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Thermal emission spectrum of the AgCr molecule

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Abstract The emission spectrum of the diatomic AgCr molecule has been investigated by exciting the mixture of silver and chromium metal in a high temperature graphite furnace in an argon atmosphere. More than 25 single headed bands, degraded to shorter wavelength side, have been photographed and assigned to the vibrational scheme of a single A – X system. Vibrational analysis has been carried out and data reduction leads to the vibrational constants for the ground state $\omega_e'' = 222.5$ cm^{-1}, $\omega_e''x_e'' = 1.25$ cm^{-1}. In light of these results, the electronic configurations giving rise to $^6\Sigma$ ground state of the AgCr are discussed

Keywords Spectra of AgCr molecule, vibrational analysis, dissociation energy

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Vapour phase intermetallic molecular systems formed at high temperature has great importance in high temperature chemistry specially in heterogeneous catalysis. Several workers in the past have identified number of diatomic gaseous species through optical spectroscopy. The diatomic AgCr molecule has been identified by Monjajeb [1] by recording its electronic emission spectrum in the region $\lambda\lambda$ 3680-3900 Å. He established ground state vibrational frequency ω_e'' for the AgCr molecule is equal to 221.5 cm^{-1}. However, the analysis is based on the spectrogram taken at low dispersion (12-40 Å/mm) using Hilger Quartz Spectrograph. Recently, we have published our results about MnSe [2], CoCu [3], and CoSe [4] molecules obtained from the thermal emission, therefore we decided to investigate the spectra of AgCr molecule at high resolution (0.1 Å) and high dispersion (7.3 Å/mm) using 2-m Plane Grating Spectrograph.

We have been able to record the emission spectrum of AgCr molecule in thermal plasma from high temperature furnace in the spectral range $\lambda\lambda$ 3650-3900 Å. We report here the vibrational analysis of A-X system, on the basis of which it is possible to draw some tentative conclusions about the nature of the ground state of AgCr molecule.

A small quantity of silver and chromium metal (BDH) was placed inside the carbon tube of Saha's high temperature graphite furnace [5]. After evacuation of the furnace chamber, argon gas was inserted at a pressure of about 40 cm of mercury to prevent rapid effusion of

molecular vapours from the open ends of the tube. The temperature was raised to 2300^{0}C with the help of 10-kVA transformer and resultant glow was recorded using first order of 2-m plane grating spectrograph with a grating blazed at λ 5600 Å and total lines 45500. An exposure time of about 4 min was found sufficient to record workable spectra on ILFORD 400 ASA black and white film. An iron arc spectra served comparison standard. The measurement of band heads were performed on a Abbe Comparator with the least count of 0.0001 cm.

The thermal emission spectrum of the AgCr molecule consists of 25 single headed, violet degraded bands in the region $\lambda\lambda$ 3650-3900 Å. The observed bands have been classified into a single system A-X. The band head data, relative visual estimates of intensity and their vibrational assignment are listed in Table 1. The analysis has yielded following vibrational constants :

$$\nu_{00} = 25932.0 \qquad \omega'_e = 213.0 \qquad \omega'_e x'_e = 1.8 \text{ cm}^{-1}$$

$$\omega''_e = 222.5 \qquad \omega''_e x''_e = 1.25 \text{ cm}^{-1}$$

Table 1. Band head data (in cm^{-1}) of the AgCr molecule A-X system

S No	ν_{vac}(cal)	ν_{vac}(obs)	(v', v'')	Int
1	27134.4	27132 0	(6,0)	1
2.	26943 0	26945.2	(5,0)	1
3	26748 0	26745 0	(4,0)	1
4	26549 4	26547 0	(3,0)	1
5	26528 0	26530 0	(4,1)	1
6	26505 5	26507 0	(5,2)	1
7	26347 2	26345 0	(2,0)	2
8	26329 4	26328 0	(3,1)	1
9.	26290 5	26292.0	(5,3)	1
10	26269 4	26270 5	(6,4)	1
11	26247.2	26249.5	(7,5)	1
12	26141.4	26142 0	(1,0)	2
13	26127 2	26129 2	(2,1)	1
14	26111 9	26113.5	(3,2)	1
15	26095.5	26097.0	(4,3)	1
16	26078 0	26079 0	(5,4)	1
17	26059.4	26061 0	(6,5)	1
18.	26039 7	26041 2	(7,6)	1
19.	25932.0	25932.0	(0,0)	3
20.	25921 4	25923.0	(1,1)	2
21	25909.7	25908 0	(2,2)	1
22	25896.9	25898.2	(3,3)	1
23.	25883.0	25884 0	(4,4)	1
24.	25712 0	25714 0	(0,1)	2
25.	25494.5	25496.5	(0,2)	2

Since the thermal emission is a low energy excitation, the electronic states involved in the transition must be low lying states. This system may correspond to the A-X system of the AuCr molecule [1] as it lies on the shorter wavelength side of the corresponding system observed in the case of AuCr. A comparison (shown in Table 2) of the ground state frequency of different gold and silver diatomic combinations with a common element shows that the ground state frequency of the gold combination was higher than the ground state frequency for the corresponding combination with silver, and here also the same trend exists. In the case of the diatomic AuCr and AgCr, we expect the same ground trend to follow, and actually it has been found to be so, as depicted below :

$$\frac{\omega_e''(\mathrm{AuAl})}{\omega_e''(\mathrm{AgAl})} \approx \frac{\omega_e''(\mathrm{AuGa})}{\omega_e''(\mathrm{AgGa})} \approx \frac{\omega_e''(\mathrm{AuIn})}{\omega_e''(\mathrm{AgIn})} \approx \frac{\omega_e''(\mathrm{AuSe})}{\omega_e''(\mathrm{AgSe})} \approx \frac{\omega_e''(\mathrm{AuCr})}{\omega_e''(\mathrm{AgCr})} \approx 1.15 \text{ to } 1.12$$

Table 2. Collection of gold diatomics and corresponding silver diatomics

Gold Diatomic	ω''_{e1} (cm^{-1})	Silver diatomic	ω''_{e2} (cm^{-1})	$\omega''_{e1}/\omega''_{e2}$
AuAl	333.0	AgAl	254.34	1.31
AuCl	382.8	AgCl	343.49	1.11
AuCu	250.0	AgCu	231.8	1.08
AuGa	226.0	AgGa	184.7	1.22
AuIn	187	AgIn	155.54	1.20
AuSe	270	AgSe	234	1.15
AuTe	212.0	AgTe	195.3	1.09
AuBi	157.0	AgBi	152.14	1.03
AuCr	252.1*	AgCr	222.5#	1.25

*ref [1], # present study and the remaining belong to ref [6]

The normal state electronic configuration of Ag and Cr atom is given by

$$_{47}\mathrm{Ag} : 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^1 \longrightarrow {}^2S_{1/2}$$

$$_{24}\mathrm{Cr} : 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, \; 4s^1 \longrightarrow {}^7S_3$$

The number of possible molecular electronic states predicted by building-up principle when a $^2S_{1/2}$ electronic state of silver is combined with a chromium $^7S_3$ ground state is two : $^6\Sigma$, $^8\Sigma$. The molecules CuCr, AgCr, AuCr, and CrH are isovalent. Thus, one can expect their molecular orbital to be comparable. In the case of CrH molecule, Ram and Bernath [7] analyzed a $^6\Sigma - {}^6\Sigma$ transition rotationally and determined spectroscopic constants for both the $^6\Sigma$ term. Therefore in analogy with the observed $^6\Sigma$ state in the case of CrH, we expect ground states character as $^6\Sigma$ for the AgCr as well. With $^6\Sigma$ lower state, the possible transitions are $^6\Sigma - {}^6\Sigma$ and $^6\Pi - {}^6\Sigma$. Since the observed bands are appeared to be single headed, therefore in all probability, A-X system involves $^6\Sigma - {}^6\Sigma$ transition.

The dissociation energy D_0 of the AgCr can be determined by using Birge-Sponer formula. In Birge formula D_0 is given by

$$D_0 = \omega_e''^2 / 4\omega_e'' x_e''.$$

Substituting values, we find $D_e = 9901.3\ \text{cm}^{-1} = 1.23\ \text{eV}$.

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