Reinvestigate the $C^2Π-X^2Π(0, 0)$ Band of AgO†

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The $C^2Π-X^2Π(0, 0)$ band of AgO has been reinvestigated by laser induced fluorescence spectroscopy with a spectral resolution of ~0.02 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 longitudinal mode optical parametric oscillator (SLM-OPO) as the laser source, high-resolution spectra of the $C^2Π-X^2Π(0, 0)$ band have been recorded for both $^{107}\text{Ag}O$ and $^{109}\text{Ag}O$ isotopologues. The spectroscopic constants of the $C^2Π$ state are consequently determined, with the $^{109}\text{Ag}O$ one being reported for the first time. The nature of the spin-orbit coupling effect in the $C^2Π$ state is proposed to be due to state mixing with the nearby repulsive $4Σ^−$ and $4Π$ states.

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

I. INTRODUCTION

The blue system, or the $C^2Π-X^2Π$ 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 $C^2Π-X^2Π$ transition was performed by Uhler [1], resulting in determination of the spectroscopic constants for $C^2Π$ $v′=0/1$ states. After that, Griffiths and Barrow [2] studied the $C^2Π-X^2Π$ emission spectrum and obtained both vibrational and rotational constants for the $C^2Π$ state of the $^{107}\text{Ag}O$ isotope. The experiment also shows that the $C^2Π$ state only has a shallow potential minimum. Supported by isotope shifts, Vujisić et al. [3] reported the improved $^{107}\text{Ag}O$ and the new $^{109}\text{Ag}O$ vibrational constants for the $C^2Π$ state. Later, through a re-analysis of the $C^2Π-X^2Π(0, 0/1)$ band spectra recorded by Uhler [1], Brien et al. [5] obtained more accurate spectroscopic constants for the $C^2Π$ $v′=0$ state of $^{107}\text{Ag}O$ isotopologue.

Considering the fact that the natural abundance ratio of silver isotopes is about 1:1, both $^{107}\text{Ag}O$ and $^{109}\text{Ag}O$ 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 $C^2Π$ state of $^{109}\text{Ag}O$. In this work, we reinvestigated the $C^2Π-X^2Π(0, 0)$ band by using a narrowband laser source [7]. The spectral resolution (~0.02 cm$^{-1}$) allows us to resolve the rotational structures for both $^{107}\text{Ag}O$ and $^{109}\text{Ag}O$ isotopologues. From a detailed analysis of the experimental data, accurate rotational constants of the $C^2Π v′=0$ state have been determined for both $^{107}\text{Ag}O$ and $^{109}\text{Ag}O$ 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 (~5%O$_2$/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 $^{107}\text{Ag}O$ and $^{109}\text{Ag}O$ 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 ~30 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 $^{107}\text{Ag}O$ and $^{109}\text{Ag}O$ isotopologues, a home-made single longitudinal mode optical parametric oscillator (SLM-OPO) is used to record the LIF spectra [7]. The SLM-OPO employs a grazing-incidence-grating.
According to the reported band origin of $^{107}$Ag$^{16}$O $C^2Π$−$X^2Π(0,0)$ band [2, 5], our experiment was performed in a frequency region of 24200–24240 cm$^{-1}$. Due to the spin-orbit coupling in both $C^2Π$ and $X^2Π$ states, the (0, 0) band consists of two subbands.

III. RESULTS AND DISCUSSION

According to the reported band origin of $^{107}$Ag$^{16}$O $C^2Π$−$X^2Π(0,0)$ band [2, 5], our experiment was performed in a frequency region of 24200–24240 cm$^{-1}$. Due to the spin-orbit coupling in both $C^2Π$ and $X^2Π$ states, the (0, 0) band consists of two subbands. IG. 1 and FIG. 2 show the recorded spectra of the two spin-orbit subbands of $C^2Π_{1/2}$-$X^2Π_{1/2}$ and $C^2Π_{3/2}$-$X^2Π_{3/2}$ 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 $^{107}$Ag$^{16}$O and $^{109}$Ag$^{16}$O isotopologues are well resolved, leaving the most dense part of the spectra, namely the R-branch head of $C^2Π_{1/2}$-$X^2Π_{1/2}$, 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 II-II 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 $^{107}$Ag$^{16}$O to $^{109}$Ag$^{16}$O (~1:1). Furthermore, the component in the lower energy side is readily recognized as the (0, 0) band of $^{107}$Ag$^{16}$O based on the previously reported spectroscopic constants [2, 5]. Therefore, the other component is assigned as the (0, 0) band of $^{109}$Ag$^{16}$O isotopologue.

It can also be seen from FIG. 1 and FIG. 2 that the rotational structure of the $C^2Π_{3/2}$-$X^2Π_{3/2}$ subband is much simpler than that of the $C^2Π_{1/2}$-$X^2Π_{1/2}$ one. For the $C^2Π_{3/2}$-$X^2Π_{3/2}$ 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 $^{107}$Ag$^{16}$O and $^{109}$Ag$^{16}$O isotope shift. For the $C^2Π_{1/2}$-$X^2Π_{1/2}$ subband (FIG. 1), in addition to the isotope shift, the A-doubling is also observed. As expected, the energy intervals within the two A-doubling components should be...
TABLE I Spectroscopic constants for the C^2Π v’=0 state of AgO.

<table>
<thead>
<tr>
<th>T/cm⁻¹</th>
<th>A/cm⁻¹</th>
<th>A_D×10⁹/cm⁻¹</th>
<th>B/cm⁻¹</th>
<th>D×10⁹/cm⁻¹</th>
<th>p/cm⁻¹</th>
<th>q×10⁵/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>109Ag₁₆O</td>
<td>24326.2532(4)</td>
<td>-97.1461(7)</td>
<td>1.3382(23)</td>
<td>0.279883(3)</td>
<td>1.3435(42)</td>
<td>0.023916(64)</td>
</tr>
<tr>
<td>107Ag₁₆O</td>
<td>24326.1267(4)</td>
<td>-97.1404(7)</td>
<td>1.290(9)</td>
<td>0.280540(3)</td>
<td>1.375(6)</td>
<td>0.024004(64)</td>
</tr>
<tr>
<td>107Ag₁₆O [5]</td>
<td>24326.1382(23)</td>
<td>-96.927(28)</td>
<td>0.828(23)</td>
<td>0.280210(32)</td>
<td>1.067(13)</td>
<td>0.02629(44)</td>
</tr>
</tbody>
</table>

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

The determined spin-orbit coupling constant for the C^2Π state is \( A=-97.1 \text{ cm}^{-1} \), which is significantly smaller than that for \( X^2Π \) (\( A=-269.3 \text{ cm}^{-1} \)) and \( D^2Π \) (\( A=-226.3 \text{ cm}^{-1} \)) states [5]. The difference indicates that the nature of the spin-orbit coupling effect in \( C^2Π \) is probably different from that in \( C^2Π \) and \( D^2Π \) states. According to discussions in Refs. [4, 6, 10], the \( X^2Π \) state correlates to two ground state atoms Ag(4d\(^5\)5s\(^1\), 2S)+O(2p\(^2\), 3P) and has significantly longer characters Ag\(^+\)(4d\(^{10}\)+O\(^-\)(2p\(^5\)) and Ag\(^+\)(4d\(^{9}\)5s\(^1\))+O\(^-\)(2p\(^5\)). The \( D^2Π \) correlates to the ground state O(2p\(^2\), 3P) atom and excited state \( \text{Ag}(4d^{9}5s^{2}, 2P \text{ or } 2D) \) atom. The spin-orbit constants for the atoms are O(2p\(^2\), \( \zeta=-151 \text{ cm}^{-1} \)), O\(^-\)(2p\(^5\), \( \zeta=-121 \text{ cm}^{-1} \)) and \( \text{Ag}(4d^{9}5s^{2}, \zeta=-1767 \text{ cm}^{-1}) \) [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 \( X^2Π \) and \( D^2Π \) states [5, 10]. In contrast, the spin-orbit coupling effect in the \( C^2Π \) state differs. Theoretical study [6] shows that the \( C^2Π \) state correlates to the Ag\(^+\)(4d\(^{10}\)+O\(^-\)(2p\(^5\)) and Ag\(^+\)(4d\(^{9}\)5s\(^1\))+O\(^-\)(2p\(^5\)). In which neither the O nor Ag atom could make contributions to the molecular spin-orbit coupling. If this holds strictly, the \( C^2Π \) state is expected free of spin-orbit splitting. However, the experiments (this work and Ref. [5]) do observe spin-orbit splitting in the \( C^2Π \) 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 \( 4Σ^- \) and \( 4Π \) states, which correlate to the dissociation limit of the ground state atoms Ag\(^+\)(4d\(^{10}\)5s\(^1\), 2S)+O(2p\(^2\), 3P) [6]. As the spin-orbit splitting in O(2p\(^2\), 3P) is \( -158 \text{ cm}^{-1} \), it is reasonable that \( C^2Π \) state gains a splitting of \( -97 \text{ cm}^{-1} \) 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-

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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.

V. ACKNOWLEDGEMENTS

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