Angle-Dependent Ionization of Small Molecules by Time-Dependent Configuration Interaction and an Absorbing Potential

Pascal Krause and H. Bernhard Schlegel*

Wayne State University, Department of Chemistry, Detroit, Michigan 48202, United States

ABSTRACT: The angle-dependence of strong field ionization of O2, N2, CO2, and CH2O has been studied theoretically using a time-dependent configuration interaction approach with a complex absorbing potential (TDCI-CAP). Calculation of the ionization yields as a function of the direction of polarization of the laser pulse produces three-dimensional surfaces of the angle-dependent ionization probability. These three-dimensional shapes and their variation with laser intensity can be interpreted in terms of ionization from the highest occupied molecular orbital (HOMO) and lower lying orbitals, and the Dyson orbitals for the ground and excited states of the cations.

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and lower lying orbitals and the Dyson orbitals for the ground state and excited states of the cations.

The ionization dynamics are simulated by solving the time-dependent Schrödinger equation for the electronic wave function:

$$i \frac{d}{dt} \Psi(t) = \left[ \hat{H}_{el} - \mu \hat{E}(t) - i \hat{V}^{\text{absorb}} \right] \Psi(t)$$

(1)

where the total Hamiltonian includes the field-free electronic Hamiltonian, \( \hat{H}_{el} \), and the electron-light interaction, \( \mu \hat{E}(t) \), treated in the semiclassical dipole approximation as a product of dipole operator and electric field component of the laser pulse. Ionization is modeled by including a CAP, \(-i \hat{V}^{\text{absorb}}\). In the present work, \( \hat{V}^{\text{absorb}} \) has a quadratic rise and a quadratic turn over to a constant value of 10 \( E_0 \) at long-range. \( \hat{V}^{\text{absorb}} \) is constructed from a set of overlapping spherical potentials around each atom at a distance of 3.5 times the van der Waals radius of each element \( r_{vdw} \) at a distance of 3.5 times the van der Waals radius of each element \( r_{vdw} \) at a distance of 3.5 times the van der Waals radius of each element \( r_{vdw} \) at a distance of 3.5 times the van der Waals radius of each element \( r_{vdw} \). The radii are chosen as a compromise between minimal absorption of the norm in the field-free case and the number of diffuse basis functions needed for interaction with the CAP.

The time-dependent wave function is expanded in the basis of the Hartree–Fock ground state and all singly excited states of the field-free, time-independent Hamiltonian:

$$\Psi(t) = \sum_{i=0} C_i(t) |\Psi_i\rangle$$

(2)

The coefficients are propagated using a Trotter factorization of the exponential of the Hamiltonian with a time step of \( \Delta t = 0.05 \ h/E_0 \) (1.2 as):

$$\Psi(t + \Delta t) = \exp(-i\hat{H}\Delta t)\Psi(t)$$

$$= \exp(-i\hat{H}_{el}\Delta t/2) \exp(V/\Delta t/2)W^T$$

$$\times \exp(iE(t + \Delta t/2)\Delta t)W \exp(V\Delta t/2)$$

$$\times \exp(-i\hat{H}_{el}\Delta t/2)\Psi(t)$$

where \( WDW^T = d \) are the eigenvalues and eigenvectors of the transition dipole matrix in the direction of the polarization of the laser field. \( W, d, \exp(-i\Delta tH) \), and \( \exp(V\Delta t/2) \) need to be calculated only once, and the propagation involves a pair of matrix-vector multiplies and the exponential of the diagonal matrix, \( d \).

The energies of the field-free states for CO\(_2\) and CH\(_2\)O were calculated with the CIS\(^4\) method, while energies of the field-free states of O\(_2\) and N\(_2\) were calculated with the CIS(D)\(^4\) method since this produced a better ordering for the excited states of the ions. More accurate methods for calculating the field free states would be desirable, but it is currently not practical to use methods such as EOMCC or MRCI to calculate the thousands of excited states and associated transition dipole and absorbing matrix elements needed for the TDCl method. The electronic structure calculations were carried out with a locally modified version of the GAUSSIAN program package\(^4\) (the same matrix elements are used for CIS and CIS(D)). Spin unrestricted Hartree–Fock was used for triplet O\(_2\), while spin restricted Hartree–Fock was used for N\(_2\), CO\(_2\), and CH\(_2\)O. The calculations employed the standard Dunning aug-cc-pVTZ basis set\(^4\) augmented with an absorbing basis (AB) containing extra diffuse functions to ensure sufficient interaction with the CAP. This absorbing basis consists of nine sets of diffuse Gaussian functions on each atom: three \( s \) functions (with exponents: 0.0256, 0.0128, and 0.0064), two sets of \( p \) functions (0.0256, 0.0128), two sets of \( d \) functions (0.0512, 0.0256, and 0.0128), and one set of pure \( f \) functions (0.0256), (for details of the development of the absorbing basis, see refs 40 and 41). The molecules were aligned with the z axis and have the following geometries: 1.160 Å for O\(_2\), and 1.067 Å for N\(_2\), \( R(\text{CO}) = 1.136 \) Å for CO\(_2\), and \( R(\text{CO}) = 1.179 \) Å, \( R(\text{CH}) = 1.092 \) Å, and \( \angle(\text{CHO}) = 121.947^\circ \).
for CH₂O. Dyson orbitals were obtained from the overlap of the ground state of the neutral and the ground and excited states of the cation computed using single determinant Hartree–Fock calculations at the same geometry (since the orbitals of the neutral and the cation are different, this involves the overlap between nonorthogonal determinants). The ground state and all singly excited electronic states were used in the time-dependent configuration interaction calculations: 1703 states for O₂, 706 for N₂, 1633 for CO₂, and 1369 for CH₂O.

In this work, we apply linearly polarized cosine squared pulses with frequency of 0.057 E₀/h(800 nm) and 7 optical cycles (9.35 fs full width at half maximum), and propagate the system for a total of 1000 h/E₀(24.2 fs). The maximal field strengths range from Eₘₐₓ = 0.04 E₀/(e₀a₀) to 0.12 E₀/(e₀a₀) correspond to peak intensities of 5.62 × 10¹³ and 5.05 × 10¹⁴ W/cm². For the molecules considered, ionization at these field strengths occurs primarily by barrier suppression rather than tunneling. The loss of norm was calculated after the pulse (18.7 fs) when the field has returned to zero and is taken as the ionization yield for the pulse. By varying the polarization direction of the pulse with a given Eₘₐₓ we obtain a three-dimensional surface, which we interpret as an angle-dependent ionization probability. For each Eₘₐₓ up to 114 points were calculated and a three-dimensional plot was generated using the ionization rate as the radial distance and the direction of the polarization as the angles. To obtain a smooth surface, the ionization rate as a function of the angles was fitted to a polynomial in cos(θ)ⁿ cos(mϕ) and cos(θ)ᵐ sin(mϕ), n = 0–9, m = 0–4.

Figures 1–4 show the total ionization rates as a function of the orientation of the laser field polarization. For a particular maximum field strength, the ionization yield is plotted as a distance from the origin as a function of the angle of the laser polarization. So that the angular dependence is easier to see in the three-dimensional plots, the ionization yield is scaled by a factor of 3 for the lowest intensity and by a factor of 1.5 for the second lowest intensity. Also included in the figures are more conventional polar plots of the angle dependent ionization rates (without scaling). The relevant Dyson orbitals are included in the figures to aid in the interpretation of the angular dependence of the ionization rate. The Dyson orbitals for the ground state and lowest two excited states of the cations closely resemble the canonical Hartree–Fock orbitals and have norms greater than 0.95 (the exceptions are 0.93 for π₊ of CO₂ and 0.94 for a₁ of CH₂O).

For O₂, the angle-dependent ionization yield is shown in Figure 1a,b. For the ²Πₗ ground state of O₂, the Dyson orbital is a π₊ antibonding orbital, shown in Figure 1c. At lower intensities, the angle-dependent ionization closely reflects the shape of the Dyson orbital. The ionization rate is lowest along the molecular axis, reaches a maximum around 45° and 135°, and decreases to a minimum at 90°, where the π₊ orbital has a node. At higher intensities, the angular dependence of the ionization shows contributions from the σ₂ orbital along the molecular axis and the π₊ orbital perpendicular to the axis. The lowest excited states of O₂ are of ²Πₗ and ³Σ⁺ symmetry and are associated with the π₊ and σ₂ Dyson orbitals. These excited states are 4–8 eV higher than the ground state of the ion.²⁷ Calculations of HHG spectra indicate that harmonic yields from the π₊ and σ₂ orbitals increase with increasing intensity.²⁷

The angular dependence of the ionization yield for N₂ shown in Figure 2a,b appears to be a mixture of two contributions even at the lowest intensities. The large ionization rate along the molecular axis is associated with the X ²Σ₁⁺ state and loss of an electron from the σ₂ lone pair orbital (Figure 2c). The increased ionization rate perpendicular to the molecular axis corresponds to the A¹Π₂⁺ state of N₂ and loss of an electron from the π₊ Dyson orbital (Figure 2d). Experimentally, the A¹Π₂⁺ state is only 1.1 eV above the ground state and
participates in strong field ionization at higher intensities.\textsuperscript{48} The experimental HHG spectra of N\textsubscript{2} are dominated by the $\sigma_g$ orbital, but contributions from the $\pi_u$ orbital can be seen in the HHG data.\textsuperscript{15} The $\pi_u$ contributions to the HHG spectra and the angle-dependent ionization grow with increasing laser intensity.\textsuperscript{18,21} Orbital tomography has been used to reconstruct both the $\sigma_g$ and the $\pi_u$ orbitals from the real and imaginary parts of the emission dipole from coherent soft X-ray emission spectra.\textsuperscript{23} SAE-TDSE calculations based on Kohn–Sham orbitals show that the $\sigma_g$ orbital dominates ionization at all angles but the $\pi_u$ orbital makes a significant contribution perpendicular to the molecular axis.\textsuperscript{9} Figure 3a,c shows the calculated angular dependence of the ionization rate for CO\textsubscript{2}. At low values of $E_{\text{max}}$, the shape reflects the $\pi_u$ Dyson orbital for ground state CO\textsubscript{2} as depicted in Figure 3d. The ionization yield shows a broad maximum around 50° and minima along the molecular axis and perpendicular to the axis. The experimental angular dependence of the ionization has a maximum at 25°,\textsuperscript{7,8} Molecular ADK theory has a sharp maximum at 25°,\textsuperscript{7} but more careful application of MO-ADK\textsuperscript{19} and more elaborate theories have broader maxima in the 30°–45° range.\textsuperscript{9,17,20,22,25,28} At higher $E_{\text{max}}$, there is a large increase in the ionization rate along the molecular axis. This is indicative of ionization to the $B^2\Sigma_u^+$ state of CO\textsubscript{2} and the Dyson orbital corresponds to the $\sigma_u$ orbital involving the oxygen lone pairs, Figure 3f. Ionization from the Dyson orbital for the $A^2\Pi_u$ state, Figure 3e, does not seem to contribute to the angular dependence. The $A^2\Pi_u$ and $B^2\Sigma_u^+$ state of CO\textsubscript{2} are 3.5 and 4.3 eV higher than the ground state, respectively.\textsuperscript{47} Fluorescence spectra indicate that strong field ionization produces the $A^2\Pi_u$ and $B^2\Sigma_u^+$ states of CO\textsubscript{2} as well as the ground state.\textsuperscript{24} Analysis of HHG spectra of CO\textsubscript{2} reveal contributions from ionization from lower lying orbitals.\textsuperscript{16,22} Calculations by other groups also show that the $\sigma_u$ orbital contributes to ionization along the molecular axis and the $\pi_u$ orbital contributes to ionization perpendicular to the axis,\textsuperscript{9,25,28} and that at higher intensities these contributions can become larger than from the $\pi_u$ orbital.\textsuperscript{28} The angular dependence of the ionization of formaldehyde (Figure 4a–c) has a richer three-dimensional structure since it lacks the cylindrical symmetry of linear molecules in this study. The Dyson orbital for the ground state of CH\textsubscript{2}O\textsuperscript{+} is an

![Figure 3. Angle dependence of the ionization yield for CO\textsubscript{2} calculated with the TDCIS-CAP approach: (a) three-dimensional plot for field strengths of 0.08, 0.10, 0.12 $E_h/\text{ea}_0$, (b) the CAP, (c) polar plot containing the molecular axis for field strengths of 0.08, 0.09, 0.10, 0.11, 0.12 $E_h/\text{ea}_0$, (d) the Dyson orbital for the $X^2\Pi_g$ state, (e) the Dyson orbital for the $A^2\Pi_u$ state, and (f) the Dyson orbital for the $B^2\Sigma_u^+$ state.]

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antibonding combination of the in-plane $p$-type lone pair on oxygen and the antisymmetric combination of the C–H bonds. The shape of the ionization probability as well as the polar plot of the in-plane ionization rate corresponds closely to this $b_2$ Dyson orbital. The lowest two excited states of CH$_2$O$^+$ have a Dyson orbital with $b_1$ ($\pi^*$) and $a_1$ ($\sigma$) symmetry and are about 3.2 and 5.4 eV higher in energy, respectively. Some evidence of ionization from the $a_1$ orbital is seen at higher values of $E_{\text{max}}$ than shown in the plots. Experimental studies of the angular dependence of ionization have not yet been reported for formaldehyde. HHG and strong field ionization of CH$_2$O have been studied by grid-based time-dependent density functional simulations. For laser polarizations aligned with the CO bond and perpendicular to the molecular plane, the response is dominated by ionization from the $b_2$ orbital with some contribution from the $a_1$ orbital but little from the $b_1$ orbital. With increasing intensity, ionization increases significantly for the $b_2$ and $a_1$ orbitals, but not for the $b_1$ orbital.

Figure 4. Angle dependence of the ionization yield for CH$_2$O calculated with the TDCIS-CAP approach: (a) three-dimensional plot for field strengths of 0.04, 0.06, 0.08 E$_h$/eBo, (b) polar plot containing the molecular axis for field strengths of 0.04, 0.05, 0.06, 0.07, 0.08 E$_h$/eBo, (c) polar plot perpendicular the molecular axis, (d) the Dyson orbital for the $^2B_2$ state, (e) the Dyson orbital for the $^2B_1$ state, and (f) the Dyson orbital for the $^2A_1$ state.
In this paper we have demonstrated the use of the TDCl-CAP approach to simulate the angular dependence of ionization of O$_2$, N$_2$, CO$_2$, and CH$_2$O. At low intensities, the angular dependence is dominated by the shape of the Dyson orbital associated with the ground state of the ion. At higher intensities, the calculated angular distributions show contributions from ionization of lower lying orbitals. The TDCl-CAP approach is readily scalable to larger polyatomic systems (unpublished results).

**AUTHOR INFORMATION**

**Corresponding Author**  
*E-mail: hbs@chem.wayne.edu.*

**Notes**  
The authors declare no competing financial interest.

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