Photoionization and Photofragmentation Dynamics of I$_2$ in Intense Laser Fields: A Velocity-Map Imaging Study

Published as part of The Journal of Physical Chemistry virtual special issue “Paul L. Houston Festschrift”.

Felix Allum,* Joseph McManus, Oskar Denby, Michael Burt, and Mark Brouard*

Cite This: J. Phys. Chem. A 2022, 126, 8577−8587

Received: June 23, 2022
Revised: October 21, 2022
Published: November 9, 2022

ABSTRACT: The photoionization and photofragmentation dynamics of I$_2$ in intense femtosecond near-infrared laser fields were studied using velocity-map imaging of cations, electrons, and anions. A series of photofragmentation pathways originating from different cationic electronic states were observed following single ionization, leading to I$^-$ fragments with distinct kinetic energies, which could not be resolved in previous studies. Photoelectron spectra indicate that these high-lying dissociative states are primarily produced through nonresonant ionization from several molecular orbitals (MO) of the neutral. The photoelectron spectra also show clear signatures of resonant ionization pathways (Freeman resonances) to low-lying bound ionic states via Rydberg states of the neutral moiety. To investigate the role of these Rydberg states further, we imaged anionic products (I$^-$) formed through ion-pair dissociations of neutral molecules excited to these Rydberg states by the intense femtosecond laser pulse. Collectively, these results shed significant new light on the complex dynamics of I$_2$ molecules in intense laser fields and on the important role of neutral Rydberg states in a full description of strong-field phenomena in molecules.

INTRODUCTION

In recent years, the interaction of molecules with intense femtosecond laser pulses has garnered considerable attention as they form the foundation of a range of experimental techniques that can be used to study ultrafast photochemistry and photophysics. Such techniques include Coulomb explosion imaging,1−14 high-harmonic spectroscopy,15−18 and laser-induced electron diffraction.11−14 A detailed understanding of the dynamics induced by intense fields is crucial to the development of these experimental approaches. However, the photoinduced dynamics of even the simplest molecules in intense laser fields may be very rich and complex,19 due to the range of processes which can be driven by the optical field. Such exotic phenomena include field-induced coupling and distortion of potential energy surfaces,16−18 charge-resonance enhanced ionization,19,20 dynamic and geometric alignment,11−23 and multielectron ionization dynamics.6,7,24−29

Studies into strong-field ionization of small molecules have demonstrated that ionization from deeper-lying orbitals than the highest-occupied molecular orbital (HOMO) may be significant.25 Ionization from these more strongly bound orbitals (HOMO−1, HOMO−2, etc.) leaves the molecular cation in electronically excited states and therefore predetermines, to a large degree, the nuclear dynamics (e.g., photodissociation pathways) following ionization. Such multielectron ionization dynamics were observed some time ago in N$_2$ using photoelectron spectroscopy,24 but they have since been observed in a series of molecules using various experimental techniques, such as photoelectron (coincidence) imaging,25−28 high-harmonic spectroscopy,6,7,29 and photoelectron angular streaking.26 Of particular interest to the current work is experiments that have established the connection between the ionized orbital and the photofragmentation dynamics observed following ionization. This includes a seminal study by Stolow and co-workers on n-butane and 1,3-butadiene using electron−ion covariance spectroscopy.30 In this work, by examining the above-threshold ionization (ATI) photoelectron spectra correlated to production of a specific photoion product, the role of ionizing to different ionic continua could be clearly interrogated. Recent work by Weinacht and co-workers,31 employing photoion−photoelectron coincidence imaging on the D$_2$O molecule could further distinguish different photofragmentation pathways leading to the same cation products with different kinetic
energy releases. The above-threshold photoelectron spectra correlated to different photofragmentation pathways encoded information about the ionization pathways in operation and how the ionization channel predetermined the ionic photofragmentation dynamics.

Here we study the dynamics of $I_2$ molecules subjected to intense femtosecond laser fields in the near-infrared (NIR) using velocity-map imaging (VMI). As $I_2$ consists entirely of heavy atoms, the role of nuclear motion during the laser field is minimized, and thus the photofragmentation dynamics can be expected to be dominated by the electronic states populated in the field. Recent work by Gibson and co-workers studied the strong-field induced fragmentation dynamics of $I_2$ also using VMI at a series of laser wavelengths. Distinct features in the kinetic energy distributions of $\Gamma$ fragments produced following single ionization were observed, and they were suggested to occur following excitation of deep-lying molecular orbitals of $I_2$. This assignment was strengthened by time-resolved measurements, which suggested that the relatively high velocity $\Gamma$ atoms observed originate from dissociative states populated directly in the laser field, not via population of the bound X and A states of the cation formed by ionization from the HOMO or HOMO−1.

In the present work, measurements with higher velocity resolution allows unambiguous distinction of at least six dissociative ionization channels, once more assigned to population of different electronic states of the $I_2^+$ cation producing fragments with different asymptotic velocities. Evidence for similar behavior underpinning the Coulomb explosion of higher parent charge states is also presented. Further experiments measuring photoelectron velocity distributions at a range of incident intensities are consistent with multiple nonresonant ionization pathways and additionally demonstrate the important role of Freeman resonances in this system. Assignments of several of the Rydberg states resonantly populated in the laser field are offered. Ion-pair dissociations from these neutral Rydberg states which may remain populated following the light−matter interaction are also studied through the detection of negative $\Gamma$ ions, which also show different photofragmentation pathways. To our knowledge, this is the first report of anion production from molecules in intense laser fields by this mechanism, but it may be expected to be a more general phenomena in (typically halogen containing) molecules with excited states of ion-pair character. Collectively, the results presented provide several new insights into the behavior of small molecules in intense laser fields, and furthermore establish $I_2$ as a fertile system for future study into molecular strong-field ionization and photofragmentation dynamics.

## EXPERIMENTAL METHODS

The experimental apparatus consists of a velocity-map imaging spectrometer, as has been described in previous work, operating in the conventional velocity-map imaging configuration. The $I_2$ sample was prepared by diluting the room temperature vapor pressure of solid $I_2$ in helium, to a total pressure of 1–2 bar (≈0.02% $I_2$). This mixture was introduced into the spectrometer as a pulsed molecular beam, using a Series 9 General Valve. Following collimation through a skimmer, the molecular beam passes through into the spectrometer’s interaction region. The fundamental pulsed output (800 nm, ≈40 fs duration) of a commercial Ti:sapphire amplifier (Spectra-Physics Solstice Ace) was used to initiate ionization. The pulses were variably attenuated by adjusting the angle of a λ/2 waveplate installed prior to a thin film polarizer. The transmitted beam was then focused by a 200 mm focal length lens into the interaction region of the spectrometer, perpendicularly intersecting the molecular beam. The peak intensity at the focus was varied in the range 30–120 TW cm$^{-2}$.

Nascent charged particles were accelerated by velocity-mapping fields to a time- and position-sensitive detector consisting of dual stacked microchannel plates (MCPs) coupled to a P47 phosphor screen. For the data presented in this work, the spectrometer was either operated in a positive potential mode to image positively charged ions or in a negative potential mode to image electrons and anions. In both cases, voltages were applied to the repeller and extractor electrodes in a 1:0.886 ratio, with other electrodes held at ground. For the majority of the data presented in the manuscript, an absolute voltage of 8 kV was applied to the repeller, while to record a high quality image of the low velocity $\Gamma$ ions discussed later in the manuscript, the repeller voltage was lowered to −1 kV. The impact of each accelerated particle at the detector produced a flash of light, which was imaged by a fast timestamping camera, the Pixel Imaging Mass Spectrometry (PImMS2) camera. This allowed the time and position of each event to be determined, enabling all particles of a given charge to be imaged in a single acquisition, with the timing of the event indicative of the particle’s mass-to-charge ratio. Images were acquired over tens of thousands of laser cycles. The experiment was operated at 10 Hz, due to limitations on the repetition rate at which the PImMS2 camera can acquire data. The recorded images, gated over a given m/z peak, represent a two-dimensional projection of the three-dimensional scattering distribution. Abel inversion of these images using the pBASEX algorithm was used to reconstruct the underlying three-dimensional velocity distribution, from which kinetic energy distributions were derived. It is important to note that under velocity-mapping conditions, signal arising from particles with very low velocity (such as parent ions) is mapped to a very small region of the detector. This leads to overlapping clusters of bright pixels recorded by the PImMS camera, and thus individual ion hits can no longer be correctly identified by the hitfinding algorithm. Furthermore, as pixels in the PImMS camera can only register four events per acquisition cycle, pixels at the center of the detector are susceptible to saturation by lighter fragments (which arrive prior to the $I_2^+$ ion) with low velocity, such as $H_2O^+$ background. In Figure 8a), these effects reduce the signal in the $I_2^+$ ion. To obtain more quantitative mass spectra, data was also recorded with spatially defocusing ion optics voltages, as presented in Figure S3 in the Supporting Information.

In order to determine the peak laser intensity at a given pulse energy, and also calibrate the VMI images, argon gas was ionized at a range of laser pulse energies. At each pulse energy, photoelectron spectra were recorded by operating the spectrometer in negative potential mode. From the observed ponderomotive shifts of the ATI peaks observed as a function of pulse energy, a reliable calibration to peak laser intensity could be made. The spacing of the ATI peaks observed (≈1.55 eV, the photon energy) was also used to calibrate the energy scale of the velocity-map images.
RESULTS

Photoion Imaging. An example velocity-map image for the I’ photoion is shown in Figure 1a), while the corresponding total Kinetic Energy Release (KER) spectrum is displayed in Figure 1b) (blue line). At least six distinct features arising predominantly from dissociation of I’ into Π+1 are observed, and labeled I–VI in order of increasing radius (i.e., I’ velocity). Signals at higher radius than feature VI originate from Coulomb explosion of multiply charged parent ions. This is confirmed conclusively through ion–ion covariance analysis (shown in the Supporting Information), and these Coulomb explosion channels will be discussed later in the manuscript. A very sharp feature at zero radius is also seen in the recorded image, which arises from undissociated I’ ions, which have identical mass-to-charge ratio as the I’ ions, but are produced with essentially zero KER, as observed previously. Immediately, the observation of a multitude of distinct photofragmentation pathways is surprising. In a previous velocity-mapping study of this system, some structure in the velocity distributions was observed, but the series of features could not be fully resolved. As discussed in more detail in the Supporting Information, we believe this is due to superior velocity resolution achieved in the current work.

If considering the photoionization process as a vertical excitation in the Franck–Condon region, the existence of these different channels implies that several dissociative electronic states of I’ are produced following ionization and/or different product channels (i.e., electronic states of the I’ or I photofragments) are accessed. Further insights into the photoexcitation and fragmentation dynamics can be gained by examining the KER distribution of I’ ions, shown in Figure 1b). The overall spectrum may be fit to a series of Gaussian contributions representing the dissociation pathways (with an additional peak at almost zero KER to account for the aforementioned I’ contribution). The parameters for these Gaussian fits (centers, amplitudes and standard deviations) are given in Table 1. Removal of the HOMO or HOMO−1 electrons yield I’ in the bound 2Πg3/2,1/2 and 2Πu3/2,1/2 states.48

Ionizing the HOMO−2 to give I’ in the 2Σu+ state does lead to dissociation, but only to very low KER fragments (0–0.15 eV).34 The states which can lead to the observed higher KER channels therefore involve ionization of rather strongly bound orbitals of I2.

Precisely assigning the origins for these different photo-dissociation channels is challenging, as there are a multitude of dissociative electronic states which may be populated (and which are not fully characterized in the literature) and various product channels to which these states could correlate. The vertical ionization energies to several cationic states have been measured previously using electron momentum spectroscopy and photoelectron spectroscopy. Thus, asymptotic KERs for dissociation pathways can be predicted from energy conservation considerations using these vertical ionization energies along with known possible product internal energies:

\[ \text{KER} = \text{VIE} - (E_1 + E_{I'}) + I_p + D_1 \] (1)

where VIE is the relevant vertical ionization energy of I2, E1 and E1− are the internal energies of the I and I’ photoproducts respectively, I_p is the ionization potential of ground-state I atoms (10.45 eV), and D_1 is the dissociation energy of I_2 (1.54 eV). This description neglects the possibility of neutral dissociation prompted by (multiple) 800 nm photon absorption, followed by ionization of the resulting neutral iodine fragments. Given the short pulse duration employed in the current study, and the expected difficulty in populating low-lying dissociative states of I_2 at 800 nm, we do not think such a process is a likely pathway. We note that this may not be the case at other wavelengths, as suggested by a previous study using intense 100 fs 610 nm fields, where neutral dissociation could be initiated on the neutral B state.44

Figure 2 compares the experimental KER distribution with KERs predicted using Equation 1. The predicted KERs are labeled according to the electronic state of the I_2 (using the labeling of refs 49 and 50) and the states of I and I’ products. A more detailed description of the KER prediction is given in the Supporting Information, including the electronic state of the I and I’ photoproducts associated with each dissociation limit (D1, D2, D3, etc.). It should be stressed that further work is required to identify the precise origins of the different electronic states of I and I’.55

Table 1. Parameters from the Fit of the I’ KER Distribution, as Shown in Figure 1b)

| channel | center (eV) | width (σ) (eV) | amplitude |
|---------|------------|----------------|-----------|
| I       | 0.23 ± 0.01| 0.05 ± 0.01    | 0.83 ± 0.11|
| II      | 0.43 ± 0.01| 0.08 ± 0.01    | 0.80 ± 0.07|
| III     | 0.93 ± 0.02| 0.26 ± 0.03    | 0.92 ± 0.04|
| IV      | 1.71 ± 0.02| 0.22 ± 0.03    | 0.97 ± 0.05|
| V       | 2.53 ± 0.05| 0.30 ± 0.07    | 0.74 ± 0.05|
| VI      | 3.37 ± 0.18| 0.31 ± 0.21    | 0.23 ± 0.05|

*Errors shown are statistical (1σ) fitting errors.*
fragmentation pathways observed in the current work. In particular, a more comprehensive theoretical characterization of the many low-lying electronic states of the I$_2$ cation would be invaluable. With this said, the comparisons shown in Figure 2 are informative. For instance, it can be seen that predicted dissociation channels from a single excited electronic state of I$_2^+$ are insufficient to explain the experimental observations, suggesting that multiple highly excited electronic states contribute to the strong-field fragmentation of I$_2^+$, supporting the claims made by previous work. The energetic widths of the different features (which can only be assessed with the higher-resolution measurements reported here) is also richly informative. Channels I and II exhibit significantly narrower KER distributions. This suggests that these dissociation pathways originate from cation potentials that are relatively shallow in the Franck–Condon region. Future work could aim to directly characterize the electronic states of the neutral I atom dissociation products for instance by photoelectron spectroscopy using a vacuum ultraviolet (VUV) pulse, to enable the definite assignment of dissociation pathways.

Figure 2. Comparison between the experimental (blue) and fitted (red) I$^+$ KER distributions with predicted KERs for a range of possible fragmentation pathways, for different combinations of I$_2^+$ states (A, B, C, C$_p$, D) and product electronic states (D$_1$, D$_2$, D$_3$, etc.). These predictions are discussed in more detail in the main text.
Finally, we consider the angular distributions associated with the VMI image shown in Figure 1a, which are plotted in Figure 5. The angular distributions associated with the I–VI channels are shown in Figure 5. The intensity distributions for all the dissociation channels peak along the laser polarization axis, as is typically observed in strong-field ionization fragmentation dissociation, due to geometric and dynamic alignment effects. There are, however, differences in the angular distributions of the different photofragmentation channels. In particular, channels I and II exhibit a “four-lobed” angular distribution, with local maxima either side of the laser polarization axis. Similar behavior was observed in a previous VMI study by Vrakking and co-workers (although individual channels could not be resolved as in the current work), and assigned to further ionization of molecules most strongly aligned to the laser polarization axis, causing a slight depletion in the yield of these ions very close to the laser polarization axis. This explanation is consistent with the observation that these channels become relatively less prominent at higher peak laser intensities (as seen in Figure 3). Other possible origins for the observed four-lobed angular distributions may include the combination of parallel and perpendicular transitions or tunneling from II orbitals.

Photoelectron Imaging. In order to shed more light on the photoionization dynamics which underpin the photofragmentation dynamics of I$_2^+$ in strong fields, we turn to photoelectron spectroscopy. Figure 6 shows an example photoelectron image recorded following irradiation of I$_2$ with 35 TW cm$^{-2}$ NIR pulses, in which single ionization was the dominant process. Contributions from ionization of background gases (O$_2$, N$_2$, H$_2$O) have been subtracted. In addition to indistinct signal spread over a broad range of energies, a number of sharp features are observed, several of which are labeled by their electron kinetic energy. The two most dominant features are observed at 0.71 and 1.01 eV, with further features occurring at approximately 1.55 eV (the photon energy) higher electron kinetic energy (eKE), arising from the next ATI order. Nonresonant ionization features are blurred by differing ponderomotive shifts of the ionic continua within the intensity profile of the focused pulse. Features with well-defined eKE are indicative of Freeman resonances—ionization via a resonant excitation state to a Stark-shifted Rydberg state. Since their first observation in rare gas atoms, Freeman resonances have since been identified in a series of species, including several small molecules.
In order to further examine the role of resonant and nonresonant ionization pathways, photoelectron images were recorded over a range of peak laser intensities, results of which are shown in Figure 7. At the intensity range studied, single ionization of I$_2$ was dominant, mainly producing stable I$_2^+$ or low velocity I$^+$ as observed in ion mass spectra. Except for the sharp features originating from Freeman resonances, the photoelectron kinetic energy spectra are generally rather structureless, with no clear peaks from individual nonresonant ionization pathways. Ionization to a single continuum would give rise to a series of broad ATI peaks. The absence of such structure can be understood if there are several prominent nonresonant ionization pathways to different ionic continua. The general structure of the recorded photoelectron spectra suggests that direct ionization of deep-lying MOs is a major contributor to the observed cation photofragmentation pathways, as opposed to initial ionization to lower-lying states of the cation which are then further excited in the field.

While the majority of the photoelectron signal in Figure 7 can be assigned to nonresonant ionization to multiple ionic continua, several sharp features are present on top of this broad signal. Such features, whose positions do not vary, are indicative of Freeman resonances, as mentioned previously. Under the assumption that the neutral Rydberg state and the final cationic state experience the same ponderomotive shifts, electron kinetic energies are determined by the field-free (rovibonic) energies of the intermediate Rydberg state $E_{\text{Rydberg}}$, the ion state $E_{\text{ion}}$, and the number of photons absorbed in the ionization step, $n$:  

$$T_e = n\hbar\nu - (E_{\text{ion}} - E_{\text{Rydberg}})$$

(2)

In principle, differences in vibrational energy between the ion and intermediate Rydberg state would lead to a broadening of the photoelectron spectrum. However, there is a very strong propensity for ionizations where $\Delta v = 0$ due to near-perfect Franck–Condon overlap, and the vibrational constants of ionic and Rydberg states are very similar. As such, Freeman resonances lead to sharp photoelectron kinetic energy distributions, even in molecules.  

Figure 7c compares the laser intensity-averaged photoelectron spectrum and predicted electron kinetic energies using eq 2 for literature energies of high-lying Rydberg states with even $l$ converging on the $^3\Sigma_{g\pm1}$ ground state of I$_2^+$, measured by (2 + 1) Resonance-Enhanced Multiple Photon Ionization Spectroscopy (REMPI).  

While resonant contributions to ionization to other excited states of the cation are likely to occur, we focus solely on the ionic ground state, which we believe is responsible for the most common resonant...
ionization pathways at these low peak laser intensities. Contributions from odd \( l \) Rydberg states can be neglected, as the \( ^1\Sigma_g^+ \) ground state of \( \text{I}_2 \) can only couple to \( g \) (\( u \)) parity excited states when absorbing an even (odd) number of photons.\(^{57}\) Odd \( l \) Rydberg states would therefore need to experience a greater ponderomotive shift to bring them into a 7-photon resonance, relative to the shift required to bring the even \( l \) states into a 6-photon resonance to contribute to any resonant ionization processes. For Rydberg states which are consistent with the observed photoelectron energies, intensities of \( \sim 30–40 \text{ TW cm}^{-2} \) are required to bring them into 7-photon resonance. The fact that all the prominent resonant features are still observed strongly at 35 TW cm\(^{-2}\), suggest that contributions from odd \( l \) Rydberg states are not significant. To confirm this conclusively, extension of the present study to lower peak intensities would be required.

Good agreement is seen between the predictions and the observed peak positions in the experimental spectrum, especially for the two most prominent Freeman resonances, matching predictions for ionization via the 6d and 7d molecular Rydberg states. \( \text{Figure 7} \) also shows that the main Freeman resonances are observed at all the peak intensities studied. This is consistent with calculating the ponderomotive shift (and therefore minimum laser intensity) required to shift these Rydberg levels into 6-photon resonance with the 800 nm field. These intensities are given in \( \text{Table 2} \), and are all lower than the lowest peak intensity used in the current study. To further disentangle the resonant ionization pathways, it would be interesting to examine lower peak intensities (which was challenging in the present study due to low signal rates), to access intensity regions at which certain Freeman resonances cannot occur. This would strengthen the current assignment, and could potentially allow the identification of other resonant features in the photoelectron spectrum. For instance, in the spectra shown in \( \text{Figure 7} \) there are indications of sharp peaks in the 0–0.7 eV which are not assigned in the current work.

We would like to stress that the \( \text{II} \) molecular cations formed by resonant ionization will remain bound, in the absence of any postionization excitation. While resonant ionization gives very clear signatures in the photoelectron spectra, the majority of ionization occurs nonresonantly, and is believed to be responsible for the dissociative cationic states. A relatively small, but still significant portion of ionization to bound cationic states is consistent with the yield of \( \text{I}_2^+ \) in the ion mass spectra (shown in \( \text{Figure S3} \) of the Supporting Information).

A promising avenue for future work would be to image photoelectrons and photoions in coincidence (or covariance\(^{30,49,72}\)), and to study the photoelectron spectra correlated to individual dissociation channels. As demonstrated in the recent work of Weinacht and co-workers studying strong-field ionized \( \text{D}_2 \text{O} \) channel-resolved ATI spectra would show characteristic shifts for the different electronic states involved, if these states are populated directly following ionization.\(^{51}\) Employing such a scheme to determine the photoelectron spectrum correlated to the individual photofragmentation channels of \( \text{I}_2^+ \) observed in the present work could therefore be particularly illuminating. Such an experiment would determine the important relationship between which MO is ionized and the ultimate photofragmentation pathway.

**Photoion Imaging.** The photoelectron data presented in the current work establishes the important role of intermediate Rydberg states of the neutral during the strong-field ionization of \( \text{I}_2 \). This raises the question of whether any neutral Rydberg states remain populated after the pulse. Previously it has been established that, following interaction with an intense laser field, population may remain “trapped” in high-lying neutral Rydberg states.\(^{73,74}\) A common explanation for this phenomenon is the high centrifugal barrier such Rydberg states may possess due to their high angular momentum. In the case of molecules, these Rydberg states may have important consequences for the ultimate photofragmentation dynamics, for instance in producing neutral atomic Rydberg fragments following dissociation of these molecular Rydberg states (as observed in \( \text{H}_2 \)\(^7\) and \( \text{O}_2 \)\(^7\)). In the case of \( \text{O}_2 \), recent work has identified dissociation channels of molecular Rydberg states specifically populated by resonant multiphoton excitation.\(^{76}\)

To identify possible consequences of resonantly excited neutral molecular Rydberg state population in \( \text{I}_2 \), we turn to the extensive literature on the properties of \( \text{I}_2 \) Rydberg states. It has been well established that many such Rydberg states act as “doorways” to ion-pair states\(^{37,39,48,70,78,79}\) which, assuming the dissociation of the ion-pair state is exceeded, can produce \( \text{I}^- + \text{I}^- \) photofragment pairs. Baklanov and co-workers have recently conducted nanosecond\(^{56}\) and femtosecond\(^{38}\) velocity-map imaging studies on the photofragmentation dynamics of 6d Rydberg states of \( \text{I}_2 \). These experiments identified a number of dissociation channels mediated by ion-pair states, either directly to ion pair products or to electronically excited atoms through lower-lying Rydberg states. As the photoelectron spectra shown in \( \text{Figure 7c} \) exhibit prominent features assigned to ionization via 6d (and higher) Rydberg states, like those studied by Baklanov and co-workers, we conducted a search for anionic products from ion pair dissociations.

When operating the VMI spectrometer in negative potential mode in order to image photoelectrons, photoanions are also accelerated under velocity-mapping conditions. The use of a fast timestamping camera allows the simultaneous imaging of photoelectrons and photoanions, with the latter recorded at significantly later times-of-flight than the prompt electron signal. We observe a (very weak) signal from anions, specifically the \( \text{I}^- \) ion, which we believe originates from ion-
pair dissociations from neutral Rydberg states. Figure 8a) compares the time-of-flight spectrum recorded for I$_2$ under

![Image](https://example.com/image.png)

Figure 8. Summary of the photoanion imaging data. (a) Time-of-flight spectra for I$_2$ upon irradiation by the 800 nm laser at a peak intensity of 60 TW cm$^{-2}$, with the spectrometer operating in positive (red) and negative (blue) voltage mode. (b) Expanded view at the time-of-flight region corresponding the I$^+$ ion. By multiplying the negative voltage signal by a factor of 1000, a clear peak corresponding to the I$^-$ ion is seen. (c) VMI image of the I$^-$ ion. (d) KER distribution for the I$^-$ ion extracted by Abel inversion of the VMI image.

which may be due to an increased probability for photodetachment, or an increased probability for ionization of the Rydberg state.

Panel c shows the image associated with the I$^-$ ion. For this data, the absolute voltage of the repeller was reduced to magnify the image associated with the I$^-$ ions, which are produced with low velocity. In contrast to the cation and electron images produced, the I$^-$ image is essentially isotropic. There are also indications of channels with distinct kinetic energies, as highlighted in panel d, which displays the KER distribution extracted from Abel inverting the image shown in panel c. A very sharp feature with zero KER is observed, along with a peak at $\sim$0.03 eV KER, and a far broader peak centered at $\sim$0.25 eV KER.

Previous work studying anion production from gas-phase molecules in intense laser fields is scarce. Molecular and fragment anion formed by irradiating small molecules (CO$_2$, CS$_2$, O$_2$) in intense laser fields has been reported in one study, an observation assigned to attachment by low energy electrons produced in the field. In this previous study, both parent and fragment anions were observed, believed to come from nondissociative and dissociative electron attachment, respectively. The fact that, in the current work, only I$^-$ ions are seen implies a different origin, as does the fact that, under the conditions of our experiment, no anions are produced from any background gases (O$_2$, N$_2$, H$_2$O), or from the Ar sample used to calibrate the spectrometer.

The isotropic I$^-$ velocity distribution seen in Figure 8c would be expected if the Rydberg states are populated via intermediate states of different symmetries, or if ion-pair dissociation is rather slow relative to the time scale of molecular rotation (albeit fast relative to the microsecond time scale of the time-of-flight measurement). This may be due to the time taken for population transfer from the initially prepared (bound) Rydberg states to the relevant dissociative ion-pair states. Recent work studying the dissociation dynamics of I$_2$ 6d Rydberg states populated by two-photon absorption in the ultraviolet have identified several such predissociation pathways with picosecond lifetimes. This study reported I$^-$/I$^+$ ion-pair dissociation products with $\sim$0.25 eV KER and an approximately isotropic angular distribution, in qualitative agreement with the higher KER feature observed in Figure 8, parts c and d. The significant broadness of this feature in the current data, in addition to the additional channels at much lower KER suggest the existence of multiple ion-pair dissociations, consistent with the observation of several Rydberg states of higher energy than the 6d the photoelectron spectra (Figure 7c).

Future work more thoroughly exploring this proposed pathway for anion production in intense laser fields would be of great interest, for instance by extending the current study to other small halogen-containing molecules or to study anion formation and subsequent photodetachment in a time-resolved manner. A thorough study of the dependence of the ion-pair dissociation KER spectra on laser intensity and pulse duration may also be illuminating, to assess how Stark shifts of the high-lying Rydberg states and the ion-pair states affect the dissociation dynamics. The single-sided velocity-map imaging spectrometer used here can only be used to measure either cations or anions in a given experimental cycle. In principle, future work using a dual-sided velocity-map imaging spectrometer could record anions and cations in coincidence. The coincident detection of I$^-$ and I$^+$ anions with equal and
opposite momenta would conclusively determine their origin as ion-pair dissociations of neutral I₂ molecules. In practice such measurements may be challenging however, given the vast overlapping background of I⁺ ions formed by cation fragmentation.

**CONCLUSIONS**

In conclusion, we have presented an experimental study of the photoionization and photofragmentation of I₂ molecules in intense femtosecond NIR laser fields, which reveal a range of interesting and complex dynamics. In particular, many different ionization pathways are believed to be in operation, leaving the I⁺ cation in multiple electronic states, as evidenced by distinct features in the ion KER distributions. At higher peak laser fields, Coulomb explosion of multiply charged parent ions is observed. The structures of the associated kinetic energy distributions again imply the existence of multiple fragmentation pathways originating from different electronic states. Photoelectron measurements provide supporting evidence that direct nonresonant ionization from several deeply bound MOs is responsible for these fragmentation channels. Clear photoelectron signal assignable to resonant ionization to low-lying, bound cationic states was also observed, and several intermediate Rydberg states identified. Interestingly, I⁻ anions were detected, which originate from several ion-pair dissociation pathways of these Rydberg states which can remain populated in the field. This is the first observation of anion production in intense laser fields by this mechanism, but may be a more general phenomena in molecules with strongly coupled Rydberg and ion pair states.⁷⁹

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.2c04379.

Detailed comparison of the I⁺ image to that reported in the literature, a summary of additional covariance imaging analysis, detailed description of the predicted KERs for I₂⁺ dissociation channels, an example of an ion mass spectrum, and further analysis of the laser intensity-dependent cation and anion imaging data (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

Felix Allum — Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, U.K.; Present Address: PULSE Institute, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025; orcid.org/0000-0002-8044-8969; Email: fallum@stanford.edu

Mark Brouard — Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, U.K.; orcid.org/0000-0003-3421-0850; Email: mark.brouard@chem.ox.ac.uk

Authors

Joseph McManus — Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, U.K.; orcid.org/0000-0002-7911-2042

Oskar Denby — Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, U.K.

Michael Burt — Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, U.K.; orcid.org/0000-0002-7317-8649

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.jpca.2c04379

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We gratefully acknowledge the support of EPSRC Programme Grants EP/L005913/1 and EP/V026690/1. M.Bu. gratefully acknowledges the support of EPSRC Grants EP/S028617/1 and EP/L005913/1. A CC-BY licence is applied to the author accepted manuscript arising from this submission, in accordance with UKRI open access conditions.

**REFERENCES**

(1) Stapelfeldt, H.; Constant, E.; Corkum, P. B. Wave Packet Structure and Dynamics Measured by Coulomb Explosion. Phys. Rev. Lett. 1995, 74, 3780–3783.

(2) Allum, F.; Burt, M.; Amini, K.; Boll, R.; Köckert, H.; Oshin, P. K.; Bari, S.; Bomme, C.; Braufé, F.; Cunha de Miranda, B.; et al. Coulomb explosion imaging of CH₄ and CH₃Cl photodissociation dynamics. J. Chem. Phys. 2018, 149, 204313.

(3) Ding, X.; Forbes, R.; Kühel, M.; Lee, K. F.; Spanner, M.; Naumov, A. Y.; Villeneuve, D. M.; Stolow, A.; Corkum, P. B.; Staudte, A. Threshold photodissociation dynamics of NO₂ studied by time-resolved cold target recoil ion momentum spectroscopy. J. Chem. Phys. 2019, 151, 174301.

(4) Endo, T.; Neville, S. P.; Wanie, V.; Beaulieu, S.; Qu, C.; Deschamps, J.; Lassonde, P.; Schmidt, B. E.; Fujise, H.; Fushitani, M.; et al. Capturing roaming molecular fragments in real time. Science 2020, 370, 1072–1077.

(5) Itatani, J.; Levesque, J.; Zeidler, D.; Niikura, H.; Pépin, H.; Kieffer, J. C.; Corkum, P. B.; Villeneuve, D. M. Tomographic imaging of molecular orbitals. Nature 2004, 432, 867–871.

(6) Li, W.; Zhou, X.; Lock, R.; Patchkovskii, S.; Stolow, A.; Kapteyn, H. C.; Murnane, M. M. Time-Resolved Dynamics in N₂O4 Probed Using High Harmonic Generation. Science 2008, 322, 1207–1211.

(7) Smirnova, O.; Mairesse, Y.; Patchkovskii, S.; Dudovich, N.; Villeneuve, D.; Corkum, P.; Ivanov, M. Y. High harmonic interferometry of multi-electron dynamics in molecules. Nature 2009, 460, 972–977.

(8) Haessler, S.; Caillat, J.; Boutu, W.; Giovanetti-Texeira, C.; Ruchon, T.; Auguste, T.; Diveki, Z.; Breger, P.; Maquet, A.; Carré, B.; et al. Attosecond imaging of molecular wavepackets. Nat. Phys. 2010, 6, 200–206.

(9) Wörner, H. J.; Bertrand, J. B.; Corkum, P. B.; Villeneuve, D. M. High-harmonic homodyne detection of the ultrafast dissociation of Br₂ molecules. Phys. Rev. Lett. 2010, 105, 103002.

(10) Wörner, H. J.; Bertrand, J. B.; Fabre, B.; Higuet, J.; Ruf, H.; Dubrouil, A.; Patchkovskii, S.;Spanner, M.; Mairesse, Y.; Blanchet, V.; et al. Comritional intersection dynamics in NO₂ probed by homodyne high-harmonic spectroscopy. Science 2011, 334, 208–212.

(11) Zuo, T.; Bandrauk, A.; Corkum, P. Laser-induced electron diffraction: a new tool for probing ultrafast molecular dynamics. Chem. Phys. Lett. 1996, 259, 313–320.

(12) Blaga, C. I.; Xu, J.; Dichiara, A. D.; Sistrunk, E.; Zhang, K.; Agostini, P.; Miller, T. A.; Dimauro, L. F.; Lin, C. D. Imaging ultrafast molecular dynamics with laser-induced electron diffraction. Nature 2012, 483, 194–197.

(13) Wolter, B.; Pullen, M. G.; Le, A.-T.; Baudisch, M.; Dobholld-Dier, K.; Sentieben, A.; Hemmer, M.; Schröter, C. D.; Ullrich, J.; Pfeifer, T.; et al. Ultrafast electron diffraction imaging of bond breaking in di-ionized acetylene. Science 2016, 354, 308–312.
