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State-to-state photodissociation dynamics of CO₂ around 108 nm: the O(¹S) atom channel

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State-to-state photodissociation of carbon dioxide (CO₂) via the 3p¹Π_u Rydberg state was investigated by the time-sliced velocity map ion imaging technique (TSVMI) using a tunable vacuum ultraviolet free electron laser (VUV FEL) source. Raw images of the O(¹S) products resulting from the O(¹S) + CO(X¹Σ⁺) channel were acquired at the photolysis wavelengths between 107.37 and 108.84 nm. From the vibrational resolved O(¹S) images, the product total kinetic energy releases and the vibrational state distributions of the CO(X¹Σ⁺) co-products were obtained, respectively. It is found that vibrationally excited CO co-products populate at as high as $v = 6$ or 7 while peaking at $v = 1$ and $v = 4$, and most of the individual vibrational peaks present a bimodal rotational structure. Furthermore, the angular distributions at all studied photolysis wavelengths have also been determined. The associated vibrational-state specific anisotropy parameters (β) exhibit a photolysis wavelength-dependent feature, in which the β -values observed at 108.01 nm and 108.27 nm are more positive than those at 107.37 nm and 107.52 nm, while the β -values have almost isotropic behaviour at 108.84 nm. These experimental results indicate that the initially prepared CO₂ molecules around 108 nm should decay to the 4¹A' state via non-adiabatic coupling, and dissociate in the 4¹A' state to produce O(¹S) + CO(X¹Σ⁺) products with different dissociation time scales.

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1. Introduction

CO₂ is one of the most significant greenhouse gases in the Earth's atmosphere. It is also found in the interstellar medium,¹ Venus² and Mars³ with extremely high abundance. Therefore, photodissociation of CO₂ is one of the most important and basic photochemistry processes in the upper layers of the CO₂-based atmospheres of solar planets, and detailed investigations of CO₂ photodissociation have attracted considerable attention over the past few decades.

Previous spectroscopic studies^{4,5} have shown that CO₂ has negligible photoabsorption at photon energies below 6.2 eV

(> 200 nm), and its absorption bands in the range of 6.2–11.0 eV (112.7–200 nm) are also very weak. Thus, lots of early experiments were performed mainly at a single photolysis wavelength of 157 nm due to the availability of commercial F₂ excimer lasers. These studies have shown that the main pathways of CO₂ photodissociation following 157 nm photoexcitation are the O(³P) and O(¹D) channels, and the branching ratio of the spin-forbidden O(³P) channel at 157 nm is about 6%.^{6,7} In 1992, Miller and co-workers⁸ measured the CO(X¹Σ⁺) product state distribution for the O(¹D) channel at 157 nm by using a VUV laser induced fluorescence technique. This experimental result showed that the CO co-products are highly rotationally excited, indicating that the dissociation occurs from a strongly bending anisotropic potential. Recently, Chen *et al.*⁹ reinvestigated the photodissociation process of CO₂ at 157 nm via the velocity map ion imaging technique. In their study, the CO(X¹Σ⁺) vibrational-state distributions and the state correlation between the O(³P_{0,1,2}) and CO(X¹Σ⁺, v) products were determined, respectively. In addition to 157 nm in this photoexcitation energy region, Yu *et al.*¹⁰ recently reported an experimental study of the O(³P) channel from CO₂ photodissociation at the photolysis wavelengths between 129.02 and 134.67 nm. It was found that the product angular distributions of the three spin-orbit channels present a notable photolysis wavelength dependent feature,

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which suggested that the different nonadiabatic interactions may play a key role in the $O(^3P)$ channel.

At shorter photolysis wavelengths (above 11.0 eV), CO_2 has significantly strong absorption bands that correspond to the transition of numerous Rydberg states converging to the ion ground state. Thus, the major photodissociation processes of CO_2 are expected to occur in this extreme VUV region. Recently, by using the velocity-map-imaging photoionization (VMI-PI) method, Ng's group performed a series of experiments to investigate state-to-state VUV dissociation dynamics of CO_2 above 11 eV.^{11–15} In 2011, they¹¹ first probed the $O(^1D)$ product from the CO_2 photodissociation in a one-color experiment at 92.21 nm. Later, photodissociation of CO_2 in the range of 90.60–91.60 nm was systematically studied *via* probing oxygen photoproducts at different levels.¹² From the ion images, they directly observed the $O(^1D) + CO(X^1\Sigma^+)/CO(a^3\Pi)$, and $O(^3P) + CO(a^3\Pi)/CO(a'^3\Sigma^+)/CO(d^3\Delta)/CO(e^3\Sigma^-)$ channels, respectively. But, the lowest dissociation channel $O(^3P) + CO(X^1\Sigma^+)$ was not found in this photoexcitation energy region. Based on the detection of VUV excited autoionizing Rydberg (VUV-EAR) states, Ng *et al.*¹³ also determined the branching ratios of the spin-forbidden $O(^3P) + CO(X^1\Sigma^+)$ and spin-allowed $O(^3P) + CO(a^3\Pi)$ channels at 102.08 nm. Then, they further investigated the $O(^1D) + CO(X^1\Sigma^+)$ channel at excitation wavelengths of 101.62–103.83 nm using two independently tunable VUV lasers.¹⁴ It was found that the $O(^1D)$ products may be produced by non-adiabatic transition from the $4^1A'$ state to the $3^1A'$ state *via* conical intersections followed by the rapid dissociation along the $3^1A'$ surface.

Besides the $O(^3P)$ and $O(^1D)$ channels, the pathway to produce $O(^1S)$ products will also be present above 11.0 eV. Lawrence¹⁶ measured the production efficiency of $O(^1S)$ between 81.2 and 121.6 nm, and determined that the $O(^1S)$ quantum yield was $\sim 30\%$ around 90 nm. Slinger and co-workers¹⁷ also measured the relative quantum yield of the $O(^1S)$ from CO_2 photolysis between 106.0 and 117.5 nm. It was found that the yield is near unity over a considerable portion of the spectral region, but there exists an abrupt dip around 108.9 nm. The state-to-state photodissociation dynamics of the $O(^1S)$ channel has also been investigated in succession by Ng's group in this extreme VUV region. In 2014, Ng *et al.*¹² measured the time-sliced velocity-mapped raw image of the $O(^1S)$ products at a single wavelength of 91.24 nm, in which two dissociation mechanisms with different dissociation time scales from the initially excited Rydberg state to the highly repulsive $4^1A'$ state were observed. Subsequently, they¹⁴ further investigated the $O(^1S)$ channel over the range of 101.62–103.83 nm. Combined with theoretical calculations, they suggested that the formation of the $O(^1S) + CO(X^1\Sigma^+)$ products occurs predominantly through the nearly exclusively $4^1A'$ state.

Though the dynamics of the $O(^1S)$ channel from CO_2 photodissociation has extensively been investigated following VUV excitation above 11 eV, rather little work has been performed around 108 nm which has been mainly assigned previously as the $X^1\Sigma_g^+ \rightarrow 3p^1\Pi_u$ transition. The present article is concerned with a detailed study of the photodissociation dynamics of the $O(^1S) + CO(X^1\Sigma^+)$ channel at the photolysis wavelengths between 107.37 and 108.84 nm. The well resolved images of the

$O(^1S)$ products were measured by using our newly constructed TSVMI-VUV FEL apparatus, in which the TSVMI technique has been combined with the tunable VUV radiation from the FEL facility. From the raw images, the vibrational state distributions of the $CO(X^1\Sigma^+)$ co-products and the product angular distributions were determined, respectively. These experimental results should be helpful in revealing the picture of CO_2 photodissociation in the whole extreme VUV region.

II. Experimental methods

The present study utilized a TSVMI-VUV FEL setup, which is based on the two-color VUV pump–probe technique, as schematically shown in Fig. 1. The VUV FEL facility has been described in detail elsewhere.^{18–20} Briefly, the VUV FEL operates in the high gain harmonic generation (HG) mode,²¹ in which the seed laser is injected to interact with the electron beam in the modulator. The seeding laser within the wavelength (λ_{seed}) range between 240 nm and 360 nm is generated from a pico-second Ti:sapphire laser. The electron beam is generated from a photocathode radio frequency (RF) gun, and accelerated to a beam energy of ~ 300 MeV by 7 S-band accelerator structures, with a bunch charge of 500 pC. The micro-bunched beam is sent through the radiator, which is tuned to the n th harmonic of the seed wavelength, and coherent FEL radiation with wavelength λ_{seed}/n is emitted. The VUV-FEL presently operates at 10 Hz, the pulse energy is 100–500 μJ per pulse and the output wavelength is continuously tunable across the range 50–150 nm. In this work, the VUV FEL laser was used as the photolysis laser, which was tuned to around 108 nm. A 1% mixture of CO_2 in He with a stagnation pressure of 800 Torr was expanded through a pulsed valve with a 0.5 mm diameter pulsed nozzle. The supersonic molecular beam was collimated by a 1 mm diameter aperture skimmer and reached the main chamber, where the CO_2/He beam was crossed at right angle by

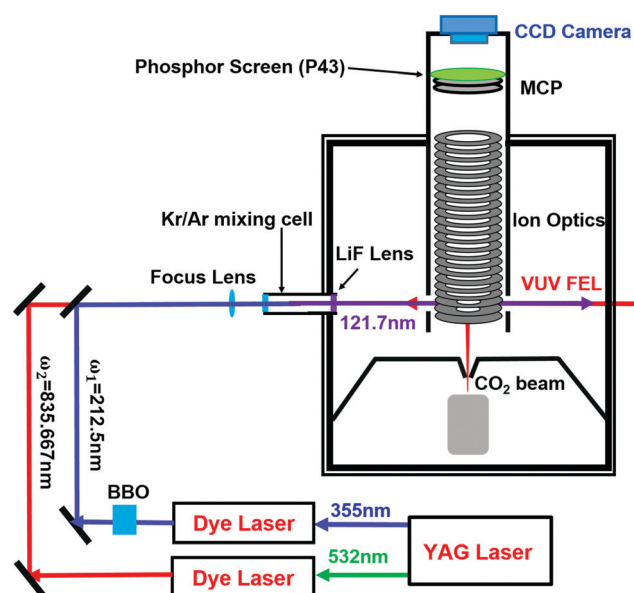


Fig. 1 Schematic diagram of the TSVMI-VUV FEL apparatus.

the VUV FEL laser. The resulting oxygen product $O(^1S)$ was then detected with about a 10–20 ns delay with respect to the VUV FEL laser, by using the TSVMI technique.^{22,23}

In this work, the photoionization of the $O(^1S)$ photoproduct was achieved through absorbing another VUV photon at 121.7 nm, *via* the autoionization transition of $O^*[2s^22p^3(^2P^o)3s(^1P_1^o)] \leftarrow O(^1S)$. The 121.7 nm photon was generated by difference four-wave mixing (DFWM) of two 212.55 nm photons and one 835.66 nm photon in a stainless steel cell filled with a 3 : 1 ratio Ar/Kr mixture. The mixing cell was sealed at both ends with a quartz window at the entrance and a LiF lens at the light exit. The laser light at 212.55 nm was produced by doubling the output of a 355 nm (Nd:YAG laser) pumped dye laser (Sirah, PESC-G-24) operating at ~ 425 nm. A 532 nm output of the same Nd:YAG laser was used to pump another dye laser (Sirah, PESC-G-18) which operated at ~ 835 nm. The resulting oxygen ions were then accelerated by the 23-plate ion optics¹⁹ and passed through a 740 mm long time-of-flight tube before hitting a position-sensitive dual Chevron-type microchannel plate (MCP) coupled to a phosphor screen (P43). A fast high-voltage switch was used to gate the central slice of the photofragments at a specific mass. The typical pulse width was about 20 ns. The resulting electron avalanche strikes a P43 phosphor screen, thereby creating an ion image, which was captured by a charge-coupled device (CCD) camera (UI-3260CP-M-GL Rev. 2, IDS) and transferred to a computer on an every shot basis for event counting²⁴ and data analysis. The final images were accumulated over 30 000 laser shots or more, depending on the signal-to-noise ratio. The timing of the pulsed valve, the photolysis and probe lasers, and the gate pulse applied to the MCP detector was controlled by using two multichannel digital delay generators (DG645, SRS). The speed of the product was calibrated using the O^+ signal from the photodissociation of O_2 at ~ 225 nm.

III. Results and discussions

Fig. 2 displays the VUV absorption spectrum of CO_2 between 107 and 109 nm.²⁵ The corresponding assigned $X^1\Sigma_g^+ \rightarrow 3p^1\Pi_u$

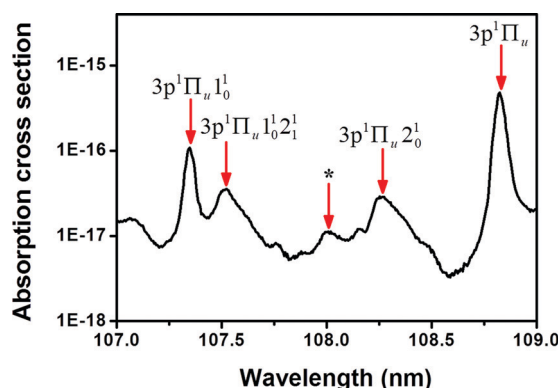


Fig. 2 VUV absorption spectrum of CO_2 between 107 and 109 nm (the data were obtained from www.uv-vis-spectral-atlas-mainz.org, adapted from ref. 25). The positions of the photolysis excitation wavelengths used in this work are indicated by downward pointing arrows.

transition²⁶ is known to be involved in bending vibrational coupling,²⁷ which is due to the Fermi resonance between the excitation of one quantum of symmetric stretching (ν_1) and two quanta of bending ($2\nu_2$) vibrational modes.²⁸ Thus, the photodissociation dynamics of CO_2 *via* the $3p^1\Pi_u$ state will be particularly complicated and interesting. As shown in Fig. 2, the VUV photolysis excitation wavelengths chosen in this work are marked by the downward pointing arrows, which correspond to different vibrational progressions of CO_2 in the $3p^1\Pi_u$ Rydberg state beside 108.01 nm. It should be noted that the initial Rydberg state has a linear configuration, and splits into one A' and/or one A'' components in bent C_s symmetry due to Renner–Teller crossings. Fig. 3 displays the raw images of the $O(^1S)$ products following CO_2 photodissociation by tuning the VUV FEL at 107.37 nm ($3p^1\Pi_u 1_0^1$), 107.52 nm ($3p^1\Pi_u 1_0^2 1_1^1$), 108.01 nm (unknown yet), 108.27 nm ($3p^1\Pi_u 2_0^1$) and 108.84 nm ($3p^1\Pi_u$), respectively. Each image was obtained by accumulating the O^+ signals over 30 000 laser shots with background subtraction. The red vertical arrow shown in Fig. 3 indicates the polarization direction of the VUV FEL laser. It is found that each $O(^1S)$ image displays a series of well-resolved rings with different intensities. Furthermore, the rings observed at 108.01 nm and 108.27 nm are more anisotropic, and the rings observed at 108.84 nm are more likely to be isotropic. This observation suggests that CO_2 photodissociation *via* the $3p^1\Pi_u$ state to form $O(^1S) + CO(X^1\Sigma^+)$ products takes place on a photolysis wavelength-dependent time scale.

The velocity distributions of the $O(^1S)$ products could be extracted by integrating the signals in the images over the angular range. From these velocity distributions, the total kinetic energy release (TKER) spectra in the center-of-mass frame are acquired according to the conservation of energy and momentum. Fig. 4 depicts the resulting TKER spectra from the photodissociation of CO_2 at all studied photolysis wavelengths. It is clear that all TKER spectra comprised of a group of well resolved peaks extending to the energy limit of the available energy.

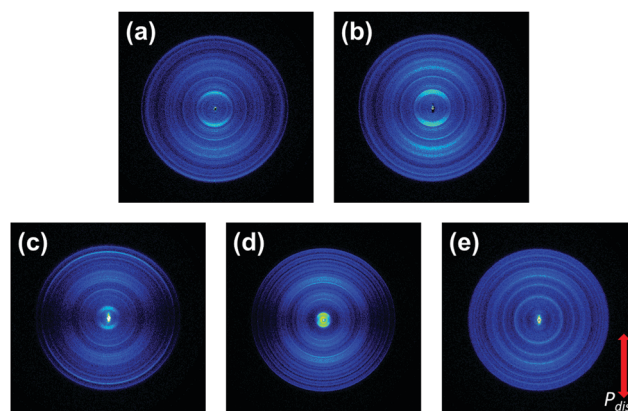


Fig. 3 Raw images of $O(^1S)$ photoproducts from photodissociation of CO_2 at (a) 107.37 nm, (b) 107.52 nm, (c) 108.01 nm, (d) 108.27 nm, and (e) 108.84 nm. The double arrow indicates the polarization direction of the dissociation laser. The ring features correspond to the rovibrational states of the coincident $CO(v)$ product.

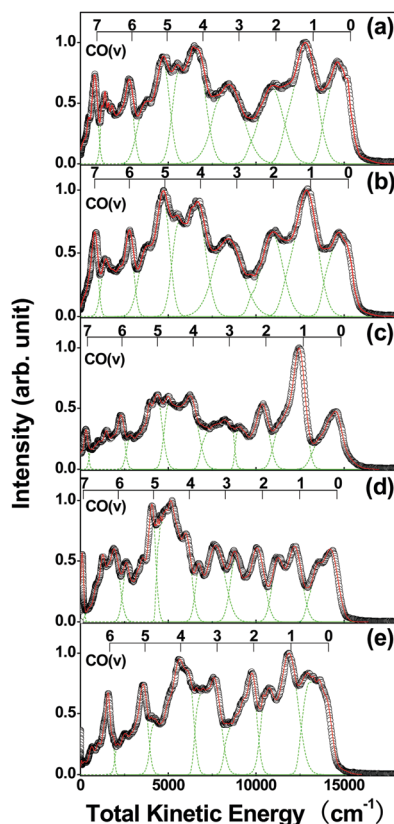


Fig. 4 Product total kinetic energy distributions (black empty circles) of the $O(^1S) + CO(X^1\Sigma^+)$ channel derived from the raw images in Fig. 3 at (a) 107.37 nm, (b) 107.52 nm, (c) 108.01 nm, (d) 108.27 nm, and (e) 108.84 nm. The red lines are the fitting results and the dashed green lines are the individual CO vibrational components.

Since the O atom product internally possesses only the electronic energy, the observed peaks in the TKER spectra correspond directly to the ro-vibrational states of the CO co-product according to the following equation:

$$E_{hv} - D_0 = E_T + E_{int}(O) + E_{int}(CO) \quad (1)$$

Here E_{hv} denotes the photon energy of photolysis laser, D_0 represents the dissociation threshold energy of the $O(^1S) + CO(X^1\Sigma^+)$ channel, which is determined to be about 9.64 eV in this work, E_T is the total kinetic energy of the photoproducts, $E_{int}(CO)$ is the internal energy of the CO product and $E_{int}(O)$ is the energy level difference between the $O(^1S)$ state and the ground state $O(^3P_2)$.

As shown in Fig. 4, we have assigned the peaks to the $CO(X^1\Sigma^+, v = 0-7)$ vibrational states. According to the assignment, the onsets of the TKER spectra are found to be in excellent agreement with the known dissociation threshold of the $O(^1S) + CO(X^1\Sigma^+)$ channel, confirming that the CO products are produced in correlation with the $O(^1S)$ atomic photoproducts. Fig. 4 shows that the CO products formed from CO_2 photodissociation *via* the $3p^1\Pi_u$ state are vibrationally excited and can populate up to the energy limit of the available energy. This phenomenon is quite different from those at the photolysis wavelengths of

101.62–103.83 nm,¹⁴ but similar to that at a single wavelength of 91.24 nm.¹² Furthermore, most of the vibrational peaks of CO products in the TKER spectra, especially the highly vibrationally excited ones exhibit a bimodal structure. Such a non-statistical product state distribution implies that the CO products are rotationally hot. As marked in Fig. 2, the photolysis wavelengths of 108.27 nm and 107.52 nm correspond to CO_2 photoexcitation to the $3p^1\Pi_u 2_0^1$ and $3p^1\Pi_u 1_0^1 2_1^1$ state with one quantum of bending excitation, respectively. Thus, it is reasonable that the bending vibration excitation of the excited CO_2 molecule at these two photolysis wavelengths may cause the final vibrational distribution of CO to have a hot rotational excitation. However, at other photolysis wavelengths, especially at 108.84 nm which corresponds to excite CO_2 to the $3p^1\Pi_u$ state with no bending excitation, the remaining bimodal rotational distribution implies that photodissociation of CO_2 in this VUV region should take place in a bent dissociative state.

In order to abstract more dynamics information, a qualitative simulation of the TKER spectra was carried out. The simulation used a multi-peak fitting method in which a set of Gaussian profiles (each peak corresponds to a rotational state of the CO co-products) were employed to fit one vibrational peak in the TKER spectra. As shown in Fig. 4, the red solid curve in each graph superimposed on the experimental TKER spectra represents the global result of a multi-peak fitting and the dashed green curves represent the individual CO vibrational components. From the fitting, the relative vibrational state populations of the CO co-products at all studied photolysis wavelengths are obtained in Fig. 5. It is found that the CO vibrational state distributions share similar profiles with a bimodal structure peaking at $v = 1$ and 4 beside 108.27 nm. This result is different from those observed in the study of CO_2 photodissociation at 101.62–103.83 nm by Ng *et al.*,¹⁴ in which most of the $CO(X^1\Sigma^+)$ co-products favor to populate low vibrational states ($v = 0-2$). The difference shows a clear influence of the initial electronic excited state on the final dissociation dynamics characteristics.

The angular distributions $I(\theta)$ corresponding to different ro-vibrational states of CO co-products could be extracted from the

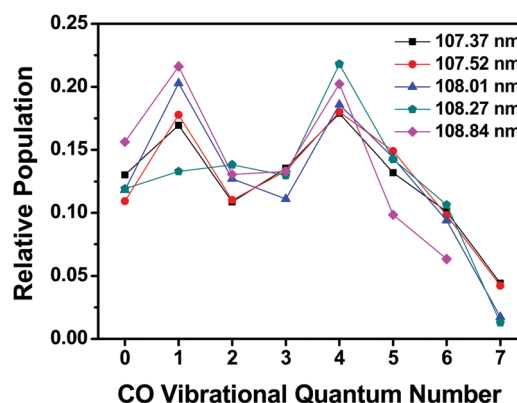


Fig. 5 Relative vibrational population of the CO co-products at different photolysis wavelengths.

images shown in Fig. 3 by integrating the intensity over a certain radial range around the most probable velocity for each vibrational peak. The $I(\theta)$ was then fitted by using the relation displayed in the equation:

$$I(\theta) = (1/4\pi)[1 + \beta P_2(\cos \theta)] \quad (2)$$

where θ is the crossing angle between the direction of the recoil velocity of the dissociative products and the polarization axis of the linearly polarized photolysis laser, β is the anisotropy parameter and $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$ is the second order Legendre polynomial. Accordingly, the β -values for each vibrational state are determined, respectively. As shown in Fig. 6, the measured β -values are plotted as a function of CO vibrational quantum number at all studied photolysis wavelengths. It is clear that the β -values for the $O(^1S) + CO(X^1\Sigma^+)$ products are all positive at five wavelengths, suggesting that the dissociation lifetimes are shorter than the rotational period of the excited CO_2 complex. However, the product angular distributions exhibit a strong photolysis wavelength dependence. The β -values observed at 108.01 nm and 108.27 nm are found to decrease roughly monotonically from 1.60 to 0.75. This trend is similar to the previous study of CO_2 photodissociation *via* $4s$ and $4s(1^1_0)$ Rydberg states by Ng *et al.*,¹⁴ in which the formation of $O(^1S) + CO(X^1\Sigma^+)$ photoproducts was suggested to occur in nearly exclusively $4^1A'$ states. At 107.37 nm and 107.52 nm, the β -values are less positive, and present a slight fluctuation near the line $\beta = 0.75$. While at 108.84 nm, the β -values further decrease to near 0.5, and the angular distribution is close to being isotropic. This observation indicates that the photodissociation time scale of the $O(^1S) + CO(X^1\Sigma^+)$ channel around 108 nm varies with the VUV photoexcitation energies.

Theoretical calculations of the potential energy surfaces (PESs) are important for understanding the CO_2 photodissociation mechanisms. So far, Grebenshchikov²⁹ has constructed the CO_2 PESs of the first ten electronic states, $1-5^1A'$ and $1-5^1A''$, corresponding to the components of the linear Π , Σ^- , Σ^+ and Δ states in bent C_s symmetry due to Renner–Teller crossings. As suggested in previous works, the low lying bent states, $1-3^1A'$ and $1-3^1A''$ correlate adiabatically to spin-allowed $O(^1D) + CO(X^1\Sigma^+)$ or $O(^3P) + CO(a^3\Pi)$ channels, respectively. As for the $O(^1S) + CO(X^1\Sigma^+)$ channel

studied in this work, previous studies suggested that only one $^1A'$ state converges towards the asymptote. On the other hand, in the CO_2 photodissociation study of the $O(^1S)$ channel around 101.62–103.83 nm by Ng *et al.*,¹⁴ it was suggested that the formation of the $O(^1S)$ channel occurs predominantly on the essentially repulsive $4^1A'$ PES. So it is deduced that the $4^1A'$ state is responsible for the $O(^1S) + CO(X^1\Sigma^+)$ channel in the extreme VUV region. However, the VUV photolysis wavelengths used in this work are around 108 nm, and the corresponding absorption bands are assigned to the $3p^1\Pi_u$ state. Because the photoexcitation energies used here are slightly low compared to those used by Ng *et al.*, the region on the $4^1A'$ PES can't be directly accessed by the Franck–Condon (FC) excitation from the ground state of CO_2 in this work. Therefore, it is expected that the possible pathway to form the $O(^1S) + CO(X^1\Sigma^+)$ products is the initially excited CO_2 molecules' non-adiabatic transit to the $4^1A'$ PES *via* the seam of conical intersection far outside the near linear Franck–Condon region, followed by the dissociation in the $4^1A'$ state eventually. However, due to the complex conical intersection existing among the high excited states, the VUV excited CO_2 may undergo more than one transition before decaying to the $4^1A'$ state. Such a complicated process is possible, the main reason being the bimodal vibrational structure at all studied photolysis wavelengths. The much hotter ro-vibrational excitation of the CO co-products observed in this energy region might be caused by the combined effect of the initial vibrational excitation mode existing in the excited CO_2 molecule and the bent OCO geometry of the final dissociative state $4^1A'$. Furthermore, the β -value distributions exhibit a wavelength dependence, in which the much more positive β -values are observed at photolysis wavelengths with one vibrational quantum in the symmetric stretching mode than those at photolysis wavelengths with only one vibrational quantum in the bending mode. One possible reason for this is that the different initial vibrational excitation modes may affect the detail route and the time scale of non-adiabatic coupling from the initially excited state to the $4^1A'$ state. In addition, the irregular shape of the dissociative state $4^1A'$ might also cause a little slow dissociation at relatively low photoexcitation energy. The observed β -values at 108.84 nm are consistent with the picture that the excited CO_2 molecules undergo the ripples of minor potential energy barriers in the $4^1A'$ state. However, due to the lack of the high accurate PESs of the Rydberg states, the detailed information on the PES couplings is not clear. To unambiguously illustrate the dissociation characteristics for the $O(^1S) + CO(X^1\Sigma^+)$ channel observed in this work, such as a bimodal vibrational structure, further theoretical calculations are required. Nevertheless, this experimental study is beneficial in understanding the dissociation mechanism for the $O(^1S) + CO(X^1\Sigma^+)$ channel following the $3p^1\Pi_u$ state excitation.

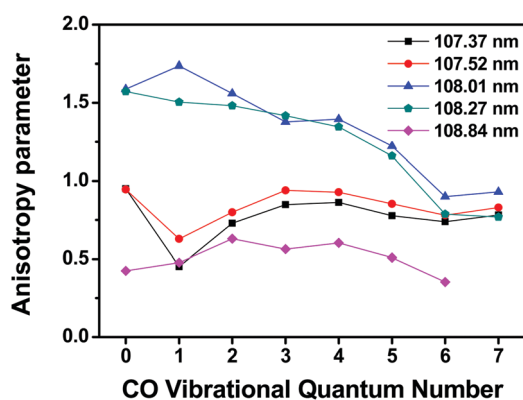


Fig. 6 Anisotropy parameters for each CO vibrational state correlated to the $O(^1S)$ state at different photolysis wavelengths.

IV. Conclusions

In this work, state-to-state photodissociation dynamics of the $O(^1S) + CO(X^1\Sigma^+)$ channel has been investigated *via* a TSVMI technique combined with a VUV FEL source. Vibrational state

resolved images of the $O(^1S)$ products have been acquired at a series of photolysis wavelengths from 107.37 to 108.84 nm. The $CO(X^1\Sigma^+)$ co-product vibrational state distributions and product angular distributions were determined by simulating the product total kinetic energy releases which were derived from the $O(^1S)$ images. It is found that the relative population of the vibrationally excited CO co-products and most of the individual vibrational peaks both exhibit a bimodal structure. Furthermore, the vibrational state specific β -values present a strong photolysis wavelength dependence, indicating that the photodissociation time scale of the $O(^1S) + CO(X^1\Sigma^+)$ channel around 108 nm varies with the VUV photoexcitation energies. The overall observations indicate that non-adiabatic pathways with different dissociation time scales could play an important role in the formation of $O(^1S) + CO(X^1\Sigma^+)$ products in this extreme VUV region.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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