O}_7$ (s)	KCl	KBr	KI	Assignment
556	580 (d)	562 (d)	550 (d)	A_1
566				s(Cr-O-Cr)
764	765	760	737	B_1
796	770 (d)	771 (d)	740 (d)	as(Cr-O-Cr)
	794	780	753	
885	899	895	885	B_1
891	905			s(CrO_3)
902	918 (d)	...	908 (d)	A_1
908				s(CrO_3)
924				
934	975	948	930	A_1, A_2
940	980	954	950	B_1, B_2
946	998	965	958	as(CrO_3)
950	1003	970	967	
956				
966				

$\sim 200 \text{ cm}^{-1}$ are obtained. In KI crystals the two sets of lines are clearly resolved as shown in Fig. 3. The spacing between the two sets of lines is $\sim 180 \text{ cm}^{-1}$. In KCl crystals the splitting could not be determined due to poor resolution and low concentration of the dichromate ions. The concentration of the dichromate ions which could be doped in KCl was small, probably due to the smaller radius of the chlorine ions. The fine structure observed has been tabulated in Table II. The spacing between various vibrational levels along with the average splittings observed in 1T_2 level for KBr and KI

matrices are tabulated.

In alkali halide crystals doped with chromate ions^{2,4} it was found that the chromate ion enters the lattice by replacing one halide ion. The chromium ion sits at the halide ion site and the four oxygens form a tetrahedron along the diagonals of the unit cell with one charge compensating vacancy created in the neighborhood. In case of the dichromate ion, since the ion is quite large, it cannot be accommodated in place of one halide ion. A possible position of such an ion in the lattice can be obtained by joining two chromate ions in the lattice such that they share one of the oxygens. The two chromium atoms sit at two halide ion sites along the $\langle 110 \rangle$ direction. The Cr-O bond involving the common oxygen is thus disturbed. Moreover no anionic vacancies are required for charge compensation. The change in one of the four Cr-O bonds of the chromate ion should lower the symmetry of the molecule. However at room temperature (300°K) no splittings could be found in the optical absorption spectra. At low temperatures the lattice contracts and the distortion is much more increased. Also the resolution of the various lines improves considerably. Each chromate ion of the dichromate molecule can be assumed to have C_{3v} symmetry with the C_3 axis lying along the common Cr-O bond. As shown in Figs. 1 and 3 the optical bands shift in energy due to the increased crystalline field at low temperatures and a splitting in the visible band due to symmetry lowering is also observed. In C_{3v} symmetry the 1T_2 level splits in to two states, namely 1A_1 and 1E . Both the transitions ${}^1A_1(t_1^6) \rightarrow {}^1A_1(t_1^5 e^1)$ and ${}^1A_1(t_1^6) \rightarrow {}^1E(t_1^5 e^1)$ are allowed transitions and therefore two bands are observed in the visible region of the optical spectra. The two sets of fine

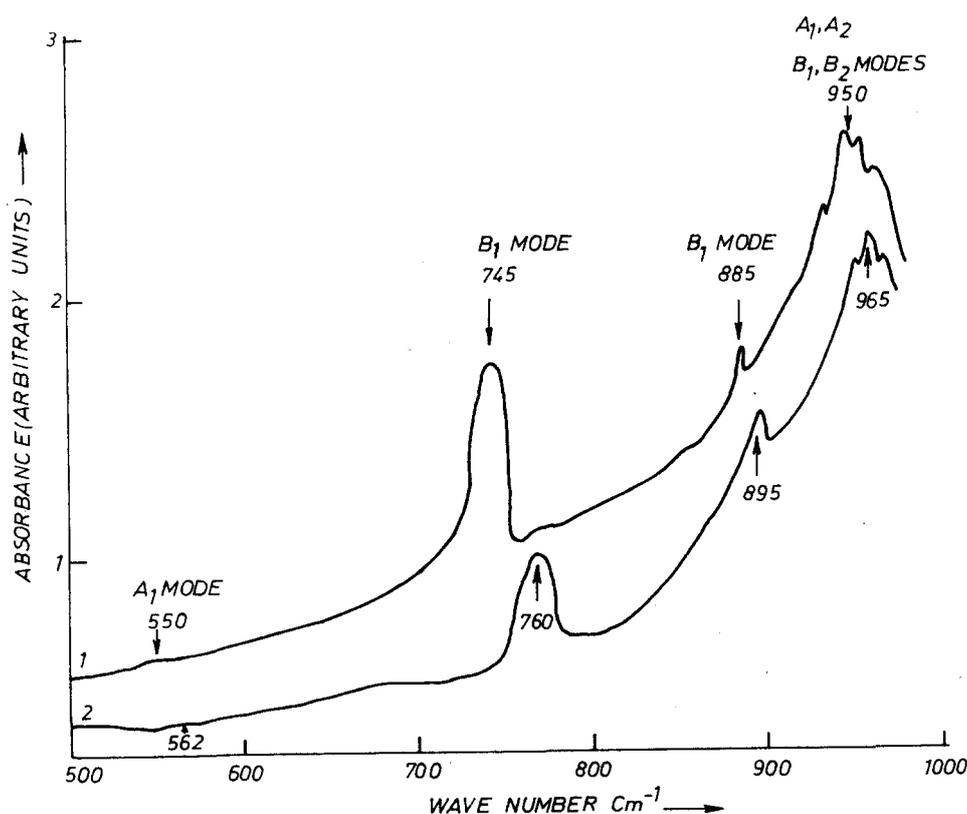


FIG. 4. Infrared spectra of KI: $\text{Cr}_2\text{O}_7^{2-}$ (curve 1) and KBr: $\text{Cr}_2\text{O}_7^{2-}$ (curve 2) crystals at 300°K .

structure lines shown in Fig. 3 arise due to the transitions from the ground state to the various vibrational overtones of the two split excited states 1A_1 and 1E . The spacing between a weak and an adjacent strong line on the low energy side gives the magnitude of splitting in the 1T_2 state. Such splittings are not observed in the spectra of chromate ion in alkali halides since each Cr-O bond is equally affected by the crystalline field.² However, similar splittings have been reported in the case of MnO_4^- ion when placed in C_{3v} symmetry.³ The splittings, however, were large, 500 cm^{-1} compared to the present case, which is only $\sim 200\text{ cm}^{-1}$. The other possibility, that these two sets of fine structure lines may arise due to the transitions from the other vibrational levels of the ground state, as observed in chromate doped alkali sulfates,¹ is ruled out in the present case since the two sets are observed only at low temperatures (77°K). The various vibrational levels of the ground state are occupied according to Boltzmann factor and so the intensity of lines which arise from higher vibrational levels of the ground state should decrease at lower temperatures and vice-versa. Experiments in the present case showed no such behavior. No structure was observed in the transition ${}^1A_1 \rightarrow {}^1T_2(t_1^5 t_2^1)$. At lower temperatures, however, some unresolved structure appeared. No splittings could be detected in this band. This indicates that the splitting in the level ${}^1T_2(t_1^5 t_2^1)$ is very small.

On x irradiation of such crystals no appreciable change could be detected in the optical bands of the dichromate ion. It was found difficult to color these crystals and irradiation doses up to 48 h resulted in a very small concentration of the F centers. No EPR signal other than that due to the F centers was detected in the irradiated samples. This shows that the dichromate ion is unaffected by x irradiation. However, on additive coloration the absorption spectra of the dichromate ion disappears and a feeble F band is formed. No other EPR signal was detected even in additively colored samples. Heat treatments up to 600°C could not restore the original spectra of the crystals. It is definite that dichromate ions are reduced, but nothing definite can be said about the new products formed.

Infrared spectra

The vibrational spectra of dichromate ion can be divided into two categories, one arising from the nonlinear Cr-O-Cr skeleton and other arising from the internal vibrations of the two trigonal pyramidal CrO_3 groups. Therefore, in the first approximation some of the vibrations of the latter type should coincide with the vibrational frequencies of the chromate ion. However, the internal and external vibrations become coupled and the difference in the frequencies is very large. Figure 4 shows the room temperature (300°K) infrared spectra of KBr and KI crystals containing dichromate ions. There are a number of lines in the spectra. Some of the lines are clearly resolved while some have an unresolved structure. In case the Cr-O-Cr had been a linear chain, the symmetry of the ion would be D_{3d} or D_{3h} . In that case one would get only six or ten infrared active

modes, respectively. The large number of lines indicate that the Cr-O-Cr chain is nonlinear and so the symmetry of the ion is C_{2v} or lower.^{8,9} In C_{2v} symmetry only 17 out of the 21 fundamental modes of vibration are infrared active.

The infrared band near 745 cm^{-1} in KI has a manifold unresolved structure and is ascribed to the B_1 antisymmetric stretching mode of the Cr-O-Cr skeletons. A feeble band appears near 550 cm^{-1} and corresponds to the A_1 symmetric mode of the Cr-O-Cr skeleton. The band around 950 cm^{-1} has a very well resolved structure. This manifold is attributed to the antisymmetric stretching A_1, A_2, B_1, B_2 modes of the trigonal pyramidal CrO_3 groups. The sharp line at 885 cm^{-1} represents the symmetric stretching B_1 mode of the CrO_3 groups. The same mode was also observed in the vibration-electronic coupled transitions discussed in the previous section. The frequency of the mode was found to be 760 cm^{-1} at 77°K in the excited state. Similar results are obtained in other crystals also. The results and the assignments are briefly summarized in Table III. The infrared spectra show that the dichromate ion has a C_{2v} or lower symmetry. The frequencies reported⁸ for $\text{K}_2\text{Cr}_2\text{O}_7$ have also been included in the table for comparison. It can be seen that the frequency values are the highest in KCl matrix implying that the dichromate ion has maximum compression in this lattice. This is evident since the lattice constant of KCl is the smallest of the three potassium halides.

Heat treatments to the samples did not cause any change to the infrared spectra of these crystals. This indicates that no charge compensating vacancies are present in the system. The bound anion vacancy should move away from the impurity ion at high temperatures. Since the anionic vacancy is less mobile in alkali halides, one would expect a change in the immediate neighborhood of the dichromate ion upon heat treatments. This would result in a change in the infrared spectra of the crystals as observed in chromate doped alkali halide crystals² where an associated anionic vacancy was present for charge compensation. Also, no dielectric loss peak was observed in the dielectric loss experiments due to impurity-vacancy dipole relaxations. Thus the model proposed satisfactorily explains all the observed optical and infrared results. It can be concluded that the dichromate ion enters the potassium halide matrices by substituting for two halide ions and that no charge compensating defects are created.

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