Photodissociation Dynamics of Carbon Dioxide Cation via the Vibrationally Mediated $\tilde{A}^2\Pi_{u,1/2}$ State: A Time-Sliced Velocity-Mapped Ion Imaging Study

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(Dated: Received on November 11, 2016; Accepted on January 25, 2017)

We report on the photodissociation dynamics of CO$_2^+$ via its $\tilde{A}^2\Pi_{u,1/2}$ state using the scheme of [1+1] photon excitation that is intermediated by the mode-selected $\tilde{A}^2\Pi_{u,1/2}(v_1, v_2, 0)$ vibronic states. Photodissociation fragment excitation spectrum and images of photofragment CO$^+$ have been measured to obtain reaction dynamics parameters such as the available energy and the average translational energy. Combining with the potential energy functions of CO$_2^+$, the dissociation mechanism of CO$_2^+$ is discussed. The conformational variation of CO$_2^+$ from linear to bent on the photodissociation dynamics of CO$_2^+$ is verified.

**Key words:** Photodissociation dynamics, Velocity map imaging, Carbon dioxide cation

I. INTRODUCTION

Photodissociation dynamics of molecular cations is a significant subject in photochemistry [1–4]. Since the prominent improvement of resolution by Eppink and Parker in 1997 [5], ion imaging method has been playing an important role in studying photodissociation dynamics of many molecular systems, like the recent reported freon [6], bromocyclopropane [7], Criegee intermediates [8], xylene [9], OCS [10], and furan [11], owning to its high detection efficiency and high velocity resolution. Many approaches come out, including time slicing in which subsets of the conventional crushed image are recorded by the gating the detector selecting a small region of $\Delta t$ and no need of the inverse-Abel for further analysis [12].

As an important molecular cation in astrophysics and atmospheric physics, CO$_2^+$ has been studied extensively during the past several decades [13–18]. Previously numerous experimental and theoretical studies on the spectrum and photodissociation dynamics of the CO$_2^+$ ion were reported [13–18], which supplied abundant information. C. Y. Ng et al. measured the vacuum ultraviolet pulsed field ionization-photoelectron spectra for CO$_2$ in the energy range of 13.6–20.0 eV, revealing vibronic structures for the $\tilde{X}^2\Pi_g$, $\tilde{A}^2\Pi_u$, $\tilde{B}^2\Sigma^+_u$, $\tilde{C}^2\Sigma^+_g$ states of CO$_2^+$, they also used theoretical calculations to provide a rationalization that the photodissociation for CO$_2^+$($\tilde{C}^2\Sigma^+_g$) to form O$^+$(4S)+CO($\tilde{X}^1\Sigma^+$) and CO$^+$($\tilde{X}^2\Sigma^+$)+O$(3P)$ most likely proceeds via the repulsive $a^4\Sigma^+_g$ and $b^3\Pi_u$ (or $b^4\Pi_1$ in a bent geometry) states [13–15]. Zhang et al. studied the mass-resolved [1+1] two-photon dissociation spectra of CO$_2^+$ via $\tilde{A}^2\Pi_u(v_1, v_2, 0)$ transitions [16–18]. The spectroscopic constants were deduced and the dissociation dynamics was discussed in their research work.

We have reported the subtle and complex photodissociation behavior in a narrow energy region ($\sim$280 cm$^{-1}$) on the photodissociation of CO$_2^+$ mediated by its different $\tilde{A}^2\Pi_{u,1/2}(v_1, v_2, 0)$ vibronic states using velocity map imaging (VMI) technology [19], nevertheless our previous work focused mainly on reporting the experimental results [19]. So we further provide details and discussion on the physical insights and dissociation mechanism in this work to explore the photodissociation dynamics of carbon dioxide cation via the vibrationally mediated $\tilde{A}^2\Pi_{u,1/2}$ state.

II. EXPERIMENTS

The experiments were performed in a home-built VMI apparatus, details of which can be found elsewhere [20, 21]. Briefly, the carbon dioxide sample seeded in Ar ($\sim$30%) at a stagnation pressure of $\sim$3 atm was expanded through a pulsed nozzle (Series 9, General Valve) with an orifice diameter of 0.5 mm in a source chamber and skimmed to form a supersonically expanded molecular beam into a differentially pumped detection chamber. The operating pressures in the source...
and detection chambers were maintained at ~10^{-6} and ~10^{-7} Torr, respectively. After passing through a 1.5 mm hole on the repeller plate, the molecular beam directed along the time-of-flight (TOF) axis was intersected at right angles by the laser beam in the detection zone. For all VMI measurements, the electric vector of the linearly polarized laser was set perpendicular to the TOF axis and thus parallel to the front face of the microchannel plates (MCP’s) that form part of the ion detection system. The ionization laser around 333 nm from the phosphor screen were captured by a charge-coupled device (CCD) camera (Image Compact QE 1376×1024 pixels, LaVision) and transferred to a computer on an every shot basis for event counting [22] and data analysis. Timing of the pulsed nozzle, the detection system. The ionization laser around 333 nm and the gate pulse applied on the MCP’s was controlled by two multichannel digital delay pulse generator (DG 535, SRS). The transient images of the ionization and dissociation lasers were simultaneously monitored during the experiment.

CO$_2^+$ ions were prepared by a [3+1] resonance-enhanced multiphoton ionization (REMPI) excitation process. Within a set of ion optics designed for the VMI measurements, photofragment CO$^+$ ions were accelerated by the focusing electric fields and projected onto a 40-mm-diameter Chevron-type dual MCP’s coupled to a P-47 phosphor screen (APD 3040FM, Burle Electro-Optics). A fast high-voltage switch (PVM-4210, DEI; typical duration ~50 ns) was pulsed to gate the gain of the MCP’s for mass selection as well as the time slicing of the ion packet. The transient images from the phosphor screen were captured by a charge-coupled device (CCD) camera (Image Compact QE 1376×1024 pixels, LaVision) and transferred to a computer on an every shot basis for event counting [22] and data analysis. Timing of the pulsed nozzle, the laser, and the gate pulse applied on the MCP’s was controlled by two multichannel digital delay pulse generator (DG 535, SRS). The photofragment excitation spectrum (PHOFEX) was acquired using a photomultiplier tube. The images were accumulated over 5×10$^4$ shots or more. The backgrounds were removed by subtracting the off-resonance images collected under the same conditions. The wavelengths calibrated by a wavemeter were scanned to cover all the speed components of the nascent fragments.

III. RESULTS AND DISCUSSION

A. PHOFEX spectrum of CO$_2^+$ (A$^2\Pi_{u} \leftarrow \tilde{X}^2\Pi_{g}$) transition

Pure CO$_2^+$ ($\tilde{X}^2\Pi_{g,1/2}(0,0,0)$) ions were generated by [3+1] REMPI at 333.06 nm via 3$p_{\pi, u}^1\Delta_u$, Rydberg state depending on the result of L. M. Zhang et al. [16], that is:

$$ \text{CO}_2^+ (\tilde{X}^2\Sigma_u^+) \rightarrow \text{CO}_2 (3p_{\pi, u}^1\Delta_u) \rightarrow \text{CO}_2^+ \left(\tilde{X}^2\Pi_{g,1/2}(0,0,0)\right) $$

After the preparation of the cations, the photodissociation laser was introduced, and PHOFEX spectrum (Fig.1) of CO$_2^+$ was obtained by scanning the wavelength of photodissociation laser and recording the photofragment CO$^+$ signals. In order to ensure that CO$^+$ was the cooperative action of two lasers, not one laser only, the power of photoionization and photodissociation laser was carefully optimized with temporally and spatially matched at the laser-molecular interaction point.

Based on previous results, assignments of our PHOFEX spectrum were carried out giving different vibronic of A$^2\Pi_{u,1/2}$ ($v_1, v_2, 0$) state. Here $v_1$ and $v_2$ denote vibrational quantum numbers for the symmetric stretching and bending modes, respectively. The vibronic coupling induces Remer-Teller splitting, giving rise to the split $\mu$ (lower) and $\kappa$ (upper) components for each A$^2\Pi_{u,1/2}$ ($v_1, v_2, 0$) state. With this spectrum, we could study the dissociation dynamics via the vibrationally mediated state using time-sliced velocity-mapped ion imaging technique.

One interesting phenomena should be noticed. The intensities of ($v_1, 2, 0$; $v_1=0-3)\mu^2\Pi_{u,1/2}$ are obviously lower than those of ($v_1, 2, 0$; $v_1=0-3)\kappa^2\Pi_{u,1/2}$ and ($v_1, 0, 0$; $v_1=1-4)\Pi_{u,1/2}$, nevertheless the intensities of ($4, 2, 0)\mu^2\Pi_{u,1/2}$ are higher than those of ($4, 2, 0)\kappa^2\Pi_{u,1/2}$ and ($5, 0, 0)\Pi_{u,1/2}$. It is known that the potential energy surface of the lower ($v_1, 2, 0)\mu^2\Pi_{u,1/2}$ state (corresponding to a bent geometry) is more complex than that of the upper ($v_1, 2, 0)\kappa^2\Pi_{u,1/2}$ state (corresponding to a linear geometry) [23], respectively. When the linear parent CO$_2^+$ cations absorb the first dissociation photon, the bent $\mu$ (lower) components for each A$^2\Pi_{u,1/2}$ ($v_1, v_2, 0$) state are relatively difficult to be excited. Nevertheless, when the linear parent CO$_2^+$ cations absorb the first dissociation photon and begin to bend, the bent $\mu$ (lower) components for each A$^2\Pi_{u,1/2}$ ($v_1, v_2, 0$) state are relatively easier to be excited. It is suggested that the conformational variation occurs in the photodissociation process.

B. Ion images and assignments of CO$^+$ vibronic distributions

The time-sliced ion images of photofragment CO$^+$ were obtained at all the vibronic transition peaks of CO$_2^+$ ($\tilde{A}^2\Pi_{g} \leftarrow \tilde{X}^2\Pi_{g}$) in the wavelength range we explored. A typical example is shown in Fig.2, in which the photodissociation is mediated via the
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FIG. 1 PHOFEX spectrum recorded by monitoring the photofragment CO$^+$ signals in the wavelength range of 278–354 nm. The assignments of the $\tilde{A}^2\Pi_u(v_1, v_2, 0)\rightarrow \tilde{X}^2\Pi_g(v_1, v_2, 0)$ vibronic transitions were used for acquiring images of CO$^+$.

$\tilde{A}^2\Pi_{u,1/2}(v_1, v_2, 0)$ states. To obtain the anisotropy parameter, $\beta$, the angular distribution $P(\theta)$ has been fitted according to:

$$P(\theta) \propto 1 + \beta P_2(\cos \theta)$$

where $\theta$ is the angle between the polarization vector of the dissociation laser and the recoil velocity vector of the fragments, and $P_2(\cos \theta)$ is the second-order Legendre polynomial.

On the basis of energy and momentum conservation, the distribution of total translational energy of fragments (CO$^+$, O) can be routinely obtained. The internal energy of CO$^+$ fragments, $E_{\text{int}}$, could be obtained using the formula below:

$$2h\nu - D_0 = E_T + E_{\text{int}}$$

where $2h\nu$ is the two-photon energy of the photodissociation laser, $D_0$ is the dissociation limit of the O($^3P_g$)+CO$^+$(X$^2\Sigma^+$) channel. $D_0$ value is 5.6724 eV [15], and the corresponding one-photon wavelength is 176.3 nm, which can not be obtained in our laboratory. So [1+1] resonance-enhanced two photons scheme is used to dissociate CO$_2^+$. $E_T$ is the total released translational energy of O and CO$^+$ fragments, which can be obtained by

$$m_{\text{CO}^+}V_{\text{CO}^+} = m_OV_O$$

and

$$E_T = \frac{1}{2}m_{\text{CO}^+}V_{\text{CO}^+}^2 + \frac{1}{2}m_OV_O^2$$

The calibration for the speed of CO$^+$ fragment was achieved by probing CO rotational bands of OCS at 230 nm [24]. $m_{\text{CO}^+}$, $m_O$, $V_{\text{CO}^+}$, and $V_O$ represent the mass and velocity of the CO$^+$ and O fragments, respectively.

Using vibrational frequency $\omega_e=2214.2$ cm$^{-1}$ and the anharmonic constant $\omega_e\chi_e=15.16$ cm$^{-1/2}$ of CO$^+(X^2\Sigma^+)$ [25], the vibronic quantum number of CO$^+(X^2\Sigma^+)$ was assigned as shown in Fig.2(b). The profile of $\beta$ versus total translational energy of fragments is plotted in Fig.2(c). The values of $\beta$ are near zero.

C. Dissociation dynamics via $\tilde{A}^2\Pi_{u,1/2}(v_1, v_2, 0)$ states

From the analysis of the raw image, the angular distribution of CO$^+$ fragments is isotropic, indicating that the CO$_2^+$ ($C^2\Sigma^+_g$) cations are predissociative. The
Rosmus and coworkers also calculated potential energy functions of CO$_2^+$, the predissociation for CO$_2^+$ channel. $E_{\text{avail}}$ denotes the available energy, $\langle E_T\rangle$: the average translation energy of CO$^+$ and O, $\langle E_T\rangle/E_{\text{avail}}$: the ratio of the average translational energy to the available energy.

<table>
<thead>
<tr>
<th>Mediated state</th>
<th>Excitation wavelength/nm</th>
<th>$E_{\text{avail}}$/eV</th>
<th>$\langle E_T\rangle$/eV</th>
<th>$\langle E_T\rangle/E_{\text{avail}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5,0,0)</td>
<td>293.64</td>
<td>2.773</td>
<td>0.349</td>
<td>0.126</td>
</tr>
<tr>
<td>(4,2,0)$\kappa$</td>
<td>294.64</td>
<td>2.744</td>
<td>0.326</td>
<td>0.119</td>
</tr>
<tr>
<td>(4,2,0)$\mu$</td>
<td>296.09</td>
<td>2.703</td>
<td>0.387</td>
<td>0.143</td>
</tr>
<tr>
<td>(4,0,0)</td>
<td>303.53</td>
<td>2.497</td>
<td>0.387</td>
<td>0.155</td>
</tr>
<tr>
<td>(3,2,0)$\kappa$</td>
<td>304.73</td>
<td>2.465</td>
<td>0.323</td>
<td>0.131</td>
</tr>
<tr>
<td>(3,2,0)$\mu$</td>
<td>306.24</td>
<td>2.425</td>
<td>0.363</td>
<td>0.150</td>
</tr>
<tr>
<td>(3,0,0)</td>
<td>314.13</td>
<td>2.222</td>
<td>0.486</td>
<td>0.219</td>
</tr>
<tr>
<td>(2,2,0)$\kappa$</td>
<td>315.65</td>
<td>2.184</td>
<td>0.482</td>
<td>0.221</td>
</tr>
<tr>
<td>(2,2,0)$\mu$</td>
<td>317.21</td>
<td>2.145</td>
<td>0.482</td>
<td>0.225</td>
</tr>
<tr>
<td>(2,0,0)</td>
<td>325.55</td>
<td>1.945</td>
<td>0.536</td>
<td>0.275</td>
</tr>
<tr>
<td>(1,2,0)$\kappa$</td>
<td>327.36</td>
<td>1.903</td>
<td>0.574</td>
<td>0.302</td>
</tr>
<tr>
<td>(1,2,0)$\mu$</td>
<td>329.01</td>
<td>1.865</td>
<td>0.508</td>
<td>0.272</td>
</tr>
<tr>
<td>(1,0,0)</td>
<td>337.93</td>
<td>1.666</td>
<td>0.504</td>
<td>0.303</td>
</tr>
<tr>
<td>(0,2,0)$\kappa$</td>
<td>340.08</td>
<td>1.619</td>
<td>0.490</td>
<td>0.303</td>
</tr>
<tr>
<td>(0,2,0)$\mu$</td>
<td>341.79</td>
<td>1.583</td>
<td>0.461</td>
<td>0.291</td>
</tr>
<tr>
<td>(0,0,0)</td>
<td>351.24</td>
<td>1.387</td>
<td>0.676</td>
<td>0.487</td>
</tr>
</tbody>
</table>

a Calculated by using the relation $E_{\text{avail}}=2h\nu - D_0$.

b Calculated by using the relation $\langle E_T\rangle=1/2m_{CO^+}\langle V_{CO^+}^2\rangle+1/2m_{O}\langle V_O^2\rangle$.

From initial analysis, the relation reaction dynamics parameters are shown in Table I. It is obvious that the ratios of the average translational energy to the available energy decrease as the energy of dissociation photon increases. As the excitation wavelength is varied from 351.24 nm to 303.53 nm, the images of CO$^+$ resemble each other, which verify that the dissociation dynamics of carbon dioxide cation in this excitation energy area is similar. This is because the excitation of bending modes does not influence the dissociation process when the parent molecule is linear. However, as the excitation wavelength is varied from 293.64 nm to 296.09 nm (photon energy varied also by $\sim$280 cm$^{-1}$), the three images of carbon oxide cation look different in small energy region [19]. The dissociation dynamics of carbon dioxide cation exists dramatic variation, which is suggested that there is an important variation in the dissociation process. According to the potential energy functions calculated by C. Y. Ng and coworkers [15], the predissociation for CO$_2^+$($\tilde{X}^2\Sigma_g^+$) to form CO$^+$(\text{X}$^2\Sigma_g^+$)+O($^3P$) most likely proceeds via the repulsive $b^4\Pi_u$ (or $b^4\Pi_d$ in a bent geometry) states. P. Rosmus and coworkers also calculated potential energy functions of CO$_2^+$, and they found that the potential energy functions of the A$^2\Pi_1$ state around $\alpha_{OCO}=130^\circ$ exhibited a barrier at $\sim$9000 cm$^{-1}$ above the energy of its equilibrium linear geometry [26]. When the first dissociation photon excitation energy exceeds the barrier height, the probability of spanning the barrier enhances, and conformational variation from linear CO$_2^+$($A^2\Pi_u$) to bent CO$_2^+$($A^2\Pi_1$) probably happen. The dissociation process of bent molecule mostly correlates with excitation of bending modes. Excitation of high level symmetric stretching modes is needed, so vibrational profiles are almost vanished for (5,0,0) [19]. The potential energy surface of the lower (4,2,0) $\mu^2\Pi_u$ (corresponding to a bent geometry) is more complex than that of the upper (4,2,0) $\kappa^2\Pi_u$ (corresponding to a linear geometry) [23], so more dissociation channels may be opened up when CO$_2^+$ ions are excited to the former surface. This causes the continuous distribution of translation energy [19].

In our research work, the carbon dioxide cation is dissociated vibrationally mediated by $A^2\Pi_{u,1/2}$($v_1$, $v_2$, 0) using [1+1] resonance-enhanced two photons scheme, and the first resonance step is a rate-decided step which plays an important role on dissociation dynamics of carbon dioxide cation. Conformational variation in the dissociation process when carbon dioxide cation is excited by dissociation laser lead to dramatic variation in the intensities of PHPFEX spectrum and vibrational distributions of CO$^+$. DOI:10.1063/1674-0068/30/cjcp1611208 ©2017 Chinese Physical Society
IV. CONCLUSION

In conclusion, we have investigated the photodissociation dynamics of carbon dioxide cation by means of time-sliced VMI. The CO$_2^+$ (C$^2\Sigma^+_g^-$) cations are predisociative. The abnormal intensities of PHOFEX spectrum and dramatic reaction dynamics variation in a narrow 280 cm$^{-1}$ region are correlated with the conformational variation in the dissociation process of CO$_2^+$.

V. ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation of Changzhou Institute of Technology (No.YN1507), Undergraduate Training Program for Innovation of Changzhou Institute of Technology (No.J150245), the China Postdoctoral Science Foundation (No.2013M531506), the National Natural Science Foundation of China (No.21273212).