

## ARTICLE

# Laser-induced Fluorescence Spectroscopy of CoS: Identification of a New Excited State Arising from the Ground State<sup>†</sup>

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Laser-induced fluorescence excitation spectra and dispersed fluorescence spectra of cobalt sulfide (CoS) have been recorded in the energy range of 22400–24400 cm<sup>-1</sup> (corresponding to 446–409 nm). A new electronic transition progression with six vibronic bands, stemming from the  $X^4\Delta_{7/2}$  state of CoS, was identified and assigned to be  $[24.00]^4\Delta_{7/2}-X^4\Delta_{7/2}$ . The new observed  $^4\Delta$  state most probably originates from the core  $[10\sigma^2][4\pi^3][11\sigma^2][1\delta^3][5\pi^3]$  electronic configuration. Strong perturbations are found to extensively exist in the transition bands of this new state. The rotational constants and lifetimes of these bands have been determined.

**Key words:** CoS, Laser-induced fluorescence, Dispersed fluorescence, Perturbation among states

## I. INTRODUCTION

The electronic spectra of transition metal sulfides have attracted much attention for the past few years, due to their important application in material science [1], catalysts [2], and being indispensable parts for understanding the bonding details between the transition metals and various ligands. Generally the d-block shells of transition metal atoms are populated by many unpaired electrons, which in turn produces a large amounts of low-lying electronic states with high values of spin multiplicity and orbital angular momentum, as well as extensive perturbations among these states [3], making the electronic spectra of transition metal sulfides congested and complicated.

Cobalt, one of first-row transition metal elements, has three unpaired electrons, so the electronic spectra of diatomic cobalt sulfide should involve various interactions among states, and the spectral investigation of CoS will be valuable for making the cause of these interactions clear and enriching our knowledge of molecular structure. However, spectroscopic information about CoS is still quite limited. For the first time Flory *et al.* reported the pure rotational spectra of CoS, the ground state of which was proven to be  $X^4\Delta_i$ , with a  $\sigma^2\delta^3\pi^2$  electronic configuration [4]. Later in 2006, Yu *et al.* carried out Fourier transform spectroscopic study of CoS in near-infrared region [5]. Two low-lying excited

states ( $A^4\Phi_i$ ,  $B^4\Pi_i$ ) were observed, developing from the  $\sigma^2\delta^3\pi^1\sigma^1$  and  $\sigma^2\delta^2\pi^3$  electronic configurations, respectively. Recently, Zhen *et al.* conducted laser-induced fluorescence (LIF) spectroscopic survey of jet-cooled CoS molecules in the 15200–22600 cm<sup>-1</sup> energy region [6, 7]. Five new electronic transition progressions rooting in the  $X^4\Delta_{7/2}$  state, and three coming from the low-lying  $A^4\Phi_{9/2}$  state, were carefully identified and rotationally analyzed. The electronic transitions from the  $A^4\Phi_{9/2}$  state of CoS have not been observed in CoO [8, 9] and NiS [10], though the molecular structures of which should be theoretically analogous to that of CoS.

In this work, we have extended the LIF excitation spectra of CoS to the energy range of 22400–24400 cm<sup>-1</sup>. A new electronic transition progression with six vibronic bands was picked out and attributed to the  $[24.00]^4\Delta_{7/2}-X^4\Delta_{7/2}$  transition system. The rotational constants and lifetimes of these bands have been determined. The perturbations among states have also been explored.

## II. EXPERIMENTS

The experimental procedure has been described in detail elsewhere [11, 12]. Briefly, the gaseous CoS molecules were produced by the reaction of H<sub>2</sub>S molecules (0.5% in argon) with cobalt atoms sputtered from a pair of pure cobalt pin electrodes. The H<sub>2</sub>S sample gas seeded in argon at a stagnation pressure of ~6 atm passed through a pulsed nozzle (General Valve Co.) with the orifice 0.5 mm diameter into the vacuum chamber. The cobalt pin electrodes employed for DC discharging the sample gas were fixed in a Teflon disk with a spacing of ~1.5 mm located 2.0 mm downstream

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the nozzle, and were supplied with a pulsed high voltage from a home-made power supply device. The background pressure of the vacuum chamber was  $5.0 \times 10^{-2}$  and  $2.0 \times 10^{-4}$  Pa, with and without operation of the free jet, respectively.

A tunable dye laser (Sirah, PRSC-LG-18) pumped by a Nd:YAG laser (Spectra Physics, GCR-190, repetition rate being 10 Hz) was used to excite the jet-cooled CoS molecules. A configuration of one 1800 line/mm grating and one mirror was applied in the dye laser system. By using the 2nd order diffraction of the Littrow grating, a spectral resolution  $\sim 0.1 \text{ cm}^{-1}$  was achieved. The output of the pulsed dye laser was introduced into the vacuum chamber and crossed the jet flow perpendicularly about 3.0 cm downstream from the point of discharge.

The LIF excitation spectra were recorded by monitoring the total fluorescence as a function of laser wavelength. The dispersed fluorescence (DF) spectra were obtained by fixing the probe laser frequency at or near a strong R-head of the vibronic bands of CoS and scanning the monochromator (Zolix Omni- $\lambda$  300) with a 1-mm-wide slit. The fluorescence signal was detected by a photomultiplier tube (PMT, Beijing Hamamatsu, CR105) and digitized by an A/D card and then transferred to a personal computer. The relative time delays among the nozzle, the discharge, the laser and the signal detection were controlled by a home-made four channel digital delay generator. A digital oscilloscope (Tektronix, TDS3032B) was used to record the fluorescence signal averaged over 256 laser shots when the lifetimes of the electronic transitions were measured. No attempt was made to normalize the spectral intensity against the laser power. The laser wavelength was calibrated by a wavemeter (Coherent, WaveMaster 33-2650) with a resolution of 0.001 nm and an accuracy of  $\pm 0.005 \text{ nm}$ .

### III. RESULTS AND DISCUSSION

LIF excitation spectra of CoS have been recorded in the energy range of 22400–24400  $\text{cm}^{-1}$ . The spectra are complicated, only one electronic transition progression has been picked out, which is shown in Fig.1. All of the bands are red-degraded and have three branches (P, Q, and R). The intensities of Q branches of these bands are stronger than that of P and R branches, indicating they all follow the  $\Delta\Lambda=0$  transition selection rule [13].

The average interval of the bands at 22475, 22981, 23491, and 24006  $\text{cm}^{-1}$  is about 510.3  $\text{cm}^{-1}$ , which comes rather close to the vibration frequency of the ground state of CoS (515  $\text{cm}^{-1}$ ) reported by Yu *et al.* [5]. With the help of the DF spectra of these bands, they were determined to arise accordingly from the  $v''=3$ ,  $v''=2$ ,  $v''=1$ , and  $v''=0$  levels of the ground state of CoS, which means all of these bands, from different vibrational levels of the  $X^4\Delta_i$  state, should be excited to the same upper state. Conditioned by the  $\Delta\Lambda=0$

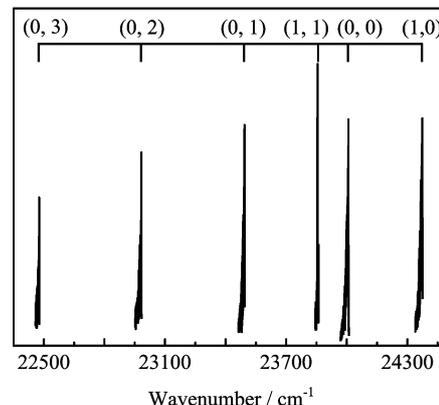


FIG. 1 LIF excitation spectra of the CoS molecule in the energy range 22400–24400  $\text{cm}^{-1}$  together with the bands assignments. The bands of the CoS, denoted as  $(v', v'')$ , are assigned to the  $[24.00]^4\Delta_{7/2}-X^4\Delta_{7/2}$  transition system. The (1, 1) band is mixed with two cobalt atom lines and quite weak in intensity.

transition selection rule, the upper state should be a  $^4\Delta$  state. Here the DF spectra of the bands at 24006 and 23491  $\text{cm}^{-1}$ , excited at 24007.9 and 23493.4  $\text{cm}^{-1}$  respectively, were taken as examples to illustrate how the intensity of the spectra peak changes with excitation at different locations, which are displayed in Fig.2 (a) and (b).

The DF spectrum of the band at 24372  $\text{cm}^{-1}$  is presented in Fig.2(c), which implies that this band comes from the  $v''=0$  level of the ground state, and the vibrational quantum number of the upper state of this band is at least 1 because of the band having one minimum. Furthermore, it is noteworthy that the location of the band at 23858  $\text{cm}^{-1}$  is consistent with the transition energy for an electron promotion from the  $v''=1$  level to the  $v'=1$  level of CoS. Above all, we finally designated the vibrational level of the upper state of the band at 24372  $\text{cm}^{-1}$  as  $v'=1$  and that of the bands at 22475, 22981, 23491, and 24006  $\text{cm}^{-1}$  as  $v'=0$ . Using Hund's case (a) [13], the bands in Fig.1 have been rotationally analyzed, and a nicely matched observed and simulated rotational resolved LIF excitation spectrum of the (0, 0) band is demonstrated in Fig.3. The upper state of this new transition procession is determined to be a  $^4\Delta_{7/2}$  state, and the rotational constants derived from the method of least square fitting are listed in Table I.

Because of heavy perturbation, it is very difficult to identify other vibronic bands belonging to the  $[24.00]^4\Delta_{7/2}-X^4\Delta_{7/2}$  transition system. To gain insight into the perturbation of the observed bands in the system, we drew the reduced energy plots for the upper states of these bands, following a similar treatment developed by Adam *et al.* [14]. Figure 4(a) gives the reduced energy plot for the upper state  $[24.00]^4\Delta_{7/2}(v'=0)$ , the variation trend is analogous to that of the strongly perturbed  $G^4\Phi_{9/2}(v'=v+3)$  state

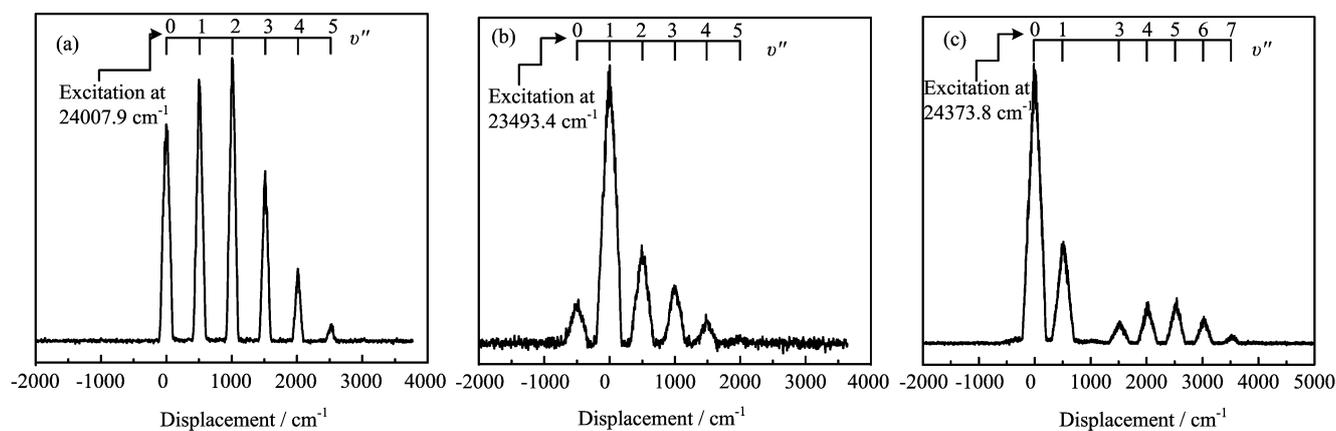


FIG. 2 The DF spectra of CoS obtained using the probe lasers fixed. (a) The R-head ( $24007.9\text{ cm}^{-1}$ ) of the (0, 0) transition band. (b) The R-head ( $23493.4\text{ cm}^{-1}$ ) of the (0, 1) band and (c) the R-head ( $24373.8\text{ cm}^{-1}$ ) of the (1, 0) band, respectively. These spectra can be readily interpreted in terms of emission solely into the vibrational manifold (indicated by ticks) of the electronic ground state.

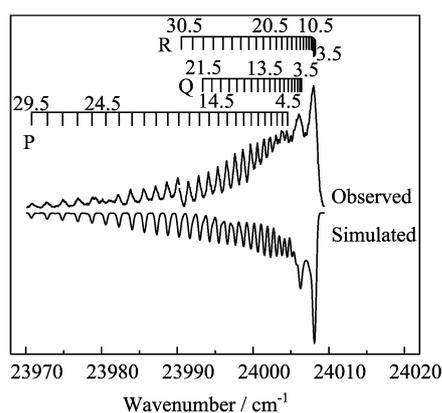


FIG. 3 Rotationally resolved LIF excitation spectrum of CoS for the (0, 0) band.

of CoO [9], which means that it is perturbed by other nearby states or even dark states somewhere. The behaviors of the reduced energy plots for the upper states of bands (0, 3), (0, 2), and (0, 1) all are quite similar to that of band (0, 0), further suggesting that the upper states of these bands are all the same, namely the  $[24.00]^4\Delta_{7/2}(v'=0)$  state, and strong perturbations are widespread in these bands. The low- $J$  part of the (1, 0) band is overlapped by another component, which also has three branches (P, Q, and R) and is attributed to a  $[24.38]\Omega'=7/2-\Omega''=7/2$  transition by rotational analysis. The reduced rotational level patterns for the  $[24.00]^4\Delta_{7/2}(v'=1)$  and  $[24.38]\Omega'=7/2$  states are displayed in Fig.4(b), there is an avoided crossing between two states. The two states have the same value of  $\Omega'$  and could interact with each other by spin-orbit coupling.

The lifetimes measurements for these bands have also been conducted. A typical fluorescence decay trace of

TABLE I Derived molecular constants for the CoS electronic states  $X^4\Delta_{7/2}$  and  $[24.00]^4\Delta_{7/2}$ . Numbers in parentheses are the uncertainties in the unit of the last quoted decimal place.

$(v',v'')$	$T_v^a/\text{cm}^{-1}$	$B_v/\text{cm}^{-1}$	$D_v/\text{cm}^{-1}$	$\tau_{v',v''}^b/\mu\text{s}$
$X^4\Delta_{7/2}$				
(0, 3)	1531.7(1)	0.2034(1)	3.42(67)	0.251(2)
(0, 2)	1025.3(1)	0.2050(1)	3.79(84)	0.253(2)
(0, 1)	514.8(1)	0.2061(1)	1.09(23)	0.316(2)
(0, 0) <sup>c</sup>	0	0.207206	1.335	
$[24.00]^4\Delta_{7/2}$				
(1, 0)	24372.9(1)	0.1715(1)	55.76(56)	0.963(5)
(0, 0)	24006.7(1)	0.1800(1)	15.38(28)	0.374(3)

<sup>a</sup> The level of the state is defined as the zero of energy.

<sup>b</sup> The lifetimes of the vibronic bands in Fig.1.

<sup>c</sup> The values are taken from Ref.[5].

the  $[24.00]^4\Delta_{7/2}(v'=0)-X^4\Delta_{7/2}(v''=0)$  band of CoS is illustrated in Fig.5. An obvious lifetime lengthening happens to the (1, 0) band, the lifetime is determined to be  $\tau=0.963\text{ }\mu\text{s}$ , twice longer than that of the other bands of the  $[24.00]^4\Delta_{7/2}-X^4\Delta_{7/2}$  transition system, due to overlapping between the (1, 0) band with the band  $[24.38]\Omega'=7/2-X^4\Delta_{7/2}$  (its lifetime being  $\tau=1.029\text{ }\mu\text{s}$ ).

In this work, all the observed transition bands arise from the  $X^4\Delta_{7/2}$  state of CoS. The electronic configuration of the  $X^4\Delta_i$  state of CoS has been proven to be  $core[10\sigma^2][4\pi^4][11\sigma^2][1\delta^3][5\pi^2]$ , where the  $10\sigma$  and  $4\pi$  bonding orbitals are mainly centered on the sulfur atom, so is  $11\sigma$  the nonbonding orbital, though the participation of the  $4p$  and  $3d$  atomic orbitals of cobalt is helpful for stabilizing the  $4\pi$  and  $11\sigma$  molecular orbitals of CoS [4]. The  $1\delta$  nonbonding and  $5\pi$  antibonding orbitals are chiefly pointed to the cobalt

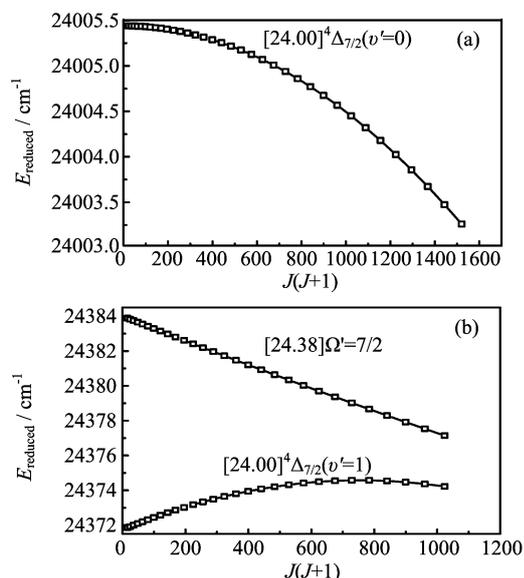


FIG. 4 Reduced energy plots for (a) the  $[24.00]^4\Delta_{7/2}(v'=0)$  state and (b) the interacting  $[24.00]^4\Delta_{7/2}(v'=1)$  state and  $[24.37]\Omega'=7/2$  states of CoS. A quantity  $B_{\text{reduced}}J(J+1) - D_{\text{reduced}}J^2(J+1)^2$  has been subtracted to increase the scale. The values of  $B_{\text{reduced}}$  are (a) 0.180 and (b)  $0.164 \text{ cm}^{-1}$ , the values of  $D_{\text{reduced}} \times 10^7$  are both  $6.0 \text{ cm}^{-1}$ .

atom. The new observed  $^4\Delta$  state is determined to lie in high level (near 3 eV) with respect to the  $X^4\Delta_i$  state of CoS. Compared to the electronic states of the CoO molecule reported in previous work [8, 9], such an energy location is thought to be quite high, here we propose that this new state should come from the  $\text{core}[10\sigma^2][4\pi^3][11\sigma^2][1\delta^3][5\pi^3]$  electronic configuration, which corresponds to a electron promotion from the  $4\pi$  orbital to the  $5\pi$  orbital, being a charge-transferred state and having covalent nature. However, it is noted that further theoretical and experimental study is imperative to clarify the electronic structure of CoS.

#### IV. CONCLUSION

A new transition progression derived from the  $X^4\Delta_{7/2}$  state of CoS, with six vibronic bands, was observed and assigned to be  $[24.00]^4\Delta_{7/2}$ - $X^4\Delta_{7/2}$  transition system. It is suggested that the new observed  $^4\Delta$  state should arise from the  $\text{core}[10\sigma^2][4\pi^3][11\sigma^2][1\delta^3][5\pi^3]$  electronic configuration. Perturbations are turned out to be quite common in the transition bands of this new state. The rotational constants and lifetimes of these bands have also been obtained.

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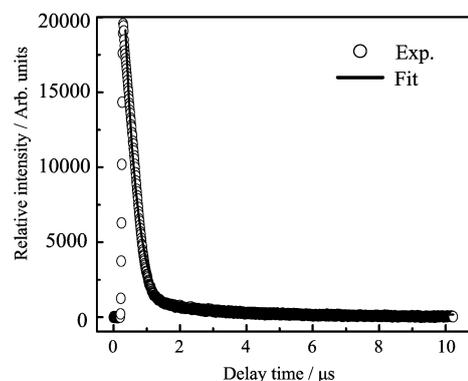


FIG. 5 A typical fluorescence decay trace of the (0, 0) band of CoS. The circle symbols denote the experimental data, while the solid curve is the exponential fit of the decay trace,  $\tau=0.374 \text{ μs}$ .

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