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Investigation of the $A^2\Sigma^-$ state of CuO by laser-induced fluorescence*

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The laser-induced fluorescence excitation spectrum of the $A^2\Sigma^- - X^2\Pi_{3/2}$ transition of CuO in the 540–620nm region has been studied, where the CuO molecule was produced by using the technique of dc discharge reaction under a supersonic condition. We have recorded and rotationally analysed the 0–0, 1–0, 2–0 and 3–0 bands. The rotational constants of the upper state $A^2\Sigma^-$ were determined and vibrational constants improved. In addition, the lifetime measurement for the $A^2\Sigma^-$ state was carried out under the collision-free condition, and the lifetimes obtained are 469±2, 456±2, 488±3 and 490±4ns for v'=0, v'=1, v'=2 and v'=3 levels, respectively.

Keywords: CuO, excitation spectrum
PACC: 3320K, 3350D, 3150

1. Introduction

Diatomic transition metal oxides have received much attention during the past 50 years.[1] Among the first row transition metal oxides, copper monoxide provides a simple model for the study of ionic bonding. The complex electronic spectra of CuO have been extensively studied in the visible and near-infrared spectral regions.[2−12] Numerous bands observed in these regions have been rotationally analysed or tentatively identified. They were assigned to several band systems, among which the most intense is the orange system. The orange $A^2\Sigma^- - X^2\Pi_i$ transition was first identified by Antic-Jovanovic *et al.*[2] using isotopic substitutions, and later the 0–0 and 1–1 bands of the transition were rotationally analysed by Appelblad and Lagerguist[3] using a low-temperature hollow-cathode technique. The electronic parity of the $A^2\Sigma$ state had been debatable until 1982. Based on the observation of the $Y^2\Sigma^+$ state and the determination of the sign of p ($X^2\Pi_{1/2}$), the parity of the $A^2\Sigma$ state has been established to be the $^2\Sigma^-$ one.[7,12−14] In all of the previous studies,[2,3] the orange system was obtained in emission spectrum. In this paper, we investigate the laser-induced fluorescence excitation spectrum of CuO in the 540–620nm range. The 0–0, 1–0, 2–0 and 3–0 bands of the $A^2\Sigma^- - X^2\Pi_{3/2}$ transition are recorded under supersonic free jet conditions. The molecular constants of $A^2\Sigma^-$ are determined from rotational analyses. The most significant result of this work is the observation of the new 1–0, 2–0 and 3–0 transitions, which allow us to determine the accurate vibrational constants. In addition, the lifetimes of the $A^2\Sigma^-$ state are measured under collision-free conditions and are compared to the previous values.[15]

2. Experiment

The experimental apparatus has been described in detail elsewhere.[16,17] Briefly, the CuO molecules were produced by the reaction of sputtered copper atoms with O_2 under the discharge condition. An O_2 molecular jet with a stagnation pressure of 5×10^5 Pa was led through a pulsed nozzle (general valve) of 0.5mm orifice diameter at a repetition rate of 10Hz into a vacuum chamber. A pair of pure copper electrodes with 1 mm separation was set for discharge outside the nozzle. The background pressures of the

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vacuum chamber were 4×10^{-2} and 5×10^{-3}Pa, respectively, for the cases with and without running of the free jet.

The light source was a tunable dye laser (Lumonics HT-500) with a linewidth smaller than 0.1cm^{-1}, pumped by a Nd:YAG laser (Spectra Physics:GCR-170), where the dyes used were C540A and KR620, which were available in the range of 535–620nm. The laser was operated at a repetition rate of 10Hz with a pulse energy of about 2mJ, the laser beam intersecting the jet at a place 30mm downstream from the nozzle. While the operation of the nozzle, discharge and laser was controlled sequentially by a homemade pulse generator.

Fluorescence from the excited CuO radical was detected by a photomultiplier (GDB-56, Beijing) situated at right angles to both the laser and the molecular jet. The output of the photomultiplier was fed into a computer for recording the spectrum, or into a transient digitizer (Tektronics TDS 380) for measuring lifetime. For calibration of the laser wavelength we used optogalvanically active neon lines.

3. Results and discussion

3.1. Spectrum

It has been well determined that the ground state of CuO is a $^2\Pi_i$ state, where $^2\Pi_{3/2}$ is the lowest state and $^2\Pi_{1/2}$ is 277cm^{-1} above.[2,3,13,14,18] Up to now, all the bands of CuO observed in the visible and near-infrared spectral regions have been connected with the $X^2\Pi_i$ ground state. In this work, we have observed four intense bands located at 606.3, 584, 563.6 and 545nm, respectively, and a weak band at 616.7nm. The difference between the 606.3 and 616.7nm bands is about 277cm^{-1}. This means that the two bands share the same upper state, but come from the two sub-states of the ground state $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, respectively. The weak band at 616.7nm is too weak to be rotationally analysed. This fact suggests that the laser excitation probes mostly the CuO molecules in the lowest $X^2\Pi_{3/2}$ state. So, in this study, we focus our attention mainly on the $A^2\Sigma^- - X^2\Pi_{3/2}$ transition, although the two sub-states of $X^2\Pi_i$ are populated simultaneously. All four intense bands show the same rotational structure. From the knowledge of the previous studies of CuO,[2,3] we can easily attribute the four bands to the 0–0, 1–0, 2–0 and 3–0 bands of the $A^2\Sigma^- - X^2\Pi_{3/2}$ transition. Only the 0–0 and 1–1 bands have been studied by emission spectrum,[3] so the 1–0, 2–0 and 3–0 transitions are observed, as far as we know, for the first time. As a typical rotational structure for the $A^2\Sigma^- - X^2\Pi_{3/2}$ transition, each vibrational band has six branches, called R_{11}, $^SR_{21}$, Q_{11}, $^PQ_{21}$, P_{11} and $^QP_{21}$, among which the R_{11} and $^PQ_{21}$ branches form the two heads when $B' < B''$. The four intense bands show the $A^2\Sigma^- - X^2\Pi_{3/2}$ transition characteristic (see Fig.1).

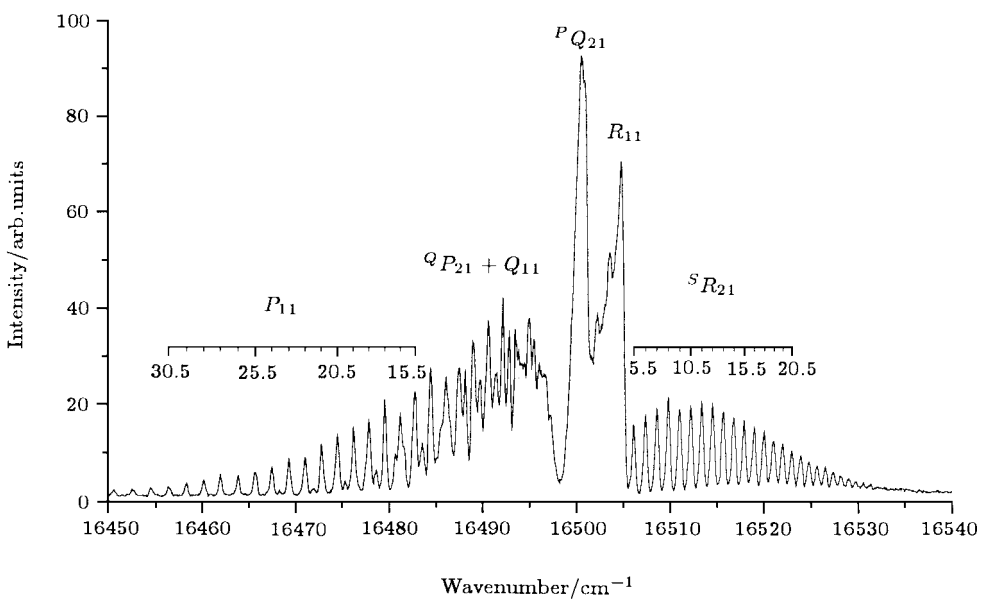


Fig.1. Fluorescence excitation spectrum of the $A^2\Sigma^- - X^2\Pi_{3/2}$ (0,0) transition in CuO.

The ground state has been well studied in a previous work and all the rotational constants have been obtained.[3] For the upper state $A^2\Sigma^-$, due to the large spin-splitting constant γ, the following expressions hold

$$F_1 = T_v + B_v N(N+1) - D_v N^2(N+1)^2 + 1/2\gamma N, \qquad N = J - 1/2, \tag{1}$$

$$F_2 = T_v + B_v N(N+1) - D_v N^2(N+1)^2 - 1/2\gamma(N+1), \qquad N = J + 1/2. \tag{2}$$

The term values of the rotational levels of $A^2\Sigma^-$ are listed in Table 1, the accuracy of the wavenumbers being about 0.07cm^{-1}.

Table 1. Term values (in cm^{-1}) of CuO $A^2\Sigma^-$ levels.

	$v'=0$		$v'=1$		$v'=2$		$v'=3$	
N	F_1	F_2	F_1	F_2	F_1	F_2	F_1	F_2
1	16493.135	16493.428	17124.307	17124.594	17743.243	17743.517	18348.293	18348.567
2	494.764	495.252	125.917	126.397	744.839	745.296	349.870	350.326
3	497.255	497.938	128.379	129.052	747.279	747.919	352.281	352.920
4	500.609	501.488	131.693	132.562	750.563	751.386	355.526	356.347
5	504.826	505.900	135.860	136.924	754.691	755.696	359.605	360.609
6	509.906	511.175	140.879	142.140	759.662	760.850	364.518	365.704
7	515.848	517.312	146.750	148.209	765.477	766.848	370.265	371.633
8	522.653	524.312	153.473	155.130	772.135	773.689	376.845	378.396
9	530.320	532.175	161.047	162.905	779.636	781.373	384.259	385.992
10	538.849	540.899	169.474	171.532	787.981	789.900	392.506	394.422
11	548.241	550.485	178.752	181.012	797.169	799.270	401.586	403.684
12	558.494	560.934	188.881	191.344	807.198	809.483	411.499	413.780
13	569.608	572.243	199.861	202.528	818.070	820.538	422.244	424.708
14	581.584	584.414	211.692	214.564	829.785	832.436	433.822	436.468
15	594.420	597.446	224.373	227.451	842.341	845.175	446.232	449.061
16	608.118	611.339	237.905	241.189	855.739	858.756	459.474	462.486
17	622.676	626.092	252.286	255.778	869.979	873.178	473.548	476.742
18	638.093	641.705	267.518	271.218	885.059	888.441	488.453	491.829
19	654.371	658.177	283.598	287.508	900.980	904.544	504.188	507.747
20	671.508	675.510	300.527	304.649	917.741	921.489	520.755	524.496
21	689.504	693.701	318.305	322.638	935.342	939.272	538.151	542.075
22	708.359	712.751	336.931	341.477	953.783	957.896	556.377	560.483
23	728.072	732.659	356.404	361.164	973.063	977.358	575.432	579.721
24	748.642	753.425	376.725	381.700	993.181	997.660	595.317	599.788
25	770.070	775.048	397.892	403.083	18014.137	18018.799	616.029	620.683
26	792.355	797.527	419.906	425.314	035.932	040.776	637.570	642.406
27	815.496	820.864	442.766	448.391	058.563	063.590	659.938	664.957
28	839.492	845.056	466.471	472.315	082.031	087.241	683.133	688.334
29	864.344	870.103	491.021	497.084	106.336	111.728	707.154	712.538
30	890.051	896.005	516.415	522.699	131.476	137.051	732.002	737.568
31	916.612	922.761	542.652	549.158	157.451	163.209	757.674	763.423
32	944.027	950.371	569.733	576.462	184.260	190.201	784.172	790.103
33	972.294	978.833	597.656	604.609	211.903	218.027	811.493	817.607
34	17001.414	17008.148	626.421	633.599				
35	031.385	038.315	656.027	663.430				
36	062.207	069.332	686.474	694.104				
37	093.880	101.200						
38	126.403	133.918						

As the rotational constants of the ground state were fixed to the result of Ref.[3], the constants for upper levels v'=0, 1, 2 and 3 are derived and listed in Table 2, in which the rotational constants of the v'=0 and 1 levels are in good agreement with the results of Appelblad *et al.* Comparing the rotational constant of v'=2, 3 to v'=0, 1, we find that the rotational constants of all four levels are reasonable. From the sub-band origins of the four different levels, we gain the vibrational constants for $A^2\Sigma^-$ (see Table 3), which are quite different from the previous result.[3] We consider that our results are more accurate than the previous ones, because the vibrational constants are derived from the four vibrational levels in this work, and the previous constants were determined from only two vibrational levels.

Table 2. Molecular constants (in cm^{-1}) for $A^2\Sigma^-$ and $X^2\Pi_{3/2}$ states of CuO.

State	v	T_v	B_v	$D_v/10^6$	γ
	0	16492.37(2)	0.4315(1)	0.79 (1)	0.197(1)
		16492.37(1)[a]	0.43150(1)[a]	0.793(2)[a]	0.1952(1)[a]
	1	17123.55(2)	0.4265(1)	0.79(2)	0.197(3)
$A^2\Sigma^-$		17123.39(1)[a]	0.42675(2)[a]	0.793(7)[a]	0.1908(2)[a]
	2	17742.49(2)	0.4220(2)	0.79(5)	0.197(5)
	3	18347.55(2)	0.4171(2)	0.79(5)	0.197(6)
$X^2\Pi_{3/2}$	0	0	0.44226(1)[a]	0.847(2)[a]	

a) from Ref.[3].

Table 3. Spectroscopic constants (in cm^{-1}) of the $A^2\Sigma^-$ state of CuO.

State	T_0	ω_e	$\omega_e\chi_e$	B_e	$\alpha_e/10^3$	$D_e/10^6$
$A^2\Sigma^-$	16492.37	644.57	6.53	0.4339	4.8	0.79
	16492.37[b]	631.01[b]	—	0.43388[b]	4.76[b]	0.79[b]

b) from Ref.[3].

It is well known that copper has two stable isotopes, ^{63}Cu and ^{65}Cu, with abundances of 69.1% and 30.9%, respectively. So the band lines and band heads of the isotopic molecule ^{65}CuO appear with a considerable intensity, and overlap the band lines of ^{63}CuO. As expected, the 0–0 band shows negligible isotopic shift while the other three bands, 1–0, 2–0 and 3–0, present observable and gradually increasing isotopic shifts. This is consistent with the vibrational analysis.

3.2. Lifetime measurement

The lifetimes of the $A^2\Sigma^-$ state were measured using a pulsed dye laser excitation. For each sub-band we choose the strongest $^PQ_{21}$ branch. To avoid fluctuations, the fluorescence decay profiles were averaged by 256 laser shots. As the CuO radical is present in the supersonic jet, the lifetime measurement of the excited state could be carried out under collision-free conditions. So the radiative lifetime of the excited state can be directly derived from the decay of the fluorescence signal. Figure 2 illustrates a fluorescence decay curve of the 1–0 band (584nm).

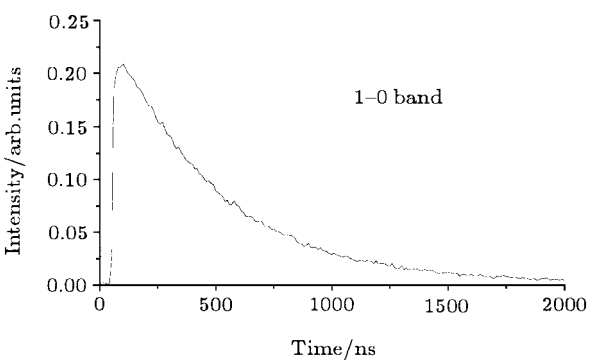


Fig.2. A fluorescence decay curve of the $A^2\Sigma^- - X^2\Pi_{3/2}$ (1,0) band.

The lifetime of each band could be easily derived by fitting the signal to a mono-exponential decay and is listed in Table 4. We can see that the lifetime of the $A^2\Sigma^-$ state in CuO measured in this work is shorter than that carried out by Delaval *et al.*[15] This is due to the fact that the radiative lifetime of $A^2\Sigma^-$ was obtained by extrapolating the measured τ to zero pressure in their case. From the regular rotational constants and the lifetime, we can conclude that the $A^2\Sigma^-$ state is an unperturbed state.

Table 4. Lifetime (ns) for the $A^2\Sigma^-$ state of CuO.

State	$v'=0$	$v'=1$	$v'=2$	$v'=3$
$A^2\Sigma^-$	469±2	456±2	488±3	490±4
	650±40[c)]			

c) from Ref.[15].

The $A^2\Sigma^-$ state is considered to correspond to the $3d^9Cu^+$ $(\sigma^2\pi^3\delta^4)$ $4sCu^+2p^5O^-$ $(\sigma^2\pi^3)$ structure.[15,18,19] This bonding has an ionic contribution arising from the donation of the Cu4s electron to the O atom, and a covalent component arising from bonds between the Cu3d and the O2p orbitals, thus resulting in the most intense band system of CuO.

4. Conclusion

The orange band system of jet-cooled CuO has been studied by laser-induced fluorescence. The 0–0, 1–0, 2–0 and 3–0 bands of the $A^2\Sigma^- - X^2\Pi_{3/2}$ transition have been recorded and rotationally analysed for the first time, as far as we know. Also, the lifetime measurement was performed for the vibrational levels $v'=0$, 1, 2 and 3, under a collision-free condition. The spectroscopic constants and lifetime of the $A^2\Sigma^-$ state are improved.

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