Directional Coulomb Explosion of Molecules in Two-Color Laser Fields

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Goal: to use strong asymmetric laser fields to induce and explore combined electronic and nuclear dynamics in small molecules.

Background

When an atom is placed in a laser field field, the laser will distort the atomic potential, lowering the barrier on the "downfield" side of the atom and raising it on this "upfield" side, as shown in **Fig. 1(a)**. The lowered potential makes it easy for one or more electrons to leave the atom, either by tunneling through the barrier (tunnel ionization) or by flying above the barrier (above the barrier ionization).

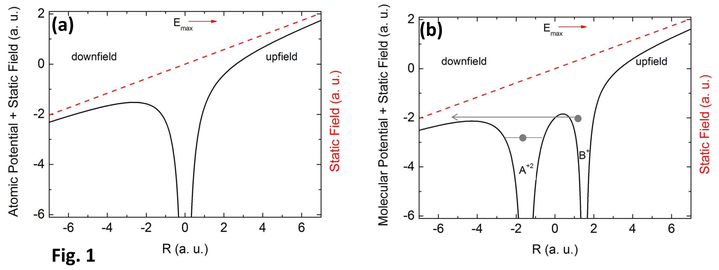
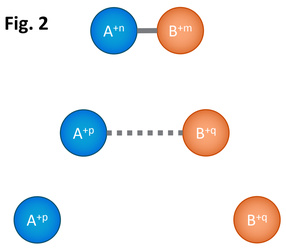


Fig. 1

The same happens for a diatomic molecule (**Fig. 1(b)**), and when one or more electrons have been removed, the molecule starts to break apart **(Fig 2)**.

Fig. 2



When the two ionic centers reach a critical internuclear separation, it becomes very easy for many more electrons localized on the upfield side of the molecule to tunnel through the inner potential barrier. This occurs at laser intensities much lower than those required to create the same degree of ionization in atoms. This process is an established mechanism for producing multiply charged ion fragments called enhanced ionization (EI)[1]. After losing so many electrons, the two ions strongly repel one another and undergo so-called *Coulomb explosion*.

The dissociation events can produce a variety of ion pairs, so we use the notation $AB(p,q)$ to refer to the $AB^{+(p+q)} \rightarrow A^{+p} + B^{+q}$ channel.

Placing molecules in asymmetric fields, those with a difference in the maximum field strength in one spatial direction than the other, can induce directional emission of ion fragments. For example, pioneering experiments on dissociative ionization of HD^{+} [2] showed that positively charged fragments were preferentially emitted "downfield," i.e. opposite to the direction of the maximum in the asymmetric field (recall **Fig. 1(b)**). Measurements on H_2^3 indicated that protons and electrons from dissociative ionization were preferentially ejected in the same direction in an asymmetric field. Both of these results were characterized as "counterintuitive," i.e. at odds with expectations based on a "naive" classical model. Subsequent theoretical work[4] provided plausible resolutions to the controversy, predicting preferential ejection of electrons in the "counterintuitive" upfield direction, provided the post-ionization interaction between a departing electron and its parent ion are properly taken into account. Further, the preferred direction of proton emission from molecular hydrogen can be upfield or downfield, depending on the vibrational state distribution of the molecular ion, as this affects the principal ionization mechanism. Clearly, directional emission of fragments from molecular dissociations is a lively topic of study.

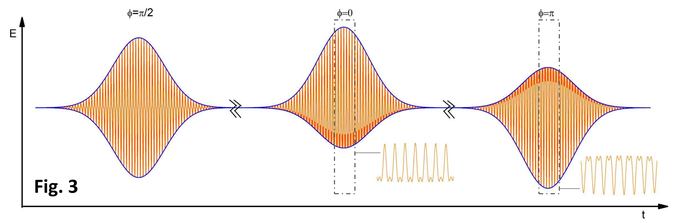


Fig. 3

Asymmetric laser fields can be created by the coherent addition of the fundamental laser field at frequency ω with its second harmonic at frequency 2ω. Depending upon the relative phase between the two components, the electric field will be stronger in one spatial direction than the other. We call this the *two-color* field method. For a linearly polarized laser field, the electric field is of the form

$$\vec{E}(t) = E_0(t)(\cos(\omega t) + \gamma \cos(2\omega t + \varphi))\hat{x} \qquad (1)$$

where $E_0(t)$ is the envelope function, γ is the relative strength of the SH field, and ϕ is the relative phase between the two components. A two-color field for a 35 fs laser pulse is shown in **Fig. 3**. Previous experiments using two-color fields to study molecular dissociations have focused on the relatively simple H_2 , D_2 or HD molecule[2,3,5] and the low-charged states from the multielectron CO molecule[6]. We extend this technique to N_2, O_2, CO, and CO_2, specifically to the highly-charged asymmetric (p ≠ q) dissociation channels[7].

Experimental Details

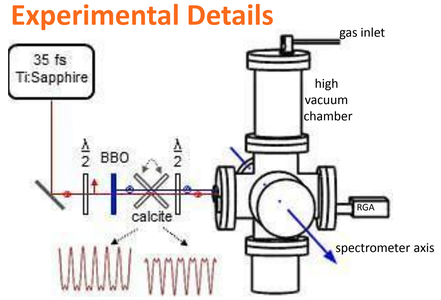


Fig. 4(a)

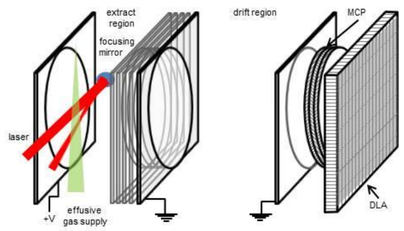


Fig. 4(b)

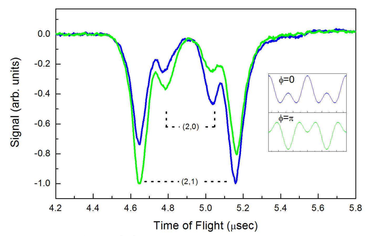


Fig. 4(c)

Laser pulses of 35 fs duration and central wavelengths of 800 nm and 400 nm are generated with a home built titanium-doped sapphire laser amplifier. See **Fig 4(a).** The total two-color field intensity is 0.8-5x10^{14} W/cm^2. Target gas is effusively introduced into a high vacuum chamber (base pressure ~5x10^{-10} Torr) where a small electric field pushes positively-charged ions towards a time- and position-sensitive detector (**Fig. 4(b)**). Generally, the laser field is polarized along the spectrometer axis, so ions have initial momentum in the forwards (towards the detector) and backwards (away from the detector) directions. This gives a double-peak structure in the time-of-flight (TOF) spectrum, shown in **Figure 4(c)** for the N^{+2} fragments from N_2 for two different values of ϕ. The resolution of the spectrometer allows us to also separate specific dissociation channels, $N_2(2,0)$ and $N_2(2,1)$. Notice that by changing ϕ, i.e. the direction in which the maximum in the two-color laser field points, more ions initially travel in the forwards (green curve) or backwards (blue curve) direction.

Results

Asymmetry Amplitude

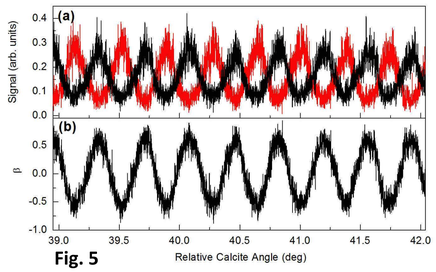


Fig. 5

We collect the channel-specific ion yield in the forward and backward directions as the calcite plate is continuously rotated. This detection method is illustrated in **Fig. 5(a)** for the $N_2(2,0)$ channel, where the black (red) curve illustrates the forward (backward) ion yield. From this raw data, we calculate the phase dependent asymmetry parameter

$$\beta(\varphi) = \frac{Y_f(\varphi) - Yb(\varphi)}{Y_f(\varphi) + Yb(\varphi)} \qquad (2)$$

which is plotted in **(b)**. Peak β values of ±0.7 are achievable for the $N_2(2,0)$ and $O_2(2,0)$ channels, and ±0.4 for the $N_2(2,1)$ and $O_2(2,1)$ channels. Comparable asymmetry levels are observed in the CO(1,2) and CO(2,2) channels while those associated with the C^{+}, C^{+2}, O^{+}, and O^{+2} fragments from CO_2 are factors of two to three smaller.

Angular Dependence

We record position and time information and calculate the ions' momenta. **Figure 6** illustrates the localization of the O^{+2} fragments from $O_2(2,0)$ and $O_2(2,1)$ along the laser polarization (vertical) axis and the $O_2(2,0)$ asymmetry observed with this method. This is also typical of the N^{+2} and O^{+2} fragments from N_2 and CO. The distributions have no ϕ- dependence beyond the forward/backward asymmetry

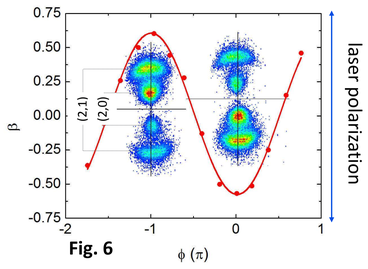


Fig. 6

Phase Relationships

The molecular ion (e.g. N_2^{+}) yield is maximized at ϕ=0 and π and has no directionality, so it exhibits oscillations at twice the frequency of the fragment asymmetry. This is illustrated for the N_2^{+} and $N_2(2,0)$ species in **Fig. 7**. Within an experimental uncertainty of 5°, the two curves are in phase. **Figure 8** shows that all dissociation channels involving multiply charged ions have $|\beta|_{max}$ at ϕ=0,π.

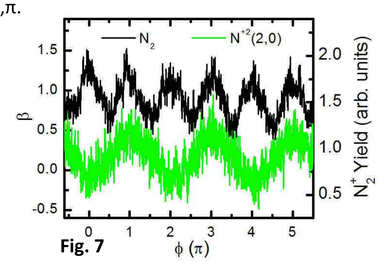


Fig. 7

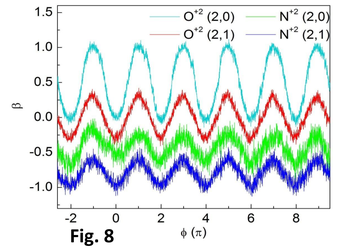


Fig. 8

Discussion: Absolute Phase

If we adopt an independent phase calibration[8], which is based on backscattered electrons from Xe and is consistent with our assignment from the $N_2(2,0)$ channel, as shown in **Figs. 6-8**, then for all channels observed in our experiments, fragments with the highest ionization potential (i.e. those that are the most difficult to produce via tunneling ionization) are preferentially emitted downfield (see **Fig. 2**). The sign of the asymmetry we observe is precisely *opposite* to that predicted by the established enhanced ionization mechanism for producing multiply-charged ion fragments[1]. One possibility for the discrepancy is that molecular dissociations at these laser intensities are not dominated by EI[9] and charge-localization of the electron on one atomic center in the separating molecule favors the observed configuration for a different reason. Another is that the phase-calibration based on backscattered electrons from Xe in a two-color field has the wrong sign[8]. In either case, the resolution of this issue may have significant implications for past and future studies of strong-field atomic and molecular dynamics.

Conclusions

In summary, we have observed strong, directional emission of multiply-charged ion fragments from dissociative ionization of a variety of molecules in two-color laser fields. All species exhibit the greatest forward/backward asymmetry when the field is maximally asymmetric. Based on an independent phase calibration, the sign of the asymmetry is opposite to that expected from the standard EI model. Once again asymmetric field experiments have brought into question the standard model of coupled electron and nuclear motion in strong field ionization in molecules. The robustness of the asymmetries in N_2, O_2, and CO makes Coulomb explosion of any of these common species a convenient *in situ*, single-shot, phase-standard for experiments involving intense two-color fields.

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