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Reinvestigate the $C^2\Pi$ - $X^2\Pi(0,0)$ Band of $\text{AgO}^\dagger$ Qiang Zhang^{a,b}, De-ping Zhang^a, Bo-xing Zhu^a, Jing-wang Gu^a, Dong-feng Zhao^{a*}, Yang Chen^{a*}*a. Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China**b. Paul Scherrer Institute, CH-5232 Villigen, Switzerland*

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The $C^2\Pi$ - $X^2\Pi(0,0)$ band of AgO has been reinvestigated by laser induced fluorescence spectroscopy with a spectral resolution of $\sim 0.02\text{ cm}^{-1}$. The AgO molecules are produced by discharging a gas mixture of O_2/Ar with silver needle electrodes in a supersonic jet expansion. By employing a home-made narrowband single longitude mode optical parametric oscillator (SLM-OPO) as the laser source, high-resolution spectra of the $C^2\Pi$ - $X^2\Pi(0,0)$ band have been recorded for both $^{107}\text{Ag}^{16}\text{O}$ and $^{109}\text{Ag}^{16}\text{O}$ isotopologues. The spectroscopic constants of the $C^2\Pi$ state are consequently determined, with the $^{109}\text{Ag}^{16}\text{O}$ one being reported for the first time. The nature of the spin-orbit coupling effect in the $C^2\Pi$ state is proposed to be due to state mixing with the nearby repulsive $^4\Sigma^-$ and $^4\Pi$ states.

Key words: Silver oxide, High resolution spectrum, Laser induced fluorescence

I. INTRODUCTION

The blue system, or the $C^2\Pi$ - $X^2\Pi$ transition of silver oxide (AgO) has been studied by several groups [1–6]. The blue system was originally named as the A - X system, and it was renamed as the C - X system by Bauschlicher *et al.* [6] following *ab initio* calculations. The first rotational analysis of the $C^2\Pi$ - $X^2\Pi$ transition was performed by Uhler [1], resulting in determination of the spectroscopic constants for $C^2\Pi\ v'=0/1$ states. After that, Griffiths and Barrow [2] studied the $C^2\Pi$ - $X^2\Pi$ emission spectrum and obtained both vibrational and rotational constants for the $C^2\Pi$ state of the $^{107}\text{Ag}^{16}\text{O}$ isotopologue. The experiment also shows that the $C^2\Pi$ state only has a shallow potential minimum. Supported by isotope shifts, Vujisić *et al.* [3] reported the improved $^{107}\text{Ag}^{16}\text{O}$ and the new $^{107}\text{Ag}^{18}\text{O}$ vibrational constants for the $C^2\Pi$ state. Later, through a re-analysis of the $C^2\Pi$ - $X^2\Pi(0, 0/1)$ band spectra recorded by Uhler [1], Brien *et al.* [5] obtained more accurate spectroscopic constants for the $C^2\Pi\ v'=0$ state of $^{107}\text{Ag}^{16}\text{O}$ isotopologue.

Considering the fact that the natural abundance ratio of silver isotopes is about 1:1, both $^{107}\text{Ag}^{16}\text{O}$ and $^{109}\text{Ag}^{16}\text{O}$ molecules should be produced simultaneously in previous experiments where isotopically pure silver samples were not used. However, limited by the experimental resolution, rotational constants have not been

obtained for the $C^2\Pi$ state of $^{109}\text{Ag}^{16}\text{O}$. In this work, we reinvestigated the $C^2\Pi$ - $X^2\Pi(0,0)$ band by using a narrowband laser source [7]. The spectral resolution ($\sim 0.02\text{ cm}^{-1}$) allows us to resolve the rotational structures for both $^{107}\text{Ag}^{16}\text{O}$ and $^{109}\text{Ag}^{16}\text{O}$ isotopologues. From a detailed analysis of the experimental data, accurate rotational constants of the $C^2\Pi\ v'=0$ state have been determined for both $^{107}\text{Ag}^{16}\text{O}$ and $^{109}\text{Ag}^{16}\text{O}$ isotopologues.

II. EXPERIMENTS

The experiment is performed in our supersonic jet laser induced fluorescence (LIF) setup that has been described in detail elsewhere [8, 9]. In brief, AgO molecules are produced by discharging a gas mixture ($\sim 5\%\text{O}_2/\text{Ar}$) between the tips of two silver needles. The needles are made from a bulk silver with natural isotopic abundances, *i.e.* $^{107}\text{Ag}^{109}\text{Ag}=1.08:1$, allowing for simultaneous production of $^{107}\text{Ag}^{16}\text{O}$ and $^{109}\text{Ag}^{16}\text{O}$ in the experiment. The discharge occurs at the beginning part of the supersonic jet expansion. The AgO molecules produced in the discharge plasma are then cooled down by supersonic expansion. At a distance of $\sim 30\text{ mm}$ downstream away from the electrodes, the molecule beam is crossed perpendicularly by a laser beam. Fluorescent emissions from laser excited AgO molecules are collected by a lens system and detected by a photomultiplier tube (PMT).

To resolve the rotational structures of the two $^{107}\text{Ag}^{16}\text{O}$ and $^{109}\text{Ag}^{16}\text{O}$ isotopologues, a home-made single longitude mode optical parametric oscillator (SLM-OPO) is used to record the LIF spectra [7]. The SLM-OPO employs a grazing-incidence-grating

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Littman-type cavity as the oscillator and a KTP (KTiOPO₄) crystal as the non-linear frequency conversion medium, and is pumped by a pulsed single-frequency 532 nm laser beam. The signal output of the OPO can be operated in the 700–1030 nm range, with an estimated bandwidth of ~ 0.004 cm⁻¹. Further details and full performance of this OPO system can be seen in Ref.[7]. In the present experiment, the signal output of the OPO is frequency doubled in a KDP (KD₂PO₄) crystal to obtain the tunable radiation in the 405–415 nm region, with an estimated bandwidth of ~ 0.006 cm⁻¹. During the experiment running, the frequency of the OPO signal output is calibrated online by a wavelength meter (High Finesse, WS7). The absolute frequency accuracy of extracted individual line positions from the recorded spectral is found to be ~ 0.006 cm⁻¹.

III. RESULTS AND DISCUSSION

According to the reported band origin of ¹⁰⁷Ag¹⁶O $C^2\Pi-X^2\Pi(0,0)$ band [2, 5], our experiment was performed in a frequency region of 24200–24420 cm⁻¹. Due to the spin-orbit coupling in both $C^2\Pi$ and $X^2\Pi$ states, the (0, 0) band consists of two subbands. FIG. 1 and FIG. 2 show the recorded spectra of the two spin-orbit subbands of $C^2\Pi_{1/2}-X^2\Pi_{1/2}$ and $C^2\Pi_{3/2}-X^2\Pi_{3/2}$ at around 24240.2 cm⁻¹ and 24412.3 cm⁻¹, respectively. These estimated band origins are in good agreement with the values reported in Refs.[1–5]. The spectral resolution is found to be ~ 0.02 cm⁻¹, which is dominated by the Doppler linewidth originating from the residual velocity distribution of AgO molecules in the supersonic jet expansion. At this spectral resolution, most rotational transition lines of both ¹⁰⁷Ag¹⁶O and ¹⁰⁹Ag¹⁶O isotopologues are well resolved, leaving the most dense part of the spectra, namely the R-branch head of $C^2\Pi_{1/2}-X^2\Pi_{1/2}$, to be partly resolved. Each spin-orbit subband consists of strong P- and R-branches, and a relatively weak Q-branch, which is characteristic for a typical $\Pi-\Pi$ transition. The R-branch can be easily recognized by its clear band head profile while the P- and Q-branches extend to the red side. With a close look at the high resolution spectrum, each subband exhibits two R-branch band heads with an energy interval of ~ 0.1 cm⁻¹. In addition, two components with nearly equal intensities are also observed in P- and Q-branches. The comparable intensities are consistent with the natural abundance ratio of ¹⁰⁷Ag¹⁶O to ¹⁰⁹Ag¹⁶O ($\sim 1:1$). Furthermore, the component in the lower energy side is readily recognized as the (0, 0) band of ¹⁰⁷Ag¹⁶O based on the previously reported spectroscopic constants [2, 5]. Therefore, the other component is assigned as the (0, 0) band of ¹⁰⁹Ag¹⁶O isotopologue.

It can also be seen from FIG. 1 and FIG. 2 that the rotational structure of the $C^2\Pi_{3/2}-X^2\Pi_{3/2}$ subband is much simpler than that of the $C^2\Pi_{1/2}-X^2\Pi_{1/2}$

FIG. 1 The high-resolution experimental spectrum of the $C^2\Pi_{1/2}-X^2\Pi_{1/2}$ (0, 0) band of ^{107/109}Ag¹⁶O (the upper black trace). The lower traces (a)–(c) show the simulated spectra using a Gaussian linewidth ~ 0.02 cm⁻¹ and a rotational temperature ~ 40 K, where (a) is the sum spectrum of ¹⁰⁷Ag¹⁶O and ¹⁰⁹Ag¹⁶O, (b) and (c) are the individual simulated spectra of ¹⁰⁷Ag¹⁶O and ¹⁰⁹Ag¹⁶O, respectively. The insert shows zoomed-in spectra in the 24232 cm⁻¹ region.

FIG. 2 Portion of the high-resolution experimental spectrum and assignments of the $C^2\Pi_{3/2}-X^2\Pi_{3/2}$ (0, 0) band of ^{107/109}Ag¹⁶O (the upper black trace). The Λ -doubling is not resolved in this subband and therefore is not indicated in the assignments. The lower traces (a)–(c) show the simulated spectra using a Gaussian linewidth ~ 0.02 cm⁻¹ and a rotational temperature ~ 40 K, where (a) is the sum spectrum of ¹⁰⁷Ag¹⁶O and ¹⁰⁹Ag¹⁶O, (b) and (c) are the individual simulated spectra of ¹⁰⁷Ag¹⁶O and ¹⁰⁹Ag¹⁶O, respectively.

one. For the $C^2\Pi_{3/2}-X^2\Pi_{3/2}$ subband (FIG. 2), individual J -lines contain two components and the energy intervals within them are J -independent. As pointed above, these two components arise from ¹⁰⁷Ag¹⁶O and ¹⁰⁹Ag¹⁶O isotope shift. For the $C^2\Pi_{1/2}-X^2\Pi_{1/2}$ subband (FIG. 1), in addition to the isotope shift, the Λ -doubling is also observed. As expected, the energy intervals within the two Λ -doubling components should be

TABLE I Spectroscopic constants for the $C^2\Pi$ $v'=0$ state of AgO.

	T/cm^{-1}	A/cm^{-1}	$A_D \times 10^3/\text{cm}^{-1}$	B/cm^{-1}	$D \times 10^6/\text{cm}^{-1}$	p/cm^{-1}	$q \times 10^5/\text{cm}^{-1}$
$^{109}\text{Ag}^{16}\text{O}$	24326.2532(4)	-97.1461(7)	1.3382(23)	0.279883(3)	1.3435(42)	0.023916(64)	1.7(10)
$^{107}\text{Ag}^{16}\text{O}$	24326.1267(4)	-97.1404(7)	1.290(9)	0.280540(3)	1.375(6)	0.024004(64)	1.6(10)
$^{107}\text{Ag}^{16}\text{O}$ [5]	24326.138(23)	-96.927(28)	0.828(23)	0.280210(32)	1.067(13)	0.02629(44)	

Note: Numbers in parentheses are 1σ of the fits, while the experimental accuracy of individual line positions is $\sim 0.006 \text{ cm}^{-1}$.

J -dependent, that is, become larger as the J increases. Because the Λ -doubling effect is much smaller in $\Omega=3/2$ components of both $C^2\Pi$ and $X^2\Pi$ states [4, 10], the Λ -doubling could not be resolved for the $C^2\Pi_{3/2}$ - $X^2\Pi_{3/2}$ subband in present study. These behaviors are also observed in previous study [2].

Based on the reported spectroscopic constants for both $C^2\Pi$ and $X^2\Pi$ states of $^{107}\text{Ag}^{16}\text{O}$ isotopologue, rotational assignments of individual transition lines are straightforward. For the $^{109}\text{Ag}^{16}\text{O}$ isotopologue, as the starting point, a set of constants are calculated firstly using isotope relations of rotational constants [11]. After that, using these calculated constants and rotational combination differences in the ground state $X^2\Pi$, the lines arising from the $^{109}\text{Ag}^{16}\text{O}$ isotopologue are also assigned. The assignments for both $^{107}\text{Ag}^{16}\text{O}$ and $^{109}\text{Ag}^{16}\text{O}$ isotopologues and the line positions extracted from the observed spectra are summarized in supplementary materials. A least square fit of the line positions is performed in the Pgpopher software [12] to obtain accurate spectroscopic constants. For the $C^2\Pi$ and $X^2\Pi$ states, a standard effective Hamiltonian [13] is used as the following:

$$\hat{H} = B\hat{N}^2 - D\hat{N}^4 + A\hat{L}_Z\hat{S}_Z + \frac{A_D}{2}[\hat{N}^2, \hat{L}_Z\hat{S}_Z]_+ - \frac{p}{2}(\hat{N}_+\hat{S}_+ + \hat{N}_-\hat{S}_-) + \frac{q}{2}(\hat{N}_+^2 + \hat{N}_-^2) \quad (1)$$

where the first two terms represent the rotation operator, the middle two terms describe the spin-orbit operator, and the last two terms represent the Λ -doubling effect in a $^2\Pi$ state. In Eq.(1), B is the rotational constant, D is the centrifugal distortion constant, A is the spin-orbit coupling constant, A_D the centrifugal distortion of the spin-orbit coupling effect, p and q are the Λ -doubling constants.

In the fits, the spectroscopic constants for $X^2\Pi$ $v=0$ state are fixed to the values reported in Ref.[10], while the $C^2\Pi$ $v=0$ state constants are set to the variable parameters. In order to obtain more accurate molecular constants, some partly resolved R-branch lines and very weak Q-branch lines are weighted by two standard deviations (see the detailed line list in supplementary materials). In total, 364 observed lines are included in the fit. The rms of the fit is $\sim 0.003 \text{ cm}^{-1}$ (weighted, unweighted average error is 0.004 cm^{-1}). The calculated line positions and observation-calculation (o-c) deviations for individual transition lines are also summarized

in supplementary materials. The resulting $C^2\Pi$ $v=0$ state constants for both $^{109}\text{Ag}^{16}\text{O}$ and $^{107}\text{Ag}^{16}\text{O}$ are summarized in Table I. The $^{109}\text{Ag}^{16}\text{O}$ constants are reported for the first time. The $^{107}\text{Ag}^{16}\text{O}$ constants are also improved in precision compared to previously reported values [2, 5], due to the fact that the spectrum in literature could be more or less contaminated by unresolved isotopologues.

The determined spin-orbit coupling constant for the $C^2\Pi$ state is $A=-97.1 \text{ cm}^{-1}$, which is significantly smaller than that for $X^2\Pi$ ($A=-269.3 \text{ cm}^{-1}$) and $D^2\Pi$ ($A=-226.3 \text{ cm}^{-1}$) states [5]. The difference indicates that the nature of the spin-orbit coupling effect in $C^2\Pi$ is probably different from that in $C^2\Pi$ and $D^2\Pi$ states. According to discussions in Refs.[4, 6, 10], the $X^2\Pi$ state correlates to two ground state atoms $\text{Ag}(4d^{10}5s^1, ^2S)+\text{O}(2p^4, ^3P)$ and has significantly ionic characters $\text{Ag}^+(4d^{10})+\text{O}^-(2p^5)$ and $\text{Ag}^+(4d^95s^1)+\text{O}^-(2p^5)$. The $D^2\Pi$ correlates to the ground state $\text{O}(2p^4, ^3P)$ atom and excited state $\text{Ag}(4d^95s^2, ^2P \text{ or } ^2D)$ atom. The spin-orbit constants for the atoms are $\text{O}(2p^4, \zeta=-151 \text{ cm}^{-1})$, $\text{O}^-(2p^5, \zeta=-121 \text{ cm}^{-1})$ and $\text{Ag}(4d^95s^2, \zeta=-1767 \text{ cm}^{-1})$ [14]. By comparing the molecular spin-orbit coupling constants with the atomic ones, we can easily conclude that both p-hole on the O (or O^-) atom and d-hole on the Ag atom account for the large spin-orbit coupling in $X^2\Pi$ and $D^2\Pi$ states [5, 10]. In contrast, the spin-orbit coupling effect in the $C^2\Pi$ state differs. Theoretical study [6] shows that the $C^2\Pi$ state correlates to the $\text{Ag}(4d^{10}5s^1, ^2S)+\text{O}(2p^4, ^1D)$ dissociation limit, in which neither the O nor Ag atom could make contributions to the molecular spin-orbit coupling. If this holds strictly, the $C^2\Pi$ state is expected free of spin-orbit splitting. However, the experiments (this work and Ref.[5]) do observe spin-orbit splitting in the $C^2\Pi$ state. Therefore, the observed spin-orbit splitting must be caused by mixing with other states. By examining the nearby electronic states, the candidates are probably the repulsive $^4\Sigma^-$ and $^4\Pi$ states, which correlate to the dissociation limit of the ground state atoms $\text{Ag}(4d^{10}5s^1, ^2S)+\text{O}(2p^4, ^3P)$ [6]. As the spin-orbit splitting in $\text{O}(2p^4, ^3P)$ is -158 cm^{-1} , it is reasonable that $C^2\Pi$ state gains a splitting of -97 cm^{-1} by partly mixing with this (these) state(s). This idea could be supported by previous studies [1, 2], where Uhler [1] observed predissociation in both $\Omega=1/2$ and $\Omega=3/2$ com-

ponents of $C^2\Pi$ $v'=1$ level. It is suggested that the predissociation is caused by interaction with a $^4\Sigma^-$ or $^4\Pi$ state because they do have the $\Omega=3/2$ component [2]. The interactions between $C^2\Pi$ state and these repulsive states can be well understood by further theoretical studies.

IV. CONCLUSION

We present a high resolution spectroscopic study on the $C^2\Pi$ - $X^2\Pi$ transition (0, 0) band of both $^{107}\text{Ag}^{16}\text{O}$ and $^{109}\text{Ag}^{16}\text{O}$ isotopologues. The spectrum of $^{109}\text{Ag}^{16}\text{O}$ is reported for the first time. From rotational analysis, accurate molecular constants have been determined for both $^{107}\text{Ag}^{16}\text{O}$ and $^{109}\text{Ag}^{16}\text{O}$. The spin-orbit splitting of $C^2\Pi$ state is suggested to be caused by interacting with the repulsive $^4\Sigma^-$ or $^4\Pi$ state, which correlates to the two ground state atoms $\text{Ag}(4d^{10}5s^1, ^2S)+\text{O}(2p^4, ^3P)$.

Supplementary materials: The list of transition lines, rotational assignments, and o-c deviations obtained from the fits are given.

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