Angular Dependence of Strong Field Ionization of Haloacetylenes HCCX (X = F, Cl, Br, I), Using Time-Dependent Configuration Interaction with an Absorbing Potential

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ABSTRACT: Strong field ionization of haloacetylenes was simulated by time-dependent configuration interaction using all single excitations and a complex absorbing potential. The angular dependence of ionization for HCCX was mapped with static electric fields in the range 0.01−0.06 atomic units and compared with the results for CH3X. HCCF ionizes primarily from the CC π orbital. HCCX (X = Cl, Br, I) compounds show increasing amounts of ionization from the halogen π-type lone pair orbitals and have a node perpendicular to the molecular axis. These shapes can be understood in terms of the energies and interactions of the halogen π-type lone pairs with the π orbitals of the CC triple bond.

INTRODUCTION

The interaction between intense light and matter is dominated by electron dynamics. Recent advances in attosecond laser pulses have made it possible to study these dynamics on their natural time scale.1−3 Early work in the field of attoscience showed that the ionization rate for CO and N2 differed for molecules aligned with the field versus molecules perpendicular to the field.4−6 Further studies have shown an angular dependence of ionization for CO2, butadiene, and other polyatomic molecules.6−10 The impact of the orientation of a molecule in the laser field on electron dynamics can also be deduced from high harmonic generation (HHG) spectra. Orbital tomography and HHG can be used to determine the shape of the highest occupied molecular orbital (HOMO).11 Lower lying orbitals have also been found to contribute to HHG spectra at high intensities.12−17

For smaller molecules, the nodal structure of the molecular orbitals serves as a qualitative indicator of the angular dependence of ionization. For ionization in the tunneling regime, a better description can be obtained using molecular Ammosov−Delone−Krainov (ADK) theory.18,19 Solving the time-dependent Schrödinger equation (TDSE) provides a more quantitative description of angular dependence of ionization and HHG spectra. The TDSE can be solved utilizing approximations such as single active electron, quantitative rescattering theory, time-dependent resolution in ionic states, time-dependent analytical R-matrix, and time dependent generalized active space configuration interaction.20−24 In previous studies, we examined the angle dependence of various small molecules using a time-dependent configuration interaction (TDCI) approach with a complex absorbing potential (CAP).25−31 In addition to a standard molecular basis, like aug-cc-pVTZ, the TDCI-CAP calculations need a large number of diffuse functions (which we termed the absorbing basis) to describe the electron density between the valence region and the complex absorbing potential (CAP).

A larger absorbing basis is needed for heavier elements, and this was developed using the methyl halides as a test case.31 Halogenated organic molecules have been the focus of several recent strong field studies.32−36 Of particular interest for this study is the measurement of the electron dynamics of charge migration in iodoacetylene. It was found that the orientation of the molecule relative to the field made a significant contribution to the control over charge migration.37 Dissociative single and double ionization of methyl iodide has recently been studied using 3D two-electron angular streaking (3D-2eAS) with double and quadruple coincidence detection of electrons and ions.38 TDCI-CAP calculations were used to identify the relative contributions of the multiple orbitals involved in the single and double ionization of CH3I and its subsequent fragmentation. A similar study of iodoacetylene is underway. In the present work, we use the TDCI-CAP method to examine the angular dependence of ionization and orbital contributions for the series of halogenated acetylenes HCCX (X= F, Cl, Br, or I) and compare the results to the corresponding series of methyl halides, CH3X. These calculations provide the background needed for the analysis of the 3D-2eAS study of iodoacetylene.

METHODS

The electron dynamics in a strong field were simulated by solving the TDSE using the time-dependent configuration interaction approach with a complex absorbing potential, TDCI-CAP,

\[
\frac{\partial}{\partial t} \Psi_{\text{el}}(t) = \left[ \hat{H}_{\text{el}} - \hat{\mu} \cdot \vec{E}(t) - i \vec{V}_{\text{absorb}} \right] \Psi_{\text{el}}(t)
\]

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The angular dependence of ionization for the haloacetylenes is shown in panel a of Figures 2–5. For HCCF, the result is essentially cylindrical with a node along the molecular axis in the +Z and −Z directions. By contrast, the plots for HCCX (X = Cl, Br, I) show an additional node perpendicular to the molecular axis, resulting from the interaction of the halogen orbitals of the CC triple bond. For HCCX, the ionization rate is larger for the CC component; for HCCI, the rates for the CC and bromine component are similar; for HCCBr, the rates for the CC and bromine component are similar.

**RESULTS AND DISCUSSION**

The angular dependence of ionization for the haloacetylenes is shown in panel a of Figures 2–5. For HCCF, the result is essentially cylindrical with a node along the molecular axis in the +Z and −Z directions. By contrast, the plots for HCCX (X = Cl, Br, I) show an additional node perpendicular to the molecular axis, resulting from the interaction of the halogen \( \pi \)-type lone pairs with the \( \pi \) orbitals of the CC triple bond. For HCCCI, the ionization rate is larger for the CC component; for HCCBr, the rates for the CC and bromine component are similar;
for HCCI, the iodine dominates. HCCCl and HCCBr also have significant ionization rates from the halogen end along the molecular axis. All of the haloacetylenes show a node in the ionization rate along the molecular axis at the hydrogen end of HCCX.

The trends in the shapes of the ionization rates for haloacetylenes are similar to the trends in the shapes for the haloacetylenes. CH$_3$F is dominated by ionization from the methyl group (Figure 3 of ref 31). For CH$_3$Cl and CH$_3$Br, there are increasing contributions from the halogen lone pair orbitals to the ionization rate (Figures 4 and 5 of ref 31). For CH$_3$I, ionization to the lowest energy cation is dominated by the iodine with very little contribution from the methyl group (Figure 6 of ref 31).

Mulliken population analysis can be used to obtain the orbital contributions to the angular dependence of the ionization rates. The contributions of the degenerate π HOMO to the ionization rate are illustrated in panel b of Figures 2–5; the molecular orbitals are shown in panel c of these figures. In HCCF, the HOMO has a small component from the fluorine, but this does not contribute significantly to the ionization rate. The component of the halogen π-type lone pairs in the HOMO of HCCX increases as X is incremented from Cl to Br to I. Because the HOMO is an out-of-phase combination of the CC π orbital and the halogen π-type lone pair orbitals, the HOMO has a node perpendicular to the molecular axis. As a result, the
The ionization rate also has a node perpendicular to the molecular axis. The contributions from HOMO−1 and HOMO−2 are much smaller than the contribution from HOMO.

The ionization yields as a function of the electric field are shown in panel d of Figures 2–5, along with the orbital components. Perpendicular to the molecular axis (X direction), the ionization yields are dominated by the HOMO, with almost no contributions from HOMO−1 or HOMO−2. Along the molecular axis, the ionization rate is higher from the halogen end of the molecule (+Z direction) than from the hydrogen end (−Z direction). In the +Z direction, the contributions of HOMO to the ionization dominate, but the contributions from HOMO−1 increase from X = Cl to Br to I. For a given field strength, the trend in the ionization rate is F < Cl < Br < I, as expected from the energies of the HOMO.

The analysis of angular dependence of the ionization rate for HCCX and CH3X shows that it is governed by the shapes and energies of the highest occupied orbitals with some contributions from HOMO−1. The energies of the π-type orbitals of HCCX and CH3X are shown in Figure 6, along with the energies for the π-type lone pairs of atomic X (ROHF calculation with the same basis set) and the π HOMOs of HCCH and CH4. Orbital π1 (HOMO) is formed from an out-of-phase combination of the π-type lone pair orbitals of the halogen and...
For CH₃X (X = Cl, Br, I), the energies of the halogen π-type lone pairs and a node perpendicular to the molecular axis. Ionization was found to occur primarily from the highest occupied molecular orbital, with smaller contributions from lower lying orbitals. The highest occupied orbitals are formed from halogen π-type lone pairs interacting with the π orbitals of the CC triple bond for HCCX and with the π orbitals of CH₃ for CH₃X. Because the π-type lone pair orbitals of fluorine are so much lower in energy than the π-type orbitals of CC or CH₃, fluorine does not contribute significantly to the highest occupied orbital or to the angular shape of the ionization. For X = Cl, Br, and I, the halogen lone pair orbitals are close enough in energy to the CC π orbitals to interact strongly. The out-of-phase interaction in the highest occupied orbital results in a node perpendicular to the molecular axis in the ionization yield. As the halogen is incremented from Cl to Br to I, ionization from the halogen end of the molecule becomes greater. For HCCX, the halogen lone pair orbitals are lower in energy than the CC π orbitals, and the shape of the ionization yield retains some CC character. For CH₃X, the halogen lone pair orbitals are higher in energy than the CH₃ π orbitals, and the shape of the ionization yield is dominated by the halogen lone pairs, especially for iodine.

### SUMMARY

The angular dependence of strong field ionization for halocetylenes was examined for static fields in the range of 0.01–0.06 atomic units. Simulations were carried out using time-dependent configuration interaction with single excitations and a complex absorbing potential. The results were compared to the angular dependence of strong field ionization of CH₃X using the same approach. HCCF ionized almost exclusively from the CC fragment; similarly, CH₃F ionized mainly from the CH₃ fragment. HCCX and CH₃X (X = Cl, Br, I) showed increasing amounts of ionization from the halogen π-type lone pairs and a node perpendicular to the molecular axis. Ionization was found to occur primarily from the highest occupied molecular orbital, with smaller contributions from lower lying orbitals. The highest occupied orbitals are formed from halogen π-type lone pairs interacting with the π orbitals of the CC triple bond for HCCX and with the π orbitals of CH₃ for CH₃X. Because the π-type lone pair orbitals of fluorine are so much lower in energy than the π-type orbitals of CC or CH₃, fluorine does not contribute significantly to the highest occupied orbital or to the angular shape of the ionization. For X = Cl, Br, and I, the halogen lone pair orbitals are close enough in energy to the CC and CH₃ π orbitals to interact strongly. The out-of-phase interaction in the highest occupied orbital results in a node perpendicular to the molecular axis in the ionization yield. As the halogen is incremented from Cl to Br to I, ionization from the halogen end of the molecule becomes greater. For HCCX, the halogen lone pair orbitals are lower in energy than the CC π orbitals, and the shape of the ionization yield retains some CC character. For CH₃X, the halogen lone pair orbitals are higher in energy than the CH₃ π orbitals, and the shape of the ionization yield is dominated by the halogen lone pairs, especially for iodine.

### REFERENCES


