Photoionization of isooctane in intense laser fields: The effect of irradiance on electron dynamics.

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We photoionized thin path length jets (60 μm) of liquid isooctane with 36-70 fs pulses of 3.1 eV photons. The decay of the transient absorption, TA, at 1200 nm (assigned as predominantly due to absorption by the electron) was examined over a time interval from 0.5 ps to 40 ps and over an irradiance range from I_{ex} =7 TW/cm^2 to I_{ex} =407 TW/cm^2. This range of irradiance covers a region that encompasses the closing of the 3 photon and 4 photon liquid ionization channels (at $\sim$ 15 TW/cm^2 and 110 TW/cm^2 respectively). We observed that the temporal behavior of the TA decay cycles with irradiance. This, to our knowledge, has never previously been observed.

This cycling in the dynamics is shown to correlate with the predicted irradiance dependence of the kinetic energy distribution of photoejected electrons. [1] The fundamental correlation between the pump laser irradiance and the electron kinetic electron kinetic energy derives from the fact that in order to photoionize a molecule with the smallest number, n, photons of energy $\hbar\omega$, requires the photons to supply both the vacuum ionization potential, $I_{\rm p}$, and any field shifting of the ionization continuum. This shifting, often referred to as the pondermotive energy, U, is simply proportional to the irradiance, $U = 0.144\ I_{\rm ex}/(\hbar\omega)^2$ eV for $I_{\rm ex}$ in TW/cm^2 and $\hbar\omega$ in eV. The most probable value of n is the smallest integer required to make $T = n\hbar\omega - I_{\rm p} - U > 0$.[1–5] Accordingly, as $I_{\rm ex}$ approaches a value where $U = n\hbar\omega - I_{\rm p}$, the n-photon process is closed and the lowest available order transitions to the $n+1$ process. We have previously observed the predicted effects of these channel closings on the irradiance dependence of the TA amplitude at two fixed pump-probe time delays, where we established a correlation between the channel closings and the rate of photoionization.[2]

To parameterize the temporal behavior of the TA we fit the experimental TA to a model of the survival probability of a pair of geminate ions diffusing in their coulomb field and disappearing by recombination. The model assumes that the diffusion starts at $t = 0$ with geminate pair thermalized at a radius of r_e with an exponential radial probability density where $\langle r_e \rangle$ is the average radius. This density function was convoluted with known analytical solutions [6, 7] to diffusion in the coulomb field. The parameter $\langle r_e \rangle$ was determined from least square fits of the diffusion model to the experimental data. As shown in Fig. 1, the irradiance dependence of the parameter $\langle r_e \rangle$ shows a peculiar cycling in magnitude.

In the regions of irradiance that lie slightly beyond the closing of a photon channel, the theoretically predicted

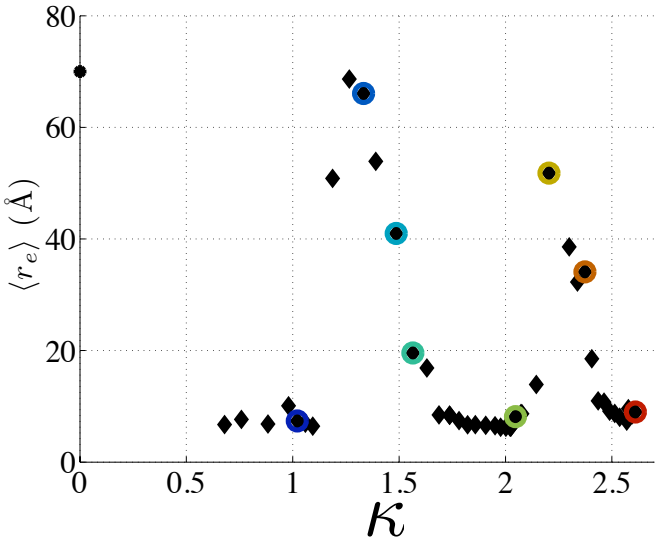

FIG. 1: The average range of electron ejection, $\langle r_e \rangle$ plotted as a function of κ (where $\kappa = \log_{10}(I_{ex})$) determined by fitting the diffusion model to the TA decay.

kinetic energy distribution of ejected electrons, $P(T)$, contain predominantly electrons that arise from a single n photon process. However, as the irradiance moves into the regions beyond these channel closings, the distribution broadens with the appearance of electrons of significantly higher energy. This effect is illustrated in Fig. 2 as a plot of the probability for generating an electron with $T > 3.1$ eV as a function of κ. The solid line is the prediction of the Reiss hydrogenic model which implicitly assumes that electron ejection is the only possible decay channel of photon absorption. The dashed line in Fig. 2 is constructed by accommodating an increase in ionization efficiency with energy. The energy dependence of this efficiency was taken to rise linearly from zero at threshold to a value of 0.45 when the excitation energy is about 1.5 eV above threshold. This would crudely accommodate the photoionization behavior of many hydrocarbon liquids. The similarity of Fig. 2 to Fig. 1 is rather striking, and lends itself to the interpretation that it is the presence of fast high energy electrons that are responsible for the peculiar cycling

However, there must be caution in the above interpretation: to place such an importance upon those electrons with kinetic energy sufficiently above the $I_{\rm p}$ of the liquid would overlook the fact that throughout the interval between channel closures the average energy of the

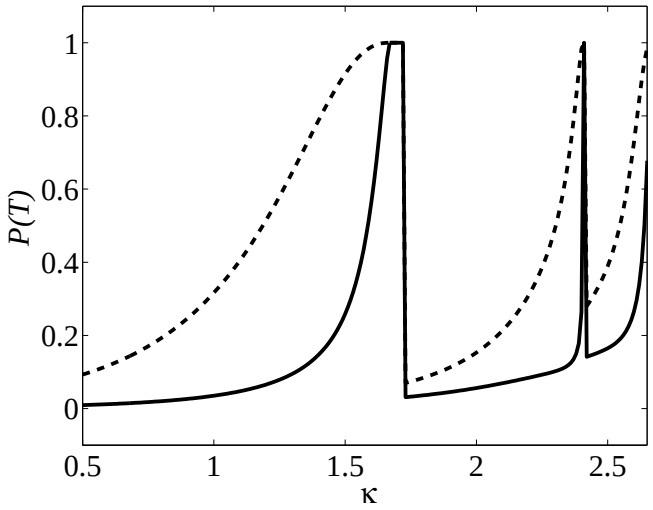

FIG. 2: The probability that an ejected electron has an electron with $T > 3.1$ eV (solid line), and the probability that an electron is ejected with $T > 3.1$ eV given an ionization efficiency that is zero at threshold and increases linearly with T to a value of 0.45 at $T = 3.1$ eV. Here, $\kappa = \log_{10}(I_{ex})$

ejected electrons continues to decrease, until the closing of a channel, at which point it abruptly increases. A simple correlation between the overall average electron kinetic energy and $\langle r_e \rangle$ could also explain the cycling of the TA with irradiance. Our data are presently insufficient to decide the question of mechanism. Additional measurements on the wavelength dependence of the TA as a function of irradiance will help to both confirm the existence, and establish the nature of, other products contributing to the TA besides the electron. Such investigations are ongoing in our laboratory.

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