

Ultrafast pump-probe measurement of CO₂ by few-cycle NIR pulses and the high-order harmonics

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When polyatomic molecules are irradiated with extreme ultraviolet (XUV) light, their cations are produced by photoionization not only in the ground electronic states but also in the electronically excited states, and the evolution of electronic, nuclear, and rotational wave packets starts. Thanks to recent advances in the ultrashort XUV light pulse generation technology, it has become possible to probe in time domain the dynamics of molecules induced by an ultrashort XUV light pulse. In the present study, we have performed pump-probe measurements of CO₂ by ionizing CO₂ by XUV light pulses generated as the high-order harmonics of few-cycle near-IR (NIR) laser pulses whose pulse duration is ~6 fs and probing subsequent ultrafast nuclear wave packet dynamics of CO₂⁺ by the few-cycle NIR laser pulses. We have revealed the ultrafast dissociation dynamics of CO₂⁺ occurring within 20 fs associated with the inner-valence photoionization and the vibrational dynamics proceeding with the period of ~30 fs associated with the outer-valence photoionization.

The yields of CO⁺ and O⁺ fragment ions whose kinetic energy release (KER) E_{KER} is in the range of $4.5 \leq E_{\text{KER}} \leq 6.5$ eV recorded as a function of the pump-probe delay time, Δt , exhibit an immediate increase at $\Delta t \sim 0$ fs followed by the decay fitted by a double exponential form with the fast time constant of 14 fs and the time constant much slower than 100 fs. We find that electronically excited singly charged ions (CO₂⁺)^{*} are produced by the inner-valence ionization by the XUV pump pulses¹ and are further ionized to CO₂²⁺ by the NIR probe pulses, resulting in the increase in the yields of the fragment ions with high E_{KER} . The subsequent decay reflects the ultrafast dissociation processes of (CO₂⁺)^{*}. On the other hand, the yield of C⁺ fragment ions in the range of $0.5 \leq E_{\text{KER}} \leq 2.5$ eV, originating from the dissociation of (CO₂⁺)^{*}, exhibits an increase with the time constant of 17 fs.

The yield of CO⁺ in the range of $0 \leq E_{\text{KER}} \leq 0.3$ eV and that of O⁺ in the range of $0.4 \leq E_{\text{KER}} \leq 0.6$ eV oscillate with the period of 27 fs. This oscillation appearing in the yields of CO⁺ and O⁺ with the low KER, both which are created via the predissociation of CO₂⁺ in the $\tilde{C}^2\Sigma_g^+$ state,² can be assigned to that of the symmetric stretching vibration of CO₂⁺ in the electronic ground $\tilde{X}^2\Pi_g$ state. The vibrational wave packet is probed by the four-photon excitation to the vibrationally excited states of the $\tilde{C}^2\Sigma_g^+$ state, decomposing into CO⁺ + O and O⁺ + CO. On the other hand, the yield of O⁺ in the range of $0 \leq E_{\text{KER}} \leq 0.3$ eV exhibits an oscillation with the period of 30 fs. This oscillation can be assigned to the symmetric stretching vibration of CO₂⁺ in the first electronically excited $\tilde{A}^2\Pi_u$ state, whose wave packet evolution is probed by the one-photon excitation to the vibrational ground state of the $\tilde{C}^2\Sigma_g^+$ state, decomposing only into O⁺ + CO.

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