

# ARTICLE

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## Angle-dependent strong-field ionization of triple bonded systems calculated by time-dependent configuration interaction with an absorbing potential

Qing Liao, Wen Li, and H. Bernhard Schlegel

**Abstract:** The angle dependence of strong field ionization has been studied for a set of molecules containing triple bonds: HCCH, HCN, HCC–CN,  $H_2N$ –CCH,  $H_2N$ –CCH, and  $H_2N$ –CC–CN. Time-dependent configuration interaction (TDCI) with a complex absorbing potential was used to model strong field ionization by a linearly polarized seven-cycle 800 nm cosine squared pulse. The ionization yields have been calculated as a function of the laser intensity and polarization direction and plotted as three-dimensional surfaces. At low field strengths, the angular dependence can be understood in terms of ionization from the highest occupied orbitals. At higher laser intensities, ionization occurs from lower lying orbitals as well as from the highest occupied orbitals, as indicated by changes in the angular dependence of the ionization yield and by variations in the population analysis of the TDCI wavefunction with the intensity of the laser field. The ionization length is increased. NH<sub>2</sub> substitution substantially increases the ionization yield along the molecular axis but has only a small effect for perpendicular directions.

Key words: strong field ionization, time-dependent configuration interaction, complex absorbing potential.

**Résumé** : Nous avons étudié l'effet de l'angle sur l'ionisation sous fort champ d'un ensemble de molécules contenant des triples liaisons : HCCH, HCN, HCC-CN,  $H_2$ N-CCH,  $H_2$ N-CC et  $H_2$ N-CC-CN. Nous avons utilisé une interaction configurationnelle à dépendance temporelle (ICDT) ainsi qu'un potentiel d'absorption de complexe pour modéliser une ionisation sous fort champ au moyen d'une impulsion en cosinus carré de 800 nm à sept cycles et à polarisation linéaire. Nous avons calculé les rendements d'ionisation en fonction de l'intensité du laser et de l'orientation de la polarisation, et nous en avons compilés sous forme de surfaces tridimensionnelles. À champs faibles, la dépendance angulaire peut s'expliquer par l'ionisation dans les orbitales les plus hautes occupées. Aux intensités de laser plus élevées, l'ionisation se produit à la fois dans les orbitales plus basses et dans orbitales les plus hautes occupées, comme en témoignent les changements de la dépendance angulaire du rendement d'ionisation et les variations de l'analyse populationnelle de la fonction d'onde de l'ICDT, en fonction l'intensité de champ du laser. Lorsque l'orientation est parallèle à l'axe moléculaire, le rendement d'ionisation croît plus rapidement en fonction de l'allongement du système conjugué que lorsque l'orientation est perpendiculaire à l'axe. La substitution par un groupe NH<sub>2</sub> entraîne une augmentation substantielle du rendement d'ionisation dans le sens de l'axe moléculaire, mais n'a que peu d'effet lorsque l'orientation est perpendiculaire à celui-ci. [Traduit par la Rédaction]

*Mots-clés* : ionisation sous fort champ, interaction configurationnelle à dépendance temporelle, potentiel d'absorption de complexe.

### Introduction

Both in the tunneling regime and in the barrier suppression regime, the angular dependence of strong field ionization is governed by electron dynamics on an attosecond and femtosecond timescale. Investigating dynamics on this timescale requires very short, intense laser pulses.<sup>1–3</sup> Early work showed that the ionization rate for  $N_2$  and CO differed significantly when the polarization of the laser field was aligned parallel versus perpendicular to the molecular axis.<sup>4,5</sup> Subsequently, the angular dependence of ionization was measured directly for  $N_2$ ,  $O_2$ , and  $CO_2$ .<sup>6,7</sup> For butadiene and some larger polyatomics, angle-dependent and channel-dependent ionization yields have been observed.<sup>8–10</sup> For high harmonic generation (HHG) spectra, the amplitudes of the various harmonics depend on the angle of the molecular orbital

(HOMO) can be reconstructed from these data using orbital tomography<sup>11</sup> under the assumption that the angle dependence of the amplitudes comes only from ionization of the HOMO. However, HHG spectra can also have contributions from direct ionization of lower lying orbitals if the intensity is high enough.<sup>12–17</sup> Earlier work also showed that an intense laser pulse can cause nonresonant multiphoton ionization of inner-valence electrons.<sup>18,19</sup>

A qualitative description of the angular dependence of ionization for simple molecules can be obtained from Dyson orbitals. These are computed from the overlap between the neutral and the ionic wavefunctions,  $\Phi_i^D = \int \Psi^{*\text{neutral}} \Psi_i^{\text{cation}} d\tau_2 \cdots d\tau_n$ . For simple molecules and high symmetry, the shapes of the Dyson orbitals closely resemble the canonical Hartree–Fock orbitals. Molecular Ammosov–Delone–Krainov (ADK) theory provides a better description of ionization in the tunneling regime.<sup>20,21</sup> More quanti-

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**Fig. 1.** First row: angular dependence of the ionization yield for acetylene HC=CH for a 800 nm seven-cycle cosine squared pulse with  $E_{max} = 0.04$  au (5.62 × 10<sup>13</sup> W/cm<sup>2</sup>), 0.08 au (2.25 × 10<sup>14</sup> W/cm<sup>2</sup>), and 0.12 au (5.05 × 10<sup>14</sup> W/cm<sup>2</sup>) (from left to right; the ionization yield is scaled by a factor of 50, 3, and 2, respectively). Second row: doubly degenerate HOMO, HOMO-1, and HOMO-2 (from left to right). Third row: Dyson orbits for the ground state and the first excited state of the cation. Fourth row: orbital populations with polarization along the *x*, *y*, and *z* directions. Populations (left hand axis) of the doubly degenerate HOMO (red and blue), HOMO-1 (green), and HOMO-2 (purple) as a function of field strength; final norm of the neutral wavefunction as a function of the field strengths (broken lines, right-hand axis). [Color online]



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tative descriptions of the angular dependence of ionization and HHG spectra can be obtained using the time-dependent Schrödinger equation (TDSE) with approximations such as single active electron TDSE, quantitative rescattering theory, time-dependent resolution-in-ionicstates, time-dependent analytical R-matrix, and time-dependent generalized active space configuration interaction.<sup>22-26</sup> In previous studies, we examined the angle dependence of strong-field ionization for  $N_2$ ,  $O_2$ ,  $CO_2$ , and  $CH_2O$ ,<sup>27</sup> a set of polyenes,<sup>28</sup> and a series of second and third period hydrides<sup>29</sup> using a time-dependent configuration interaction (TDCI) approach using atom-centered basis functions. The TDCI approach is well suited for describing response properties<sup>30-34</sup> and can also be used to simulate HHG spectra.34,35 When atom-centered basis functions are used, ionization can be simulated by including a complex absorbing potential (CAP) to absorb the fraction of the electron density that is distorted toward ionization by the laser field.<sup>27–29,36</sup> This approach is suitable not only for strong-field ionization in the barrier suppression regime but also for tunneling ionization. The TDCI-CAP approach is in good agreement with accurate grid-based calculations for ionization of the hydrogen atom as a function of field strength and for changes in the rate of ionization of  $H_2^+$  as a function of bond length.<sup>36</sup> The calculated three-dimensional shapes for ionization of polyatomic systems showed that direct ionization occurred not just from the HOMO but also from lower lying orbitals.<sup>27–29</sup>

In the present work, we have used the TDCIS-CAP approach to examine the angle-dependent strong-field ionization of a set of molecules containing triple bonds: individual triple bonds –HCCH and HCN, triple bonds in conjugation –HCC–CN, and triple bonded systems interacting with the lone pair of an amine  $-H_2N$ –CCH,  $H_2N$ –CN, and  $H_2N$ –CC–CN.

#### Methods

The electron dynamics were simulated by solving the timedependent Schrödinger equation: **Fig. 2.** First row: angular dependence of the ionization yield for HC $\equiv$ N for a 800 nm seven-cycle cosine squared pulse with  $E_{max} = 0.06$  au (1.26 × 10<sup>14</sup> W/cm<sup>2</sup>), 0.10 au (3.51 × 10<sup>14</sup> W/cm<sup>2</sup>), and 0.14 a.u. (6.88 × 10<sup>14</sup> W/cm<sup>2</sup>) (from left to right; the ionization yield is scaled by a factor of 60, 5, and 3, respectively). Second row: doubly degenerate HOMOs, HOMO-1, and HOMO-2 (from left to right). Third row: Dyson orbits for the ground state and the first excited state of the cation. Fourth row: orbital populations with polarization along the *x*, *y*, and *z* directions. Populations (left hand axis) of the doubly degenerate HOMOs (red and blue), HOMO-1 (green), and HOMO-2 (purple) as a function of field strength; final norm of the neutral wavefunction as a function of the field strengths (broken lines, right-hand axis). [Color online]



(1) 
$$i\frac{\partial}{\partial t}\Psi_{\rm el}(t) = [\hat{\mathbf{H}}_{\rm el} - \hat{\mu}\vec{E}(t) - i\hat{\mathbf{V}}^{\rm absorb}]\Psi_{\rm el}(t)$$

where  $\hat{\mathbf{H}}_{el}$  is the field-free electronic Hamiltonian. The electronlight interaction is treated in the semiclassical dipole approximation, where  $\hat{\mu}$  is the dipole operator and  $\vec{E}$  is electric field component of the laser pulse. The absorbing potential used to model ionization,  $-i\hat{\mathbf{V}}^{\text{absorb}}$ , is constructed from a set of overlapping spherical potentials around each atom, as described in our earlier papers.<sup>27–29,36</sup> Each spherical potential has a quadratic rise starting at 3.5 times the van der Waals radius of each element ( $R_{\rm H} = 5.051$  Å,  $R_{\rm B} = 7.145$  Å,  $R_{\rm C} = 6.739$  Å,  $R_{\rm N} = 6.405$  Å,  $R_{\rm O} = 6.125$  Å,  $R_{\rm F} = 5.887$  Å) and a quadratic turnover to constant value of 10 hartree at approximately R + 7 Å. At any given point, the total absorbing potential is equal to the minimum of the values from the atomic absorbing potentials. The radii of the spherical potentials are 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 wavefunction is expanded in the basis of the Hartree–Fock ground state and all singly excited states of the field-free, time-independent Hamiltonian:

(2) 
$$\Psi(t) = \sum_{i=0}^{\infty} C_i(t) |\Psi_i\rangle$$

The time-dependent coefficients are propagated using a Trotter factorization of the exponential of the Hamiltonian:

(3)  

$$\begin{aligned}
\Psi(t + \Delta t) &= \exp(-i\,\hat{\mathbf{H}}\Delta t)\Psi(t) \\
&= \exp(-i\,\hat{\mathbf{H}}_{el}\Delta t/2)\exp(-\hat{\mathbf{V}}^{absorb}\Delta t/2)\mathbf{W}^{T} \\
&\times \exp(i\,E(t + \Delta t/2)\mathbf{d}\Delta t) \\
&\times \mathbf{W}\exp(-\hat{\mathbf{V}}^{absorb}\Delta t/2)\exp(-i\hat{\mathbf{H}}_{el}\Delta t/2)\Psi(t)
\end{aligned}$$

where  $WDW^T = d$  are the eigenvalues and eigenvectors of the transition dipole matrix **D** in the direction of the polarization of

**Fig. 3.** First row: angular dependence of the ionization yield for cyanoacetylene HC $\equiv$ C-C $\equiv$ N for a 800 nm seven-cycle cosine squared pulse with  $E_{max} = 0.04$  au (5.62 × 10<sup>13</sup> W/cm<sup>2</sup>), 0.08 au (2.25 × 10<sup>14</sup> W/cm<sup>2</sup>), and 0.12 au (5.05 × 10<sup>14</sup> W/cm<sup>2</sup>) (from left to right; the ionization yield is scaled by a factor of 75, 5, and 2, respectively). Second row: doubly degenerate HOMOs, doubly degenerate HOMO-1s, and HOMO-2. Third row: Dyson orbits for the ground state and the first two excited states of the cation. Fourth row: orbital populations with polarization along the *x*, *y*, and *z* directions. Populations (left hand axis) of the doubly degenerate HOMO (red and blue), doubly degenerate HOMO-1 (green and purple), and HOMO-2 (yellow) as a function of field strength; final norm of the neutral wavefunction as a function of the field strengths (broken lines, right-hand axis). [Color online]



the laser field. **W**, **d**,  $\exp(-i\hat{\mathbf{H}}_{el}\Delta t/2)$  and  $\exp(\hat{\mathbf{V}}^{absorb}\Delta t/2)$  need to be calculated only once because they are time independent. The propagation involves a pair of matrix–vector multiplies and the exponential of the diagonal matrix, **d**. A time step of  $\Delta t = 1.2$  as (0.05 au) was used for the propagation. Earlier tests showed that reducing the time step by a factor of 2 changed the norm at the end of the pulse by less than 0.1%, suggesting that the choice of the time step and the Trotter factorization are satisfactory.<sup>36</sup>

The integrals needed for the TDCIS simulations were calculated with a locally modified version of the Gaussian program package.<sup>37</sup> The standard Dunning aug-cc-pVTZ basis<sup>38,39</sup> was augmented with an absorbing basis containing extra diffuse functions to ensure sufficient interaction with the CAP. This absorbing basis consisted of nine sets of diffuse Gaussian functions on each atom (including hydrogens): three *s* functions (with exponents 0.0256, 0.0128, and 0.0064), two sets of *p* functions (0.0256 and 0.0128), three sets of pure *d* functions (0.0512, 0.0256, and 0.0128), and one set of pure *f* functions (0.0256). For the most diffuse functions, the matrix elements of  $\hat{\mathbf{V}}^{\text{absorb}}$  are of the order of 0.1, and the largest eigenvalues of the  $\hat{\mathbf{V}}^{\text{absorb}}$  matrix are of the order of 0.5. Details of the development and testing of the absorbing basis can be found in Krause et al.<sup>36</sup> In particular, this choice of exponents and CAP radii yields good agreement with accurate grid-based calculations for the ionization of hydrogen atom and H<sub>2</sub><sup>+</sup> as a function of field strength and bond length, and adding more diffuse basis functions does not change the ionization yield appreciably.<sup>36</sup>

The simulations used a seven-cycle, linearly polarized cosine squared pulse:

(4) 
$$E(t) = E_{\max} \cos^2(\pi t/2\sigma) \cos(\omega t + \phi)$$
 for  $-\sigma \le t \le \sigma$ ,  
 $E(t) = 0$  otherwise

with a wavelength of 800 nm (9.35 fs FWHM) and  $\phi = \pi$ . The system was propagated for 24.2 fs (1000 au) with intensities from 0.56 × 10<sup>14</sup> to 7.90 × 10<sup>14</sup> W cm<sup>-2</sup> (electric field strengths of 0.04–0.15 au).

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**Fig. 4.** First row: angular dependence of the ionization yield for ethynamine  $H_2NC\equivCH$  for a 800 nm seven-cycle cosine squared pulse with  $E_{max} = 0.04$  au (5.62 × 10<sup>13</sup> W/cm<sup>2</sup>), 0.08 au (2.25 × 10<sup>14</sup> W/cm<sup>2</sup>), and 0.12 au (5.05 × 10<sup>14</sup> W/cm<sup>2</sup>) (from left to right; the ionization yield is scaled by a factor of 30, 5, and 4, respectively). Second row: HOMO, HOMO-1, HOMO-2, and HOMO-3 (from left to right). Third row: Dyson orbits for the ground state and the first excited state of the cation. Fourth row: orbital populations with polarization along the *x*, *y*, and *z* directions. Populations (left hand axis) of the HOMO (red), HOMO-1 (blue), HOMO-2 (green), and HOMO-3 (purple) as a function of field strength; final norm of the neutral wavefunction as a function of the field strengths (broken lines, right-hand axis). [Color online]



pression rather than by 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. The angle dependence of the ionization yield is obtained by varying the polarization direction of the pulse with a given  $E_{max}$ . Three-dimensional plots were generated using the ionization yield as the radial distance and the direction of the polarization as the angles. For the lower  $E_{max}$  in each set, the radial distances were scaled so that the shape of the surface would not be obscured by the molecular structure. To obtain smooth surfaces, the ionization yields as a function of the angles were fitted to polynomials in  $\cos(\theta)^n \cos(m\varphi)$ and  $\cos(\theta)^n \sin(m\varphi)$ , n = 0-9, m = 0-4.

#### **Results and discussion**

The angular dependence of the ionization yield for the two simplest triple bonded species, HCCH and HCN, are shown in Figs. 1 and 2, respectively, along with their molecular orbitals. In both cases, the HOMO is a doubly degenerate  $\pi$  orbital and HOMO-1 is a  $\sigma$  orbital. The Dyson orbitals derived from the ground state and lowest excited state of the cations are nearly identical to the canonical molecular orbitals, as expected for these simple, high-symmetry molecules. The angular dependence of the ionization at low field strengths reflects the cylindrical symmetry of the HOMO. At higher field strengths, there is a substantial increase in the ionization yield along the molecular (z) axis for HCN, but not for HCCH. The change in the orbital population with field strength shows that this is due to ionization from HOMO-1, which is a nitrogen  $\sigma$  lone pair orbital in HCN. The orbital energy of HOMO-1 in HCN (-0.581 au) is close to that for HOMO (-0.506), resulting in a large contribution when a strong field is directed along the z-axis. For HCCH, the difference is much greater (-0.685 au for HOMO-1 and -0.416 au for HOMO) and very little ionization is seen from HOMO-1 when the laser polarization is along the z-axis.

**Fig. 5.** First row: angular dependence of the ionization yield for cyanamide  $H_2NC\equivN$  for a 800 nm seven-cycle cosine squared pulse with  $E_{max} = 0.04$  au (5.62 × 10<sup>13</sup> W/cm<sup>2</sup>), 0.08 au (2.25 × 10<sup>14</sup> W/cm<sup>2</sup>), and 0.12 au (5.05 × 10<sup>14</sup> W/cm<sup>2</sup>) (from left to right; the ionization yield is scaled by a factor of 30, 2, and 1, respectively). Second row: HOMO, HOMO-1, HOMO-2, HOMO-3, and HOMO-4 (from left to right). Third row: Dyson orbits for the ground state and excited states of the cation. Fourth row: orbital populations with polarization along the *x*, *y*, and *z* directions. Populations (left hand axis) of the HOMO (red), HOMO-1 (blue), HOMO-2 (green), HOMO-3 (purple), and HOMO-4 (yellow) as a function of field strength; final norm of the neutral wavefunction as a function of the field strengths (broken lines, right-hand axis). [Color online]



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Figure 3 shows the angular dependence of the ionization when these two triple bonds are coupled together to form HCC–CN. The HOMO-1 and HOMO are both doubly degenerate and are composed of the in-phase and out-of-phase combinations of the CC and CN  $\pi$  orbitals, respectively. HOMO-2 is the  $\sigma$  lone pair orbital on the nitrogen. The ionization yield has cylindrically symmetry, as expected from the shape of HOMO and HOMO-1. If the ionization occurred only from HOMO, one would expect a decrease in the ionization yield in the *xy* plane as a result of the node in the HOMO. However, the orbital populations show that in addition to ionization from HOMO, there is significant ionization from HOMO-1, which does not have a node perpendicular to the molecular axis. For higher field strengths, there is a substantial increase in the ionization yield when the polarization is aligned with the molecular axis.

When one of the hydrogens in HCCH and HCN is replaced by  $NH_2$ , the  $\pi$  orbitals of the triple bond can interact with the  $NH_2$  lone pair and NH bonding orbitals, as shown in Figs. 4 and 5. This splits the degeneracy of the  $\pi$  orbitals by approximately 0.06 au. The HOMO and HOMO-1 are still primarily  $\pi$  orbitals but interacting in an out-of-phase manner with the  $NH_2$  lone

pair and the antisymmetric combination of the NH bonds, respectively. At low field strengths, ionization is primarily from the HOMO and the angular dependence reflects the nodal structure of the HOMO. Ionization is also seen from HOMO-1, perpendicular to the molecular plane (y direction). At higher field strengths, HN<sub>2</sub>-CCH also shows contributions from HOMO-2, a  $\pi$  orbital that is the in-phase combination of the NH<sub>2</sub> lone pair and the CC  $\pi$  orbital. HOMO-2 of H<sub>2</sub>N–CN is a  $\sigma$  orbital that is primarily the nitrogen lone pair of the CN group. It contributes to ionization along the molecular axis (z direction), since its orbital energy is similar to HOMO-1 and HOMO (-0.553 versus -0.473 and -0.411 au, respectively). For the corresponding highest  $\sigma$  orbital of H<sub>2</sub>N–CCH, the orbital energy difference is much greater (-0.683 au for HOMO-3 versus -0.338 au for HOMO), and it does not contribute significantly to ionization, even at higher field strengths.

The results for acetylene substituted with both NH<sub>2</sub> and CN are shown in Fig. 6. HOMO to HOMO-3 and HOMO-5 are the out-of-phase and in-phase interactions of the CC-CN  $\pi$  orbitals with NH<sub>2</sub> (orbital energies from -0.367 to -0.580 au), while HOMO-4 is the nitrogen lone pair of the CN group (-0.565 au).

**Fig. 6.** First row: angular dependence of the ionization yield for  $H_2NC\equiv C-C\equiv N$  for a 800 nm seven-cycle cosine squared pulse with  $E_{max} = 0.04$  au (5.62 × 10<sup>13</sup> W/cm<sup>2</sup>), 0.08 au (2.25 × 10<sup>14</sup> W/cm<sup>2</sup>), and 0.12 au (5.05 × 10<sup>14</sup> W/cm<sup>2</sup>) (from left to right; the ionization yield is scaled by a factor of 60, 7, and 5, respectively). Second row: HOMO, HOMO-1, HOMO-2, HOMO-3, HOMO-4, HOMO-5, and HOMO-6 (from left to right). Third row: Dyson orbits for the ground and excited states of the cation. Fourth row: orbital populations with polarization along the *x*, *y*, and *z* directions. Populations (left hand axis) of the HOMO (red), HOMO-1 (blue), HOMO-2 (green), HOMO-3 (purple), HOMO-4 (yellow), HOMO-5 (orange), and HOMO-6 (cyan) as a function of field strength; final norm of the neutral wavefunction as a function of the field strengths (broken lines, right-hand axis). [Color online]



Ionization occurs from HOMO, HOMO-2, and HOMO-5 when the laser polarization is in the *x* direction and from HOMO-1 and HOMO-3 when the laser polarization is in the *y* direction. The ionization yield along the molecular axis is more than twice as large as perpendicular to the axis. This may be the result of increased electron dynamics in the extended, delocalized  $\pi$  system. A similar enhancement of strong field ionization yield with increased conjugation length was seen in the ethylene, butadiene, and hexatriene series.<sup>28</sup>

Table 1 compares the maximum ionization yield at three different field strengths with the ionization potentials calculated by  $\Delta$ SCF and OVGF<sup>40</sup> and the available experimental ionization potentials. As expected, HCN, with the highest ionization potential, has the lowest yield in strong field ionization at each of

the different field strengths, and  $H_2NCCH$ , with the lowest ionization potential, has the highest yield. The trend the ionization yield for HCN, HCCH, and HCC–CN is nearly linear with the ionization potential, as is the trend for  $H_2N$ –CN,  $H_2N$ –CCH, and  $H_2N$ –CC–CN.

Table 2 examines the effect of  $NH_2$  substitution on the triple bonded systems for strong field ionization perpendicular to the molecular axis (*x* and *y* directions) and parallel to the molecular axis (*z* direction). The effect of  $NH_2$  substitution is relatively small for ionization perpendicular to the axis, changing the average ionization yield by approximately 20% or less. However, along the molecular axis,  $NH_2$  substitution has a much larger effect, changing the ionization yield by a factor of 2.5 for HCCH to  $H_2N$ –CCH, 4.3 for HCN to  $H_2N$ –CN, and 1.7 for HCC–CN to  $H_2N$ –CC–N. Sub-

	IP (eV) (ΔSCF)	IP (eV) (OVGF)	IP (eV) (experimental <sup>a</sup> )	Maximum yield (%) $(E_{\text{max}} = 0.04 \text{ au})$	Maximum yield (%) $(E_{\text{max}} = 0.08 \text{ au})$	Maximum yield (%) $(E_{\text{max}} = 0.12 \text{ au})$
HC≡N	13.28	13.88	13.71	0.42	15	73
$HC \equiv C - C \equiv N$	10.50	11.87	11.56	1.7	32	92
HC≡CH	10.18	11.46	11.40	2.2	59	96
$H_2N-C=N$	9.43	10.59	10.4	1.6	30	79
$H_2N-C\equiv C-C\equiv N$	8.44	9.66		4.3	54	88
$H_2N-C=CH$	7.77	8.99		9.2	72	99

Table 1. Calculated ionization potentials (IP) and maximum ionization yields as a function of maximum field strength.

aFrom http://webbook.nist.gov/chemistry/.

**Table 2.** Effect of NH<sub>2</sub> substitution on ionization yield for directions parallel and perpendicular to the molecular axis ( $E_{max} = 0.08$  au).

	Yield (%) in the x direction	Yield (%) in the y direction	Yield (%) in the z direction
HC≡CH	59	59	24
$H_2N-C=CH$	67	52	60
HC≡N	15	15	7
$H_2N-C=N$	21	15	30
$HC \equiv C - C \equiv N$	26	26	32
$H_2N-C \equiv C-C \equiv N$	25	22	54

stitution by  $\rm NH_2$  increases the conjugation length along the molecular axis, but does not alter molecular dimensions perpendicular to the molecular axis. When the laser polarization is parallel to the molecular axis, this increased conjugation length may allow for enhanced electron dynamics during ionization, which could contribute to the greater ionization yield seen in the simulations.

#### Summary

Time dependent configuration interaction with an absorbing boundary has been used to simulate the strong field ionization of a series of triple bonded systems: HCN, HCCH, HCC-CN and H<sub>2</sub>N-CN, H<sub>2</sub>N-CCH, H<sub>2</sub>N-CC-CN. The shape of the highest occupied orbital dominates the angular dependence of the ionization yield at low intensities. At higher intensities, ionization also occurs from lower lying orbitals, as judged by the angular dependence and population analysis of the TDCI wavefunction. Comparing HC-C-CN with HCCH and HCN shows that increasing the conjugation length increases ionization yield parallel to the molecular axis relative to the yield perpendicular to the axis. NH<sub>2</sub> substitution substantially increases the ionization yield along the molecular axis, but has only a small effect for directions perpendicular to the axis. The greater ionization yield parallel to the molecular axis with increased conjugation length and with NH2 substitution may be due to enhanced electron dynamics along the long axis of the molecules.

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