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$A^1\Sigma^+$ State Lifetime and Predissociation of CuH

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A combined cavity ringdown (CRD) and laser induced fluorescence (LIF) spectroscopic study on the $A^1\Sigma^+$-$X^1\Sigma^+$ transition of CuH has been presented. The CuH molecule, as well as its deuterated isotopologue CuD, are produced in a supersonic jet expansion by discharging H_2 (or D_2) and Ar gas mixtures using two copper needles. Different profiles of relative line intensities are observed between the measured LIF and CRD spectra, providing an experimental evidence for the predissociation behavior in the $A^1\Sigma^+$ state of CuH. The lifetimes of individual upper rotational levels are measured by LIF, in which the J'-dependent predissociation rates are obtained. Based on the previous theoretical calculations, a predissociation mechanism is concluded due to the strong spin-orbit coupling between the $A^1\Sigma^+$ state and the lowest-lying triplet $^3\Sigma^+$ state, and a tunneling effect may also be involved in the predissociation. Similar experiments are also performed for CuD, showing that the $A^1\Sigma^+$ state of CuD does not undergo a predissociation process.

Key words: CuH molecule, Laser induced fluorescence, Predissociation

I. INTRODUCTION

Many transition metal hydrides have been identified in the atmospheres of cool stars via observations of their electronic transitions in the optical range, attracting great interest to chemical physicists in the laboratory experimental studies on their electronic spectra and chemical properties [1−3]. The copper hydride (CuH) molecule has been identified in sunspot spectra [4] and possibly in the spectrum of the star Piscium 19 [5]. In addition, because of the simplest closed d-shell structure in the electronic configuration, CuH represents a prototypical system for a detailed understanding of the transition metal-hydrogen bonding properties.

Laboratory experiments have been performed to study the electronic transition spectra of CuH, resulting in accurate values of spectroscopic constants of low-lying electronic states [6−9]. For the $A^1\Sigma^+$-$X^1\Sigma^+$ electronic transition of CuH, a remarkable phenomenon of rotational line intensity distributions in the emission spectrum of the (0, 0) band was found by Schüler *et al.* in 1939 [10], and has led to a long discussion on the nature of this phenomenon in the past century [8, 11−14]. In Schüler's experiment, CuH molecules were produced and excited in a hollow cathode discharge lamp. It is noted that the intensity of the P(1) line is predominant in the band, and intensities of all other rotational

lines rapidly decrease with increasing J'. Schüler *et al.* suggested that this anomalous intensity distribution is due to formation process of CuH molecules under a hollow cathode discharge condition. Later, Herzberg and Mundie [11] proposed an entirely different explanation that the anomalous intensity probably results from predissociation of the $A^1\Sigma^+$ state, via an intersystem crossing with a $^3\Sigma^+$ state that can be directly dissociated to atomic H and Cu. This also explains the anomalously strong P(1) line, for which the upper ($A^1\Sigma^+$, $J'=0$) rotational level does not interact with a $^3\Sigma^+$ state according to Kronig's selection rules [15]. Hulthén [12] presumed the anomalous intensity was caused by predissociation of the $A^1\Sigma^+$ state into the continuum of $X^1\Sigma^+$ state. In the following experimental studies [8, 13, 14], this question still kept disclosed. Both explanations, chemical formation and $A^1\Sigma^+$ state predissociation, have got additional support from the measurement of the $B^3\Pi$-$X^1\Sigma^+$ transition of CuH and/or the electronic spectrum of CuD. In addition, in a recent *ab initio* study by Marian [16], the predissociation of the $A^1\Sigma^+$ state to a $^3\Sigma^+$ state was predicted. Based on the detailed calculations on the potential energy surfaces, as well as transition dipole momenta and spin-orbit couplings of the low-lying electronic states of CuH, it is suggested that the lowest-lying $^3\Sigma^+$ state, which undergoes an avoided crossing with a higher-lying $^3\Sigma^+$ state, may be responsible for the experimentally observed intensity anomalies.

In this contribution, we present a combined cavity ringdown (CRD) and laser induced fluorescence (LIF) spectroscopic study on the $A^1\Sigma^+$-$X^1\Sigma^+$ transition of

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CuH, aiming for a more in-depth understanding on the nature of the intensity anomalies. Here, CRD is used to record direct absorption spectra with relatively reliable line intensities, and LIF is used to measure the lifetimes of individual $A^1\Sigma^+$ state rotational levels. The latter measurement allows us to confirm the intensity anomalies of CuH to be due to a slow and rotation-dependent predissociation process in the $A^1\Sigma^+$ state.

II. EXPERIMENTS

The experiment is performed using our supersonic jet setup that has been described in detail elsewhere [17−19]. In brief, CuH or CuD molecules are produced by a corona discharge of a gas mixture of ∼3% H_2 or D_2 diluted in argon using two copper needles as electrodes. The gas mixture with a stagnation pressure of ∼6 bar is supersonically expanded into a vacuum chamber via a pulsed nozzle (General Valve, Series 9, 0.5 mm orifice). Two copper needles are mounted on a specially machined Teflon plate with ∼1 mm spacing, ∼1.5 mm downstream from the nozzle orifice and perpendicular to the jet expansion. High voltage pulses (∼2000 V, ∼20 μs) are applied to the copper needles to ignite the discharge, producing CuH or CuD molecules in the jet for spectroscopic studies.

Two different spectroscopic techniques, CRD and LIF, are employed. A pulsed dye laser (Sirah, Cobra-stretch) pumped by a third harmonic output of a Nd: YAG laser (Spectra Physics, Lab-190) is split into two laser beams to record the CRD and LIF spectra, respectively. In the latter measurement, the laser beam, which is attenuated to ∼10 μJ/pulse by a neutral density filter, is injected into the vacuum chamber. The laser beam is aligned perpendicularly crossing the gas jet and ∼30 mm away from the copper needles. Fluorescence emitted by the laser excited CuH/CuD molecules is collected by a telescope lens system and detected by a photomultiplier tube (PMT) (Hamamatsu, R928). The output signal of the PMT is digitized in an oscilloscope (Keysight, DSOX2024A) and then transferred to a personal computer for further processing.

The CRD measurement is performed in an optical cavity, which is formed by two highly reflective plano-concave mirrors mounted on precision alignment tools, ∼60 cm apart on opposite sides of the same vacuum chamber as for LIF measurement. The cavity axis is aligned perpendicularly crossing the gas jet at the same position as LIF excitation beam. The angle between the cavity axis and the LIF excitation laser beam is designed to be ∼10°. Three sets of highly reflective cavity mirrors are used in the present experiment, with reflectivity $R \approx 99.96\%$ at 385 nm, $R \approx 99.98\%$ at 405 nm, and $R \approx 99.98\%$ at 440 nm, respectively. In order to ensure the mirrors retaining their high reflectivity throughout the plasma discharge, small Ar flow is injected in front of the reflective surface of each mirror, acting as a protective gas curtain. The ringdown decay signal is de-

tected by a PMT detection, which is digitized in an oscilloscope.

The whole experiment runs at 10 Hz and a pulse generator is used to guarantee that gas and discharge pulses, as well as laser pulses, coincide in time to obtain the best signal intensity. A LabVIEW program is used to record the CRD and LIF spectra, wavelength tuning of the dye laser, as well as the measurement of fluorescence decay traces. The absolute frequency of the dye laser output is simultaneously calibrated by a wavelength meter (Coherent, Wavemaster) during the experiment running, which provided a frequency accuracy better than 0.04 cm^{-1} in the recorded spectra.

III. RESULTS AND DISCUSSION

We have measured the $A^1\Sigma^+$-$X^1\Sigma^+$ (0, 0) and (1, 0) band spectra of CuH, locating at ∼429 and ∼401 nm, respectively, by both LIF and CRD techniques to get a straightforward view of rotational line intensities. Fig.1 shows a comparison of the recorded $A^1\Sigma^+$-$X^1\Sigma^+$(1, 0) band spectra by LIF and CRD. The observed transition frequencies for individual lines, are in good agreement with the previously reported spectroscopic constants [9]. However, we notice that, relative line intensities between spectra recorded by LIF and CRD are rather different. It can be clearly seen from Fig.1 that, compared to the CRD spectrum, individual line intensities in the LIF spectrum decrease much more rapidly with increasing upper rotational quantum number J'. This behavior is the same as that has been found by Schüler *et al.* [10].

Because the LIF and CRD spectra are simultaneously recorded with the same CuH source, the different line intensities shown in Fig.1 cannot be explained by the chemical formation process in the discharge source. A simulation of the CRD spectrum using the Pgopher software [20] shows that, the overall band profile recorded by CRD can be well reproduced with a rotational temperature of ∼50 K, *i.e.*, the rotational populations of the ground state CuH molecules in our supersonic jet expansion follow a Boltzmann population. Because the derived ground state population is also applicable for the LIF spectra, observed intensity anomalies can only be explained by other dynamical processes in the upper $A^1\Sigma^+$ state.

Since the spectra intensity of LIF can be significantly affected by additional loss of fluorescence emitters via non-radiative processes in the upper state, such as predissociation or internal conversion to other states, knowledge on the upper state lifetimes can provide additional information to understand the observed intensity anomalies. This is realized by recording the decay traces of the time-resolved fluorescence signals with an average of 1000 pulses. FIG. 2 shows two typical fluorescence signals recorded by excitation of P(1) and P(2) lines of the $A^1\Sigma^+$-$X^1\Sigma^+$ (0, 0) band, respectively, where the background discharge glow and laser scat-
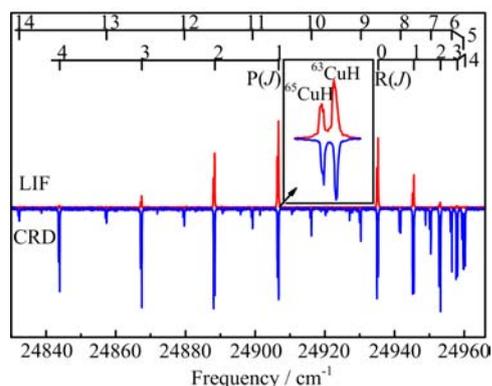
FIG. 1 LIF and CRD spectra of the $A^1\Sigma^+$-$X^1\Sigma^+$ (1, 0) band of CuH. The insert shows the zoomed-in of $^{63/65}$Cu isotope resolved P(1) line in both spectra.
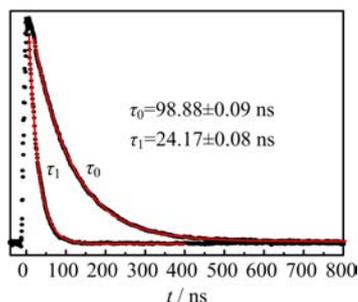

FIG. 2 Typical fluorescence signals of P(1) and P(2) transitions in the $A^1\Sigma^+$-$X^1\Sigma^+$ (0, 0) band of CuH. The red traces represent the mono-exponential fits, from which upper state lifetimes (τ_0 and τ_1) are determined. Errors given in figure are one standard devitation of the fits, which is much smaller than the pulse duration of the dye laser used in the present experiment.

tering have been subtracted. A mono-exponential fit on the falling edge of each recorded fluorescence decay curve results in a fluorescence decay time of ∼99 ns for P(1) transition and ∼24 ns for P(2) transition, respectively. Since the measurement is performed in the collision-free zone of a supersonic jet, the derived fluorescence decay time is the same as the upper state radiative lifetime, i.e., the lifetimes (τ) of $J'=0$ and 1 rotational levels in the $A^1\Sigma^+$ $v'=0$ state are 99 ± 5 and 24 ± 5 ns, respectively, where the uncertainty is limited to the pulse duration of our dye laser system.

We have measured upper state lifetimes for rovibrational levels with $J'=0-3$, as plotted in FIG. 3. For higher J' levels, the fluorescence decay time is found to be comparable to or smaller than the laser pulse duration, and thus cannot be accurately measured. No obvious differences are found between the measured lifetimes for the two copper isotopologues, ^{63}CuH and ^{65}CuH. On the other side, as shown in FIG. 3, a significant J'-dependence can be clearly seen that that $1/\tau$ increases approximately linearly with increasing J' value for both $A^1\Sigma^+$ $v'=0$ and $v'=1$ state. Furthermore, $1/\tau$
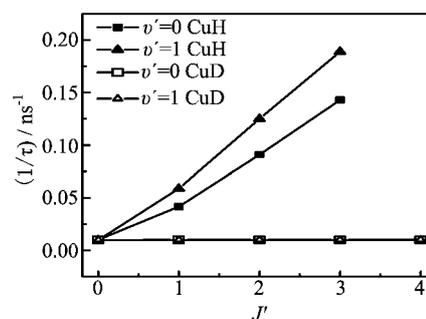

FIG. 3 Plots of $1/\tau$ versus rotational quantum number J' for both CuH and CuD.

TABLE I The $A^1\Sigma^+$ state predissociation rate k_{pre} of CuH.

J'	$k_{\text{pre}}/\text{ns}^{-1}$	
	$v'=0$	$v'=1$
1	0.032	0.049
2	0.081	0.115
3	0.133	0.180

of $J'=0$ has almost an identical value for both $v'=0$ and $v'=1$ levels. This further confirms Herzberg and Mundie's suggestion [11] that the $J'=0$ level is not affected by non-radiative processes in the upper state. According to Kronig's selection rules [15], only states with the same value J and the same symmetry can interact with each other. But for $^3\Sigma^+$ state, the only level with $J'=0$ has the opposite symmetry to that of the $J'=0$ level of $A^1\Sigma^+$ state.

Since the $J'=0$ level is not predissociative, we are able to calculate the J'-dependent dissociation rate for the $A^1\Sigma^+$ state of CuH using the following equation:

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{nat}}} + k_{\text{pre}} \tag{1}$$

where k_{pre} is the predissociation rate in unit of ns^{-1}, and $\tau_{\text{nat}}=\tau$ ($J'=0$) is the upper state natural lifetime. The derived predissociation rates for the $A^1\Sigma^+$ state of CuH are summarized in Table I.

In a similar way, we have also measured the $A^1\Sigma^+$-$X^1\Sigma^+$ (0, 0) and (1, 0) band spectra of the deuterated isotopologue CuD. The overall profiles of the resulting CRD and LIF spectra are found to be nearly identical. The measured fluorescence decay times for individual lines with $J'\leq5$ in both (0, 0) and (1, 0) bands of CuD are all within the range of 105 ± 5 ns, and are independent on the upper state rotational quantum number J'. FIG. 3 shows a comparison of the $A^1\Sigma^+$ state lifetimes between CuH and CuD. It is noticed that $J'=0$ levels of CuH and CuD have almost the same lifetime, indicating that the $A^1\Sigma^+$ state of CuD does not undergo a predissociation process.

In Ref.[16], it is suggested that the $1^3\Sigma^+$ state lying nearby the $A^1\Sigma^+$ state is a bonding state and undergoes an avoided crossing with a higher-lying $2^3\Sigma^+$

TABLE II The lifetimes (ns) of $A^1\Sigma^+$ ($v'{\geq}2$) state rotational levels for both CuH and CuD.

	v'	Lifetime/ns	
		$J'=0$	$J'=1$
CuH	2	108 (2, 0)	14 (2, 0)
	3	167 (3, 1)	40 (3, 1)
	4	116 (4, 2)	9 (4, 2)
	5		
CuD	2	104 (2, 2)	104 (2, 2)
	3	106 (3, 1)	105 (3, 1)
	4	108 (4, 2)	107 (4, 2)
	5	107 (5, 3)	105 (5, 3)

state, resulting in a barrier in the dissociation pathway of the $1^3\Sigma^+$ state. Since the excitation energies of $A^1\Sigma^+$ $v'=0$, 1 (23311 and 24922 cm^{-1}) states are significantly below the calculated barrier of the $1^3\Sigma^+$ state, different behaviors between CuH and CuD may be due to a tunneling effect in the predissociation. This hypothesis is consistent with a common understanding that the tunneling effect of a hydrogen atom can be orders of magnitude faster than a deuterium atom. To test this, we have also extended the fluorescence lifetime measurement to higher ro-vibrational levels, following the previously reported transition frequencies of hot bands in the wavelength region of 375−440 nm [9]. The results are summarized in Table II. Unfortunately, these results do not provide either positive or negative supports in the existence of a dissociation barrier in the $1^3\Sigma^+$ state, or a tunneling effect in the predissociation. For CuH, the measured lifetimes of $A^1\Sigma^+$ $v'{\geq}2$ levels involve severe perturbations of other electronic states, such as $B^3\Pi$ and $C^1\Pi$ state, which have been discussed in previous spectroscopic studies [7−9]. Such perturbations do not allow for straightforwardly evaluating the change of state lifetimes around the dissociation barrier. Further, previous *ab initio* calculations by Marian [16] have shown that, wavefunctions of low-lying electronic excited states of CuH are strongly mixed with each other via spin-orbit coupling, yielding almost all the low-lying triplet states are of a singlet-state character. Such couplings do not allow for qualitatively modelling the measured upper state lifetimes using the previously reported perturbations [7−9]. On the other side, the nearly constant lifetimes for CuD $v'=0-5$ levels may be due to a deuteration effect that the strength of the avoided crossing between $1^3\Sigma^+$ and $2^3\Sigma^+$ states are much weaker than that in CuH, yielding a much higher predissociation barrier in CuD.

IV. CONCLUSION

The difference of relative line intensities in the measured LIF and CRD spectra has provided an experimental evidence for the prediccociation process in the $A^1\Sigma^+$ state of CuH. Based on the lifetimes of individual upper rotational levels measured by LIF, and combined with previous theoretical calculations by Marian, the predissociation mechanism is concluded due to strong spin-orbit coupling between the $A^1\Sigma^+$ state and the lowest-lying triplet $^3\Sigma^+$ state, and a tunneling effect may also be involved in the predissociation. In contrast, the $A^1\Sigma^+$ state of CuD molecule does not undergo a predissociation process.

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