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Photodissociation of the carbon monoxide dication in the $^3\Sigma^-$ manifold: Quantum control simulation towards the C$^2+$ + O channel

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The photodissociation and laser assisted dissociation of the carbon monoxide dication $X^3\Pi$ CO$^2+$ into the $^3\Sigma^-$ states are investigated. Ab initio electronic structure calculations of the adiabatic potential energy curves, radial nonadiabatic couplings, and dipole moments for the $X^3\Pi$ state are performed for 13 excited $^3\Sigma^-$ states of CO$^2+$. The photodissociation cross section, calculated by time-dependent methods, shows that the C$^2+$ + O$^+$ channels dominate the process in the studied energy range. The carbon monoxide dication CO$^2+$ is an interesting candidate for control because it can be produced in a single, long lived, $v = 0$ vibrational state due to the instability of all the other excited vibrational states of the ground $^3\Pi$ electronic state. In a spectral range of about 25 eV, perpendicular transition dipoles couple this $^3\Pi$ state to a manifold of $^3\Sigma^-$ excited states leading to numerous C$^+$ + O$^+$ channels and a single C$^2+$ + O channel. This unique channel is used as target for control calculations using local control theory. We illustrate the efficiency of this method in order to find a tailored electric field driving the photodissociation in a manifold of strongly interacting electronic states. The selected local pulses are then concatenated in a sequence inspired by the “laser distillation” strategy. Finally, the local pulse is compared with optimal control theory.

I. INTRODUCTION

The dication CO$^2+$ has been widely studied both theoretically and experimentally since its first detection in 1930 using techniques such as electron impact, Auger spectroscopy, electron loss and double electron capture collisions, threshold photoelectrons coincidence spectroscopy, translational energy spectroscopy, photoion-fluorescence photon coincidence, and single-photon or multiphoton ionization of CO with ultrashort pulses. In the last 20 years, many works have focused on the study of CO$^3+$ in ion storage rings, allowing for more accurate measurements of its spontaneous dissociation and of its dissociative recombination. Apart from its intrinsic interest as a metastable species, CO$^2+$ is believed to play an important role in extreme environments, as encountered in astrophysics. As other diatomic dications, the ground electronic state $X^3\Pi$ presents a shallow potential energy curve (PEC) situated above the dissociation limit corresponding to the Coulomb explosion dissociation limit. All the vibrational states are, therefore, metastable, and in the case of CO$^2+$, all the vibrational states have a lifetime shorter than a microsecond, except for the $v = 0$ state which has a lifetime estimated to be between a few milliseconds and several seconds.

The recent experimental closed-loop control of the vibrational population performed by Wells et al. is of particular interest. A genetic algorithm was used to optimize a laser pulse which predominantly ionizes CO into either non-dissociative CO$^2+$ in a metastable state or dissociative CO$^2+$, leading to the detection of its fragments C$^+$ + O$. This amounts to controlling the double ionization of CO to form CO$^2+$ in either the $v = 0, 1$ levels of the $X^3\Pi$ state and the $v = 0$ level of the lowest $^1\Sigma^-$ state, or in higher excited vibrational levels and dissociative electronic states. Another experimental control of the emission direction of C$^2+$ from charge asymmetrical dissociation and ionization of CO$^2+$ has been carried out recently with intense laser fields. In the present work, we theoretically explore another form of control: starting from CO$^2+$ in the metastable $v = 0$ level of the $X^3\Pi$ electronic state, we optimize laser pulses that selectively photodissociate the ion through its first $^3\Sigma^-$ channel correlating to the C$^2+$ + O fragments. This scheme allows us to take advantage of the fact that vibrationally pure CO$^2+$ can be obtained experimentally without a vibrational cooling step, simplifying the control scheme for future implementations.

The photodissociation of the dication prepared by a Franck-Condon transition predominantly occurs through the $^3\Pi \rightarrow ^3\Sigma^-$ perpendicular transition, making the $^3\Sigma^-$ states a better target for laser control. In an energy range of about 25 eV, the manifold of $^3\Sigma^-$ excited states is formed of numerous.
C\(^+\) + O\(^+\) dissociative channels and only a single C\(^2+\) + O channel. This particular configuration corresponds to a specific diabatic state crossing all the Coulomb channels, leading to strong nonadiabatic interactions. This is, therefore, a challenging target for quantum control. Unfortunately, very little information is available on the 3Σ\(^-\) highly excited electronic states of CO\(^2+\), so that our study required extensive \textit{ab initio} calculations of the electronic structure of the ion up to the C\(^2+\) + O channel.

The possibility of tailoring electric fields of laser pulses by shaping the spectral amplitudes and the phases has opened the very wide and appealing area of quantum control.\(^{24-30}\) Many applications extend from atomic\(^31\) to complex molecular systems\(^32,33\) and address various topics from photochemistry,\(^34\) to information processing.\(^{35-37}\) The control of the basic two-state Landau-Zener model\(^38\) has been addressed recently by optimal control.\(^39\) We focus here on a control involving dissipative continua and many strong nonadiabatic interactions. It remains an open question to what extent the control can be achieved in a continuum.\(^40\) The benchmark prototype of nonadiabatic photodissociation control has often been the NaI molecule, for which several strategies have been studied theoretically\(^41-47\) and experimentally.\(^48-51\) Only very few excited states are however involved in the dissociation of NaI, whereas many competing dissociation channels exist in the present case of CO\(^2+\).

Several control algorithms have proven their efficiency, particularly the optimal control theory (OCT)\(^52-54\) and the local control theory (LCT).\(^55-56\) The first strategy is global in time since it optimizes the field on a temporal grid with a predetermined pulse duration. On the contrary, LCT does not impose the pulse duration but exploits the instantaneous dynamics in order to construct a field which increases or decreases the average value of an observable. This observable may be chosen as the energy of the field-free Hamiltonian or the projector on a defined state, for instance, a particular vibrational state of a chromophore in a complex system.\(^61\) The laser control in the continuum presents additional challenges. Contrarily to control in a discrete subspace, the target is usually not a well defined wave function but addresses the modification of a fragmentation yield, in other words the total population in a dissociation channel. LCT seems particularly appealing to build a field initializing the photodissociation control without fixing a pulse duration. This pulse is expected to be short since the algorithm works as long as there is some dipole coupling between the initial vibrational state and the wave packets in the excited electronic states, which are repulsive in this case so that the wave packet leaves the Franck-Condon region very fast. This LCT pulse could subsequently be concatenated in the spirit of the “laser distillation” strategy.\(^25,62\) This concept of repeated pump-dump sequences or only pump pulses has been proposed for the purification of entanglers and applied in different contexts.\(^63\) We analyze here this scenario for this photodissociation process. Finally, one LCT pulse can be used as a guess field for iterations with OCT.

Quantum control also needs to address the crucial problem of the feasibility of the optimized pulses obtained by numerical simulations. Several experimental constraints\(^64\) can be accounted for such as spectral constraints,\(^65-69\) total laser fluence,\(^68\) and time-integrated zero area of the control field.\(^69\)

The paper is organized as follows. In Sec. II, we present the results of our \textit{ab initio} calculations on CO\(^2+\): adiabatic potential energy curves, nonadiabatic radial couplings, transition dipoles, and diabatic states derived from the adiabatic data. Sec. III contains the results of our field-free calculations of the photodissociation cross section. A summary of the LCT algorithm and the results are given in Sec. IV while our OCT calculations are discussed in Sec. V.

### II. MOLECULAR DATA

As stated in the Introduction, our aim is to investigate the photodissociation of CO\(^2+\) into C\(^+\) + O\(^+\) and C\(^2+\) + O fragments via perpendicular transitions. In order to do so, we computed the PECs, nonadiabatic couplings, and permanent and transition dipole moments for the ground \(^1\Sigma^+\) state and for the 13 lowest \(^3\Sigma^-\) states of CO\(^2+\), most of which had never been described theoretically before. The dissociative fragments corresponding to these electronic states are given in Table I. It can be seen that in the asymptotic region, the \(^3\Sigma^-\) channel that dissociates into C\(^2+\) + O is the ninth molecular state of that symmetry. In order to improve the description of this state, which will be the target of the laser control, we also included the four \(^3\Sigma^-\) states that correspond to the two closest asymptotic atomic states. From a practical point of view, it should be noted that studying the photodissociation into the C\(^2+\) + O fragment through the \(^1\Pi\) molecular states would require much more computational effort, since this channel corresponds to the 14th excited state of the \(^1\Pi\) manifold.

All the computations have been carried out at the complete active space self-consistent field (CASSCF)\(^70,71\) and CI level\(^72,73\) as implemented in the MOLPRO quantum chemistry package.\(^74\)

The ground \(^1\Pi\) state of CO\(^2+\) has been described in several previous studies.\(^17,20,75-80\) These studies provide equilibrium distance values between 2.23 a.u. and 2.46 a.u., which serves to illustrate the difficulty of accurate electronic structure calculations on dications. The PEC of the \(^1\Sigma^+\) state was computed with the AV5Z basis set at the multiconfiguration reference interaction level including the Davidson correction, providing a higher accuracy than for the \(^3\Sigma^-\) states.

#### Table I. CO\(^2+\) electronic states used in this work, and corresponding atomic fragments. The \(^2\Sigma^-\) states are numbered in ascending order of energy of their fragments (NIST values).

<table>
<thead>
<tr>
<th>Designation</th>
<th>Symmetry</th>
<th>Corresponding fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>(^1\Pi)</td>
<td>C(^2)(2s2p^2D)+O(^2)p^1(S)</td>
</tr>
<tr>
<td>1</td>
<td>(^3\Sigma^-)</td>
<td>C(^2)(2s2p^2D)+O(^2)p^1(S)</td>
</tr>
<tr>
<td>2,3</td>
<td>(^3\Sigma^-)</td>
<td>C(^2)(2s2p^2D)+O(^2)p^1(S)</td>
</tr>
<tr>
<td>4</td>
<td>(^3\Sigma^-)</td>
<td>C(^2)(2s2p^2D)+O(^2)p^1(S)</td>
</tr>
<tr>
<td>5</td>
<td>(^3\Sigma^-)</td>
<td>C(^2)(2s2p^2D)+O(^2)p^1(S)</td>
</tr>
<tr>
<td>6</td>
<td>(^3\Sigma^-)</td>
<td>C(^2)(2s2p^2D)+O(^2)p^1(S)</td>
</tr>
<tr>
<td>7,8</td>
<td>(^3\Sigma^-)</td>
<td>C(^2)(2s2p^2D)+O(^2)p^1(S)</td>
</tr>
<tr>
<td>9</td>
<td>(^3\Sigma^-)</td>
<td>C(^2)(2s2p^2D)+O(^2)p^1(S)</td>
</tr>
<tr>
<td>10</td>
<td>(^3\Sigma^-)</td>
<td>C(^2)(2s2p^2D)+O(^2)p^1(S)</td>
</tr>
<tr>
<td>11,12,13</td>
<td>(^3\Sigma^-)</td>
<td>C(^2)(2s2p^2D)+O(^2)p^1(S)</td>
</tr>
</tbody>
</table>
(see below). We found that the basis set had a noticeable effect on the PEC of the ground state, and, in particular, on the shape of its potential energy barrier. This affects the vibrational wave functions, with important consequences as the photodissociation cross sections depend directly on the vibrational wave function of the ground state (see Section III). We obtained an equilibrium distance of 2.357 a.u., in agreement with the values of Ref. 80. The rovibrational energies and wave functions were obtained by solving the radial Schrödinger equation using a B-spline method. The energy of the $v = 0$ level was found to be 712.9 cm$^{-1}$ (0.088 eV) above the minimum of the well, which can be compared to the value of 732.7 cm$^{-1}$ (0.090 eV) reported from the most accurate calculations including the spin-orbit interaction and to the experimental values of 677.1 cm$^{-1}$ (0.084 eV) or 806.7 cm$^{-1}$ (0.100 eV) obtained by Hochlaf et al. and Dawber et al., respectively. The energy of the $v = 1$ level was found to be 2103 cm$^{-1}$ (0.261 eV), while the values reported in Ref. 20 are 2101 cm$^{-1}$ (0.260 eV) and 2139 cm$^{-1}$ (0.265 eV). The value obtained for the rotational constant, $B_r = 1.57$ cm$^{-1}$ (1.947 $10^{-4}$ eV), is in good agreement with previously reported values.

The literature contains very little data on the $^3\Sigma^-$ states of CO$^2+$. Wetmore et al. included the five lowest $^3\Sigma^-$ states; however, the relatively low accuracy of these calculations makes comparisons uneasy. Moreover, their result for the lowest $^3\Sigma^-$ state is in disagreement with that of subsequent studies, as they predict the state to be quasibound instead of purely dissociative. Our calculations of the excited electronic states of $^3\Sigma^-$ symmetry were rendered difficult by severe convergence issues that required the use of a very small spatial step $\Delta R$ between two successive computations (as small as 0.001 a.u. in some regions) to ensure convergence. Starting from computations at values of the internuclear distance $R$ for which the algorithm converged well, several series of computations were performed towards lower and higher values of $R$ in order to obtain a complete picture of the potential energy curves from $R = 1.5$ to 100 a.u. Due to the large number of states included in our calculations and the need for a very small spatial step between two calculations in some regions, our main series of calculation was performed with the AVTZ basis set to keep the computational time within reasonable limits. Additional calculations were however performed with the AVQZ, AV5Z, and AV6Z basis sets and compared to the AVTZ results. Although, as can be expected, the absolute energies of the states vary from one basis to another (up to 0.272 eV), the variation of the energy difference between the various states is small in comparison (0.082 eV at most). In the end, we had to choose between using a large basis and using a fine spatial grid to ensure convergence and a good description of the nonadiabatic radial couplings. Given the large number of avoided crossings among the electronic states of CO$^2+$ (see Fig. 1), the important role played by the couplings in the photodissociation dynamics, and the relatively small impact of the basis set on the relative energies, we chose to perform calculations in the AVTZ basis set and to use a very fine spatial grid. All calculations were performed with active space ($6a_1,2b_1,2b_2$) as it was found to have good convergence properties.

Fig. 1(a) shows the adiabatic potential energy curves of the $X^3\Pi$ state and of the 13 first $^3\Sigma^-$ states of CO$^2+$ as computed in this work. It can be seen that PECs of the $^3\Sigma^-$ states of CO$^2+$ exhibit a large number of avoided crossings. The nonadiabatic radial couplings $F_i = \langle \zeta_i | \partial_R | \zeta_j \rangle$, where $\zeta_i$ are the adiabatic electronic wave functions, were directly computed in MOLPRO using the 3-point finite difference method with the origin of the electronic coordinates at the center of mass. The most important nonadiabatic radial couplings in the short-range region are shown in Fig. 2. The numbering of the states

![Fig. 1](image1.png)

**FIG. 1.** (a) Adiabatic and (b) diabatic PECs of the $X^3\Pi$ (in blue) and of the 13 lowest $^3\Sigma^-$ states (in black) of CO$^2+$. The diabatic state dissociating into CO$^+$ + O is shown in red. (c) and (d) zoom on the short internuclear distances showing the excited states up to 25 eV. The zero of energy is set at the minimum of the well of the $X^3\Pi$ state.

![Fig. 2](image2.png)

**FIG. 2.** Dominant nonadiabatic radial couplings $F_{ij} = \langle \zeta_i | \partial_R | \zeta_j \rangle$ between the $^3\Sigma^-$ states of CO$^2+$. The state numbers are defined in Table I.
throughout this article is defined by the diabatic states of increasing asymptotic energy, as given in Table I. The series of intense and very narrow couplings between state 9 and states 6, 7, and 8 near \( R = 7 \) a.u. look like delta peaks and they are not represented for clarity. The shape of these couplings lets us anticipate a completely diabatic behavior in that region.

The narrowness of the nonadiabatic couplings pose numerical difficulties, and to study dynamical processes it is often more advantageous to work in the diabatic representation. The transformation matrix \( D(R) \) is defined by the equation

\[
\partial_R D(R) + F(R) \cdot D(R) = 0, \tag{1}
\]

which was solved by continuity with the initial condition \( D(\infty) = I \), in order to ensure that the adiabatic and diabatic representations are identical at large internuclear distance. The diabatic potential energy curves are shown in Fig. 1(b).

Fig. 3 displays the transition dipoles \( d_{x,i} \) between the \( \chi \Sigma^+ \) electronic state and the 13 \( \Sigma^- \) states calculated with the origin of the coordinates at the center of mass. At large internuclear distances, the only non-vanishing transition dipoles are the \( d_{X,6} \) and \( d_{X,10} \) corresponding to \( ^2P \rightarrow ^2D \) and \( ^2P \rightarrow ^2S \) transitions in \( C^+ \), in agreement with atomic electric dipole selection rules.

### III. PHOTODISSOCIATION CROSS SECTIONS

The partial cross sections towards each decay channel were extracted from time-dependent wave packet propagations by using the method introduced by Balint-Kurti et al.,\(^8\) which has been described in detail and compared to other approaches in Refs. 83 and 84. The promoted wave packets \( \Phi_{<j}(R,t = 0) \) on the excited electronic states \( j \) are obtained by multiplying the nuclear wave function of the ground state \( \psi_{<j}(R) \) by the appropriate adiabatic transition dipole moments \( d_{X,<j}(R) \), \( \Phi_{<j}(R,t = 0) = d_{X,<j}(R) \psi_{<j}(R) \). The wave packets are then propagated in time in the diabatic representation, using the split-operator method.\(^83,85,86\) The partial cross sections are given by the Fourier transform of the component of the wave packets reaching an internuclear distance \( R_\infty \) located in the asymptotic region where both adiabatic and diabatic representations coincide,

\[
\sigma_{<j}(E) = \frac{4\pi^2\alpha a_0^2 k_j}{\mu} E|B_{<j}(E)|^2, \tag{2}
\]

\[
B_{<j}(E) = \frac{1}{\sqrt{2\pi}} \int \Phi_{<j}(R_\infty,t) e^{i(E_{<j}+E)t/\hbar} dt, \tag{3}
\]

where \( \mu \) is the reduced mass of the system, \( \alpha \) is the fine structure constant, \( a_0 \) is the Bohr radius, \( E = h\nu \) is the photon energy, and \( k_j = \sqrt{2\mu(E_{<j} + E - E_\infty)} \) is the wave number in the electronic state \( j \) with an asymptotic energy \( E_\infty \).

The propagations were performed on a spatial grid of \( 2^{12} \) points spanning from an internuclear distance \( R_{\text{min}} = 1.5 \) a.u. up to \( R_{\text{max}} = 70 \) a.u. The Fourier transform was performed at \( R_\infty = 50 \) a.u. and we placed a quadratic optical potential starting at \( R = 60 \) a.u. in order to avoid reflection of the wave packets at the edge of the grid. The propagation was performed for times up to \( 2 \times 10^4 \) a.u. with a time step of 0.5 a.u.

Fig. 4 displays the partial photodissociation cross sections for angular momentum \( J = 0 \). One observes that the dissociation cross sections towards the \( \Sigma^- \) states are mainly centered in the range from 11 to 25 eV. The cross section can be decomposed in three peaks at 2.4 eV, 11.2 eV, and 14.5 eV, and of a broad structure at higher energies. Apart from the first peak, which can be attributed to a single electronic state (the first \( \Sigma^- \) state), the cross section is determined by the strong nonadiabatic interactions between the excited states. The cross section to the \( C^{2+} + O \) channel (thick curve) is smaller than that of most other \( \Sigma^- \) states. It presents a peak with very weak intensity at 14.5 eV and another one at 20.36 eV. The ratio \( C^{2+}/C^+ \) at this energy is 0.54 so that \( C^{2+} \) dominates only slightly in this narrow range.

Fig. 5 shows the diabatic populations during the field-free propagation of the promoted wave packet. One sees that it leaves the Franck-Condon region after 8 fs during which strong nonadiabatic transitions occur. The asymptotic region with constant population in each channel is reached after about 40 fs. Contrarily to the prediction of the photodissociation...
cross section at 20.36 eV, the C$^2+$ + O channel is reached with a very low yield of only 3%.

Finally, we calculated the cross section for different initial rotational states up to $J = 20$. We observed small variations in the cross section of the order of 1% at most. This can be explained by the fact that the wave function of the ground electronic state, which defines the initial wave packet, varied only slightly with $J$. The rotational temperature would therefore not affect the photodissociation process, and rotational excitation can be neglected in the quantum control of the photodissociation.

IV. LOCAL CONTROL

A. Theory

The molecules are assumed to be oriented in the laboratory and the polarization is chosen along the direction $OX$ perpendicular to the molecular axis. LCT provides at each time step the electric field $E(t)$ which optimizes the rate of variation of an observable $O$. The latter is given by the Ehrenfest theorem and reads, for a time independent observable,

$$i \frac{d}{dt} \langle O \rangle = \langle [H(t), O] \rangle,$$

where $\hbar$ is set equal to 1, $\langle O \rangle = \langle \psi(t)|O|\psi(t)\rangle$, and the Hamiltonian, expressed here in the diabatic representation, is

$$H(t) = H_0 + E(t)W,$$

with

$$H_0 = \sum_{i,j=1}^{N} |\Phi_i^d\rangle \langle T \delta_{ij} + V_{ij}^{dia}(R)|\Phi_j^d\rangle.$$

$N$ is the number of diabatic electronic states $|\Phi_i^d\rangle$ under consideration and $T = -(1/2\mu)\partial^2/\partial R^2$ where $\mu$ is the reduced mass. The interaction with the field is written in the dipolar approximation

$$W = -\sum_{i,j=1}^{N} |\Phi_i^d\rangle d_{ij}^{dia}(R)|\Phi_j^d\rangle,$$

where $d_{ij}^{dia}(R)$ are the diabatized perpendicular dipole transition matrix elements.

When the observable commutes with the field-free Hamiltonian, the control field ensuring a monotonic increase of the observable average is defined by

$$E(t) = \lambda(-i\langle \psi(t)|[O,W]|\psi(t)\rangle),$$

where $\lambda$ is an adjustable parameter limiting the amplitude of the field. As discussed recently, a constraint may be added in order to minimize at all times the instantaneous area of the pulse $A(t) = \int_0^t E(t')dt'$. This can be useful when the LCT field contains also a Stark component which is not an optical pulse. However, as shown below, the pulse shape is here very simple. The algorithm does not find any Stark field which can be confirmed by no zero or very low frequencies in the Fourier transform. The zero-area constraint has not been applied in this work.

When the photodissociation is dominated by numerous nonadiabatic transitions, it becomes irrelevant to choose as observable for LCT the projector on an adiabatic or diabatic electronic state which correlates with the dissociation limit of the target fragment. Instead, we have recently showed that a judicious procedure consists in taking the projector on the scattering states correlating with the desired exit channel since these states do not diagonalize $H_0$. However, the scattering states are not computed by stationary methods but obtained from time-dependent methods owing to the Møller operator formalism. At all times, the excited wave packet is propagating field-free up to the asymptotic region so that finally the LCT algorithm can anticipate nonadiabatic transitions which will take place at a later time. The observable is thus defined by

$$O = \sum_{p \in S} \int dk |\xi_p^-(k)\rangle \langle \xi_p^+(k)|,$$

where $S$ represents the channels leading to the target fragments. The local control field now reads

$$E(t) = \lambda \text{Im} \left[ \sum_{p \in S} \int dk \langle \psi(t)|\xi_p^-(k)\rangle \langle \xi_p^+(k)|d_2\psi(t) \right].$$

The ingoing scattering states $|\xi_p^-(k)\rangle$ are calculated using a time-dependent approach based on Møller-operators defined by

$$|\xi_p^-(k)\rangle = \lim_{t \to \infty} e^{iH_0t}e^{-iH_f t}|p,k\rangle,$$

where $|p,k\rangle$ is the outgoing plane wave in channel $p$ with energy $k^2/2\mu$ and $H_f$ is the Hamiltonian operator of the fragments where all couplings have vanished asymptotically. Using this expression, the field becomes

$$E(t) = \lambda \text{Im} \left[ \sum_{p \in S} \int dk \lim_{t \to \infty} \langle \psi(t)|e^{iH_0t}|p,k\rangle \langle p,k|e^{-iH_0t}|d_2\psi(t) \right].$$
This integral involves the momentum distribution in every channel of two wave packets obtained after a field-free propagation up to the asymptotic region. The first one is the controlled wave packet \( |d\psi(t)\rangle \) and the second one is the same state multiplied by the electronic dipolar matrix \( \{d, \psi(t)\} \). At each time step, the algorithm requires two field-free propagations and fast Fourier transforms to get the momentum distribution in each exit channel.

This control strategy remains local in time but can preemptively account for nonadiabatic transitions that occur later in the dynamics.

### B. Results

We computed a control laser pulse \( E(t) \) to maximize the objective (Eq. (9)) with \( p = 9 \), corresponding to the \( C_2^+ + O \) channel. The time step is \( \delta t = 0.1 \) a.u. for the propagation driven by the laser field and it becomes \( \delta t = 10 \) a.u. for the field-free evolution. The spatial grid extends from 1.5 a.u. to 50 a.u. (all the couplings vanish after 25 a.u.). The number of grid points is \( 2^{12} \) ensuring a good sampling of the wave number \( k \) with a maximum \( k_{\text{max}} = \pi/dR \) where \( dR \) is the spatial interval. The parameter is adjusted to limit the maximal amplitude of the electric field to about \( E_{\text{max}} = 0.05 \) a.u. \( (2.57 \times 10^{10} \text{ Vm}^{-1}) \). Fig. 6 shows the evolution of the objective (Eq. (9)) with \( p = 9 \) up to convergence for different \( \lambda \). The maximum amplitude reached is indicated. One sees that when \( \lambda \) increases, a higher objective is reached after a shorter pulse but at the price of a too high field amplitude. The value \( \lambda = 8 \) is a good compromise between the field amplitude constraint and the objective which is here the yield in the chosen channel. However, even if it is not controlled here, the ratio \( C_2^+ / C^+ \) is important. The value predicted by the photodissociation cross section is about 0.5. This ratio increases from 0.7 for \( \lambda = 7.5 \) and 0.8 for \( \lambda = 8 \) to 0.95 for \( \lambda = 11 \).

The field for \( \lambda = 8 \), which leads to an objective of 11% after about 25 fs, is shown in the upper panel of Fig. 7. The corresponding spectrogram is shown in the lower panel of Fig. 7. Several points appear. First, the LCT algorithm finds a single short pulse. The algorithm is initiated by a seed in the excited states to allow coherence between the ground state and the excited state. The LCT field stops as soon as the excited wave packet leaves the Franck-Condon region, the only domain where dipolar coupling is possible. The final field is then used without any seed to obtain the populations in the excited states. Second, as confirmed by the Fourier transform, the LCT algorithm finds the two main frequencies predicted by the photodissociation cross section to obtain \( C_2^+ + O \) fragments. The early used frequency corresponds to the transition at 20 eV and the very weak peak is centered at 14.5 eV. The field shape found by the LCT is very simple and can be almost perfectly approximated by two Gaussian functions. The envelope of the sum of two Gaussian pulses \( G(t) = A_i, \text{max}\exp(-(t-t_i)^2/\sigma_i^2)\cos(\omega_i t) \) is shown in dark full line in Fig. 7. The parameters are \( t_1 = 3.0 \) fs, \( \sigma_1 = 3.74 \) fs, \( A_1 = 0.0049 \) a.u., and \( \omega_1 \) corresponding to 14.5 eV; \( t_2 = 16.0 \) fs, \( \sigma_2 = 5.79 \) fs, and \( A_2 = 0.0562 \) a.u. and \( \omega_2 \) corresponding to 20.3 eV. Indeed, using these parameters, the analytical pulses lead to almost identical results, underlining the robustness of the obtained control fields.

Fig. 8 shows the population in the diabatic (panel a) and adiabatic (panel b) electronic states. The control objective, i.e., the average of the target projector (Eq. (9)), is also drawn (black dashes). The yield ratio between both types of fragments is now \( C_2^+/C^+ = 0.8 \). The ratio is slightly increased with respect to the value given by the photodissociation cross section.
FIG. 8. Population in the diabatic (upper panel) and adiabatic (lower panel) excited electronic states during the control. The population of the ground state is not drawn. The state numbers are defined in Table I.

FIG. 9. Upper panel: population in the target diabatic state leading to the C$^2+$ + O during the control with sequences of LCT pulse of 25, 36, and 50 fs for the case $\lambda = 8$. Lower panel: evolution of the ratio C$^2+$/C$^+$ during the same sequences.

section. As expected the evolution of the population in the adiabatic or diabatic electronic state correlated to the target asymptote is not the same in the early evolution. It is noteworthy that in this case the population in the scattering states in the exit channel used in the control objective (Eq. (9)) nearly coincides with that of the diabatic state having the same asymptote. The LCT objective and the population in the C$^2+$ + O diabatic state are nearly superposed.

In order to increase the yield, we use a series of pulses in the spirit of the laser distillation scheme. According to this scenario, if the system returns to a situation very close to the initial one after the first pulse, it will produce a similar response to a second one and the process can be repeated. The return close to initial conditions can be favored by dissipation. Here, it is expected that the component of the driven wave packet in the ground electronic state remains very close to the initial vibrational state except the decrease of its norm and that the other metastable vibrational states are very weakly populated. The system seems then to be a good candidate to respond to a sequence of pulses without intermediary delay to recover the initial situation. Rotation of the molecule can be discarded since the rotational period is 3.4 ps, much longer than the pulse duration. The two main control parameters are then the pulse duration and the repetition interval. The objective becomes stationary after about 25 fs when $\lambda = 8$.

In Fig. 9 (lower panel) gives this ratio C$^2+$/C$^+$ during the pulse sequences. The ratio remains constant when using four pulses of 25 fs or two pulses of 50 fs. However, the sequence with three pulses of 36 fs is a little bit less favorable because the final ratio is smaller. To understand the result, we show in Fig. 10 the average position of the wave packet component in the ground electronic state for the three sequences. The mean slightly oscillates and comes back close to the initial equilibrium position with a period of about 25 fs. We also examine the oscillatory pattern of the population in the excited vibrational states. Only the population in level $v = 1$ oscillates with a maximum value of about 8% and the periodicity is again about 25 fs. Except for its norm, the component in the ground electronic state is nearly the initial wave function after 25 fs. This explains the similarity between the sequences with pulses of 25 and 50 fs and the smaller performance of the sequence with pulses of 36 fs. Fig. 11 shows the details of the population evolution with a sequence of 5 pulses of 25 fs.

In Sec. V, we briefly examine whether OCT could improve the yield of the short pulse of 36 fs by imposing a similar total integrated intensity.
the ground vibrational state of the $X^3\Pi$ state. Variation of $\psi$ leads to an equation with a final condition $O(\psi(t_f))$. The optimization is performed by the Zhu and Rabitz monotonic algorithm.\(^{56}\) At each step $k + 1$ of the iterative process, a new field is generated,

$$E_{k+1}(t) = E_k(t) + \frac{S(t) \text{Im}[\langle \chi_k(t)|W|\psi_{k+1}(t)\rangle]}{2\alpha_0}, \quad (16)$$

where $|\psi_{k+1}(t)\rangle$ is the state of the system at the $k$th iteration, $|\chi_k(t)\rangle$ is the state obtained from backward propagation of the target $O(\psi(t_f))$, $E_k$ and $E_{k+1}$ are, respectively, the control fields at steps $k$ and $k + 1$, and $A_k$ is the corresponding time-integrated area when accounted for. As shown by the field-free propagation of the promoted wave packet, the asymptotic region is reached before 40 fs. So by choosing a pulse duration 36 fs, $O(\psi(t_f))$ corresponds to the component of the total wave packet in the target channel. In order to constrain the integrated field intensity

$$F = \int_0^{t_f} |E(t)|^2 \, dt \quad (17)$$

to a constant value $F_0$, the $\alpha_0$ parameter is recalculated at each iteration $k$ by\(^{66}\)

$$\alpha_0^k = (\int_0^{t_f} |E^k(t)|^2 \, dt / F_0)^{1/2}. \quad (18)$$

\textbf{B. Results}

The LCT field with $\lambda = 8$ and $t_f = 36$ fs is used as a guess field. $\alpha_0$ is calibrated in order to maintain the total integrated intensity constant, here $F_0 = 0.44 \text{ a.u.}$ The initial value of $\alpha_0$ is $\alpha_0 = 100 \text{ a.u.}$ and it is recalculated according to Eq. (18). This pulse yields a fraction of dissociation into the desired $C^{2+} + O$ channel of 0.11.

Even after 20 iterations, OCT does not succeed in improving the yield without increasing the field intensity. Fig. 12 compares the square modulus of the Fourier transform of the LCT and OCT fields. The spectrum reveals very weak difference between the two pulses. Only the contribution of the frequencies around 14 eV is weaker in the OCT case. The population evolution in the diabatic electronic state corresponding

![Average position of the vibrational wave packet in the ground electronic state during the sequence of LCT pulse of 25, 36, and 50 fs with $\lambda = 8$.](image1.png)

![Population in the diabatic excited electronic states during the control with a sequence of five LCT pulses of 25 fs with $\lambda = 8$. The state numbers are defined in Table 1.](image2.png)

\textbf{V. OPTIMAL CONTROL}

\textbf{A. Theory}

Contrarily to the local algorithm, OCT is global in time since it optimizes the electric field on a temporal grid for a pulse of duration $t_f$. The field maximizes under constraints a cost functional built on an objective which is the average value of an observable $\langle \psi(t_f)|O|\psi(t_f)\rangle$ at time $t = t_f$ taking into account different constraints,

$$J^{\alpha_0} = \langle \psi(t_f)|O|\psi(t_f)\rangle - C_1 - C_2. \quad (13)$$

The first constraint

$$C_1 = 2 \text{Re} \int_0^{t_f} (\chi(t)) \frac{d}{dt} + iH(t)|\psi(t)\rangle \, dt \quad (14)$$

ensures that the time-dependent equation is satisfied at all times. The second one

$$C_2 = \alpha_0 \int_0^{t_f} E(t)^2 / S(t) \, dt \quad (15)$$

is the penalty constraint of the laser fluence where $S(t) = \sin^2(\pi t / t_f)$ is an envelope providing a smooth beginning and ending of the field. Finally, other experimental constraints such as the zero-area constraint for an optical field could be added.\(^{69}\)

The variation with respect to $\chi$ leads to the usual time-dependent equation with an initial condition which is here

![Fourier transform square modulus of the LCT and OCT fields. The LCT field is used as guess field for OCT and the integrated intensity (Eq. (17)) is constrained.](image3.png)
to the C$^{2+}$ + O fragments is completely similar when driven by the LCT or OCT pulse. The lack of efficiency of the OCT as compared to LCT is intriguing, and it is interesting to analyze to which extent this result depends on the initial guess used for the OCT iterations. To this end, we use different initial guess fields, obtained either from the LCT fields by adding noise to it or by considering a Gaussian pulse. In all cases, the integrated intensity was kept fixed. For the initial guess fields that include noise, we have modified the field amplitude $E(t)$ according to $E(t)(1 + R)$ where $R$ is a random number in a uniform distribution in the range $[-0.25, +0.25]$. After the first iteration, the yield becomes 0.15 but the intensity is larger than $F_0$ and with the intensity constraint the final yield is again 0.11. A stronger noise has also been checked with $E(t) + RE_{\text{max}}$ leading to a rather strong deformation and a higher intensity but the final value is 0.10 after the recalibration of the intensity. Similar results are obtained by adding noise in the real and imaginary parts of the spectrum before going back to the temporal domain. In a second test, the guess field was chosen as a Gaussian pulse of frequency 20.3 eV and width $\sigma_2$ but with different midtimes and amplitudes $A_{\text{max}}$. They lead also to a yield of about 0.11 with the intensity constraint. Gaussian pulses with different frequencies provide lower yields as expected from the photodissociation cross section. We have not explored the whole parametric space of possible guess field mainly for amplitude and mid-time of the pulse but however it seems that the LCT field, which by construction exploits the dynamics of the system, provides an excellent guess field, which is robust with respect to the noise we have used here. As a main result of this test, we conclude that the control field obtained by the LCT, and which could not be improved on by subsequent OCT iterations mainly due to the constrained intensity, provides a robust solution, which is an interesting result with respect to possible future experimental realisations.

VI. CONCLUSIONS

The CO$^{2+}$ dication is an interesting candidate for photodissociation control since it can be prepared in the ground vibrational level of the electronic X $^3\Sigma^-$ state owing to the metastability of the excited vibrational states. The target exit channel C$^{2+}$ + O ($^3\Sigma^-$) is coupled to numerous C$^+$ + O$^+$ channels leading to a complex nonadiabatic dynamics. We have illustrated the efficiency of LCT in order to find a simple and experimentally feasible pulse. LCT exploits the frequencies which could be expected based on the photodissociation cross sections and determines the best pulse envelope in agreement with the dynamics in the Franck-Condon region. The shape of the pulse is experimentally feasible since the field corresponds to a quasi-Gaussian pulse with a very small integrated area, i.e., a purely optical pulse. In the photodissociation, the dynamics of the field-free evolution of a promoted Franck-Condon wave packet should lead to negligible C$^{2+}$ production with a ratio C$^{2+}$/C$^+$ = 0.025. The cross section at 20.36 eV which should correspond to an energy resolved situation with infinite pulse duration predicts a ratio of 0.5. This ratio is significantly increased up to 0.7 when the dissociation is driven by the LCT pulse with a reasonable field amplitude ($\lambda = 8$). We have shown that the dication CO$^{2+}$ is a good candidate for applying a pulse sequence in the spirit of the laser distillation. This comes from the fact that the excited vibrational states are weakly transitory populated and the wave packet component in the ground electronic state recovers periodically the initial form, except for its norm. When judiciously choosing the repetition interval and the pulse duration, a similar response is obtained after each pulse with decreasing amplitude reflecting the decrease of the norm. Therefore, the optimal sequence scenario empties the ground state in a short time but does not modify the ratio C$^{2+}$/C$^+$. We have assumed a linear polarization and used perpendicular transition dipoles so that only transitions via the ground state are possible. However, coupling the electronic states inside the $^3\Sigma^-$ manifold by parallel transitions could also improve the control. Optimizing the selectivity by the paralysis strategy, i.e., by blocking the occupation of some electronic state is also a possibility. However, in a strongly nonadiabatic regime, it is not obvious that the blockage of some transitions could ameliorate the control towards a specific exit channel. Besides, all the excited potential energy curves are repulsive so that no resonances exist to trap and transitorily protect some population in undesirable channels. In this example, OCT has not found another mechanism and has not improved the yield. OCT only leads to an increase of the intensity of the field. In fact, LCT is here very close to the spirit of OCT since at any time, the further asymptotic dynamics is probed. This particular LCT strategy adapted for control in the continua is a good compromise. It is computationally time consuming but does not require any guess field and no iteration, only some trials in order to calibrate the $\lambda$ parameter. The control involves here X-ray ultra violet photons, i.e., the XUV spectral domain where shaping is difficult. Nevertheless, the pulses are very simple and an experimental control could be implemented.

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1 R. Conrad, Phys. Z. 31, 888 (1930).