Available online at www.sciencedirect.com

ScienceDirect

Journal of Molecular Spectroscopy 240 (2006) 45–51

Journal of
MOLECULAR
SPECTROSCOPY

www.elsevier.com/locate/jms

Identification of new bands in the red system of CoO

Jingru Guo, Tingting Wang, Zhaoxia Zhang, Congxiang Chen, Yang Chen *

Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, PR China

Received 25 February 2004; in revised form 6 August 2006
Available online 12 August 2006

Abstract

The laser-induced fluorescence excitation spectrum of jet-cooled CoO molecules has been studied in the range of 540–725 nm. Beside all the parallel-polarized and perpendicular bands observed previously by Barnes and co-workers [M. Barnes, D.J. Clouthier, P.G. Hajigeorgiou, G. Huang, C.T. Kingston, A.J. Merer, G.F. Metha, J.R.D. Peers, S.J. Rixon, J. Mol. Spectrosc. 186 (1997) 374–402], 59 new bands have been recorded. Rotational constants have been derived and three new vibrational progressions identified. These three new band systems have been designated $[13.99]^4\Pi_{5/2}$–$X^4\Delta_{7/2}$, $[14.20]^4\Pi_{5/2}$–$X^4\Delta_{7/2}$ and $[15.85]^4\Pi_{5/2}$–$X^4\Delta_{7/2}$. In addition, lifetime measurements have been carried out for most of the bands under collision-free conditions.

Keywords: CoO; LIF; Spectrum

1. Introduction

The diatomic transition metal monoxides have received much attention during the past 50 years because of their importance in astrophysics and high-temperature chemistry [1–3]. It is difficult to carry out an analysis of the molecular electronic spectra due to their complicated electronic structure, which is responsible for the many low-lying states of high spin multiplicity. A detailed understanding of the electronic spectra of transition metal monoxides remains a difficult undertaking. The spectra of later 3d transition metal monoxides, such as CoO and NiO, are especially complicated because the changes in bond length in the electronic transitions from the ground state are much greater so that the intensity is spread over many more vibrational bands. Among the first row transition metal oxides, not much is known for cobalt oxide. The first electronic spectroscopic study of CoO was reported by Malet and Rosen in 1945 [4], who observed many bands in the region 520–920 nm. Since then, several subsequent experimental and theoretical studies of CoO [5–14] have been reported. Green et al. [5] studied the infrared spectrum of CoO in an argon matrix and obtained the vibrational frequency of 853.75 cm^{-1} from Co^{16}O and Co^{18}O. Krauss and Stevens [6] predict a $^4\Sigma^-$ ground state on the basis of their calculations, while the calculations of Dolg et al. [7] show that the ground state should be a $^4\Delta$ state and the $^4\Sigma^-$ electronic state should lie above the ground state. However, no rotational analysis was carried out until 1987 because of the great complexity of CoO. Adam et al. [8] analyzed three strong bands in the red region of the spectrum by laser-induced fluorescence. From their analysis they concluded that the observed transitions have $\Omega'' = 7/2$ and $\Omega'' = 5/2$ in the ground state and have a vibrational interval of 851.7 cm^{-1}. The excellent agreement between the matrix [5] and the gas-phase values suggests that the ground state is $^4\Delta_i$. Later, a detailed examination of the structure of the $^4\Delta_i$ ground state of the gaseous CoO was carried out, using the method of intracavity laser-induced fluorescence [9]. The $(4s\sigma)^2(3d\delta)^3(3d\pi)^2\ {}^4\Delta_i$ electron configuration ground state of CoO was established. Also the bond length, the spin–orbit splitting, and the hyperfine parameters were given. More recently,

---

* Corresponding author. Fax: +86 551 3607084.
E-mail address: yangchen@ustc.edu.cn (Y. Chen).

0022-2852/$ - see front matter © 2006 Published by Elsevier Inc.
doi:10.1016/j.jms.2006.08.006

Namiki and Saito [14] have recorded the microwave spectrum of the ground state of CoO. Near-infrared emission near 5700 cm^{-1} was assigned to the $\Omega = 5/2$–$7/2$ and $\Omega = 3/2$–$5/2$ sub-bands of the $A^4\Pi_i$–$X^4\Delta_{7/2}$ transition by Ram et al. [10]. Barnes et al. [11] observed nearly 100 bands arising from the $^4\Delta_{7/2}$ spin component of the ground state in the 430–720 nm region using Doppler-limited intracavity spectroscopy and supersonic jet-cooled molecular beam methods. They analyzed and determined the molecular constants of five electronic states of CoO. In the nearly 100 bands, the great majority of the bands in the spectrum of jet-cooled CoO are parallel-polarized, with $\Omega' = 7/2$ upper levels. Only about a dozen perpendicular bands were found, most of them with $\Omega' = 9/2$ upper levels, while no $\Omega' = 5/2$ bands with any appreciable intensity have been assigned.

In the current work we reinvestigated the fluorescence excitation spectrum of CoO in the range of 540–725 nm under supersonic jet-cooled conditions. In addition to the three $\Omega = 7/2$–$7/2$ band systems and the $\Omega = 9/2$–$7/2$ band system, whose upper state were assigned as $D^4\Pi$ by Barnes et al. [11], many new bands have been recorded and three new perpendicular transitions with $\Omega' = 5/2$ upper levels have been assigned.

2. Experimental

The experimental apparatus has been described in detail elsewhere [15,16]. Briefly, the CoO molecules were produced by the reaction of sputtered cobalt atoms with O_2 molecules under discharge conditions. The sample gas seeded in Ar (5% O_2 in Ar mixture) at a stagnation pressure of 5 atm passed through a pulsed nozzle (General Valve) of 0.5 mm orifice diameter at a repetition rate of 10 Hz into the vacuum chamber. A pair of pure cobalt pins with 1 mm spacing was set for discharge at 1.5 mm downstream from the nozzle. The discharge voltage was about 2 kV. The background pressures of the vacuum chamber were 3×10^{-4} and 2×10^{-5} Torr, respectively, with and without the running of the free jet.

A Nd:YAG laser (Spectra Physics:GCR-170) pumped tunable dye laser (Lumonics : HT-500) was used to excite the jet-cooled CoO molecules. The output of the pulsed dye laser (with a linewidth of 0.1 cm^{-1} and a pulse width of 5 ns) was introduced into the chamber perpendicularly to the beam of molecules approximately 3 cm downstream from the point of the DC discharge. In order to minimize the scattered light, the laser beams passed through a system of irises. The operation of the nozzle, the discharge and the laser were controlled sequentially by a home-made pulse generator. The excitation spectrum was recorded by monitoring the total fluorescence. The fluorescence signals were recorded with a photomultiplier tube (R928, Hamamatsu). To minimize the collection of scattered light, this photomultiplier tube was set perpendicularly to both the excitation laser and to the axis of the beam of molecules. The output of the photomultiplier was averaged with a computer data acquisition system, which allowed setting more than five integration gates to record the spectrum at one time. The gates were set after some proper delay time, which was determined by the nature of the monitored fluorescence decay. For lifetime measurements, fluorescence detected by the PMT was fed directly into a digital oscilloscope (Tektronics TDS 380) and the LIF decay curves were recorded by averaging the signals for 256 laser shots.

3. Results and discussion

The laser-induced fluorescence spectrum of jet-cooled CoO has been measured in the region of 540–725 nm. Beside all the bands observed by Barnes and co-workers [11], 59 new bands have been recorded. Fig. 1 presents a survey spectrum, represented as a stick diagram. Approximate relative intensities of the bands are indicated by the height of the sticks in the figure. Least squares fitting was performed on every band. The results are given in Table 1. The rotational constants for the $X^4\Delta_{7/2}$ component of the ground state were found to be consistent with those from the earlier laser work [8,9], so we fixed the rotational constants of the ground state to $B'' = 0.50058\ \text{cm}^{-1}$, $D'' = 6.5 \times 10^{-6}\ \text{cm}^{-1}$. The simulated spectrum of the $[13.99]^4\Pi_{5/2}$–$X^4\Delta_{7/2}$ (0,0) band is shown in Fig. 2, where it is seen to be in good agreement with the experimental one. In the simulation, the lineshape was taken as a Lorentzian function and the intensities of the rotational lines were assumed to follow a Boltzmann distribution for a rotational temperature of about 50 K. Unlike the results of Barnes and co-workers [11], we found many bands corresponding to $\Omega = 5/2$–$X^4\Delta_{7/2}$. Although they are weaker than the parallel-polarized bands, these bands are strong enough to be rotationally analyzed. These bands can be classified into three vibrational progressions with vibrational frequencies of about 490, 620, and 560 cm^{-1}, respectively. The 0–0 bands of the three progressions appear to be at 13998.58, 14202.89, and 15858.19 cm^{-1}, respectively. Since the letters from A to G have already been used for labeling the excited states, we use the notation $[T_0/1000\ \text{cm}^{-1}]$ to denote the new observed excited states instead of the conventional letter notation.

The rotational structure of the three new progressions is different to those of the $^4\Delta_{7/2}$–$X^4\Delta_{7/2}$ transition assigned by Barnes et al. [11]. Bands of the new progressions have strong Q and P branches, while the R branch is much weaker than the other two. This is indicative of $\Delta\Omega = -1$ type transitions. A typical band is shown in Fig. 2. It is strongly red-degraded, with the low J lines of the R branch forming a head. The first lines of all the R, Q and P branches are from $J'' = 3.5$, so the transitions are unambiguously identified as $\Omega' = 5/2$–$\Omega'' = 7/2$. For CoO, where the spin coupling is Hund case (a), the selection rule $\Delta\Omega = \Delta\Lambda$ applies. Assuming that the upper states are quartet spin multiplicity, they must therefore be $^4\Pi_{5/2}$. The three new progressions have been assigned as $[13.99]^4\Pi_{5/2}$–$X^4\Delta_{7/2}$ ($v' = 0$–6 to $v'' = 0$), $[14.20]^4\Pi_{5/2}$–$X^4\Delta_{7/2}$ ($v' = 0$–6 to