Simulation of time-dependent population transfer among the electronic states of linear CO_2^+ in ultrashort intense laser fields

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Air lasing is an interesting phenomenon where coherent, unidirectional light in the ultraviolet and visible wavelength range is emitted from population-inverted nitrogen molecular ions created by intense femtosecond laser pulses focused in air.[1] This type of lasing can also be induced using other molecular species. It was reported that, when CO_2 is irradiated with intense laser pulses, the lasing of the $\tilde{A}^2\Pi_u \rightarrow \tilde{X}^2\Pi_g^+$ emission of CO_2^+ occurred at 351 nm. However, the mechanism of the population inversion in CO_2^+ required for the lasing has not been clarified. The energy diagram of CO_2^+ shown in Fig. 1 suggests that CO_2^+ is expected to respond differently to intense laser fields having different wavelengths.

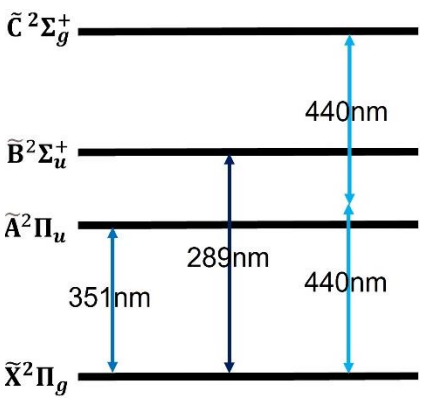

Figure 1. Energy diagram of CO_2^+

In the present study, we investigate the population transfer dynamics among these electronic states of linear CO_2^+ occurring within an ultrashort intense laser pulse to clarify the mechanism of the population inversion required for the lasing action. We adopt a laser field intensity in the non-perturbative regime of laser-molecule interaction, $I = 3.5\times10^{14}$ W/cm^2, a pulse width of $\Delta t = 50$ fs, and vary the laser field wavelength λ in the range of $300 \leq \lambda/\mathrm{nm} \leq 650$. The O-C-O molecular axis is assumed to be tilted with respect to the laser polarization direction by an angle of 25° so that both parallel and perpendicular dipole transitions occur. We calculate the time-dependent electronic wave function $\Phi(t)$ of CO_2^+ by solving the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\Phi(t) = (\boldsymbol{H}_0 + \mathbf{E}(t)\cdot\boldsymbol{D})\Phi(t),$$

where $\boldsymbol{H}_0$ is a diagonal matrix with the diagonal matrix elements representing the electronic level energies, $\boldsymbol{D}$ is a matrix composed of the transition dipole moments, and $\mathbf{E}(t)$ is an electric field vector of the laser pulse. We calculate the numerical values of the matrix elements of $\boldsymbol{H}_0$ and $\boldsymbol{D}$ by Molpro[3] using the aug-cc-pVTZ basis set and the CASSCF(9,7) method.

We have found that, when Δt = 50 fs, I = 3.5×10^{14} W/cm^2, and θ = 25°, the population inversion between the $\tilde{X}^2\Pi_g$ state and the $\tilde{A}^2\Pi_u$ state is achieved at λ = 310 nm, corresponding to the $\tilde{A}^2\Pi_u \leftarrow \tilde{X}^2\Pi_g$ transition, and the population inversion between the $\tilde{X}^2\Pi_g$ state and the $\tilde{C}^2\Sigma_g^+$ state is achieved at λ = 450 nm, corresponding to a two-photon resonance $\tilde{C}^2\Sigma_g^+ \leftarrow \tilde{X}^2\Pi_g$ transition.

References

1) H. Xu, E. Lötstedt, A. Iwasaki and K. Yamanouchi, *Nat. Commun.* **6**, 8347 (2015). 2) W. Chu et al., *EPL* **97**, 64004 (2012). 3) H.-J. Werner et al., *J. Chem. Phys.* **152**, 144107 (2020).