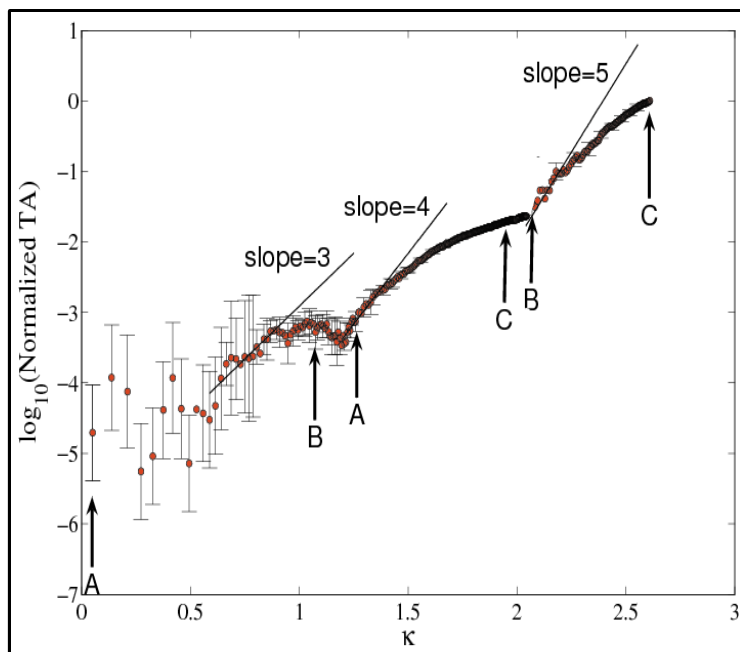


Photoionization of Isooctane and n-Octane in Intense Laser Fields

Effect of Irradiance on Ionization Rates

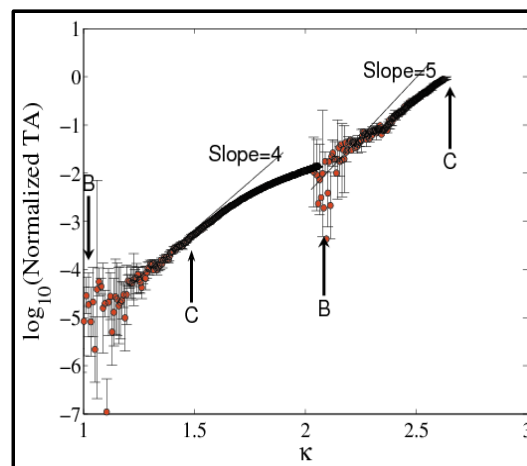
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Neat liquid Isooctane and n-octane are photoionized in intense laser fields up to 410 TW/cm^2 . These molecular liquids are photoionized by an intense 400 nm (3.1 eV) pump pulse. The effect of laser irradiance, I_{ex} , on the rate of ionization is determined by measurement of the transient absorbance (TA) of the ejected electron at 1200 nm at time delays of 0.7 ps and 2.5 ps . As the irradiance of the pulse is varied over a range from 4 TW/cm^2 to 410 TW/cm^2 , the dependence of TA on I_{ex} exhibits the periodic structure theoretically predicted for multiphoton channel openings and closings. The dependence of the TA on I_{ex} in the regions of channel openings and closings is predicted by the non-perturbative, strong field approximation (SFA) developed by Reiss. Results in n-octane parallel those in isooctane. The primary factor in the determination of the channel openings and closings is the liquid phase ionization potential, I_p , which is similar in both fluids ($\sim 8.6 \text{ eV}$).



\log_{10} (Normalized TA) as a function of κ (where $\kappa = \log_{10}(I_{ex})$ and I_{ex} is in TW/cm^2) for isooctane (above) and n-octane (right) at $t = 2.5 \text{ ps}$. Straight lines of slope = 3, 4 and 5 are drawn for visual reference. Vertical arrows labeled A, B and C identify the beginning and end of overlapping data.

A gravity-fed liquid jet apparatus was used to generate $60 \mu\text{m}$ thick sample. Evaporation compensation and flow stabilization controls allowed the jet to flow unbroken for days during the investigation.



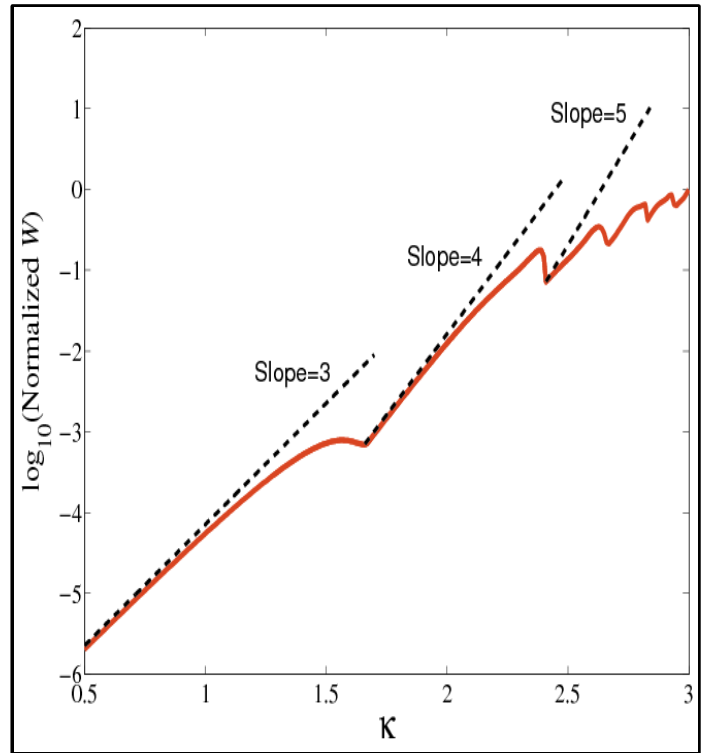
At low irradiance, this lowest order is $n = 3$ for both isooctane and octane. However, as I_{ex} increases, 3 photons soon become inadequate to ionize. The reason is that the electron is being ejected into an increasingly strong electrical field, $|E| = 2.74 \times 10^7 (I_{ex})^{1/2}$ V/cm (I_{ex} in TW/cm²) and, accordingly, is “born” with an energy (in the gas phase), averaged over a field cycle, of magnitude (in eV),

$$U = \frac{e^2 E^2}{4m_e \omega^2} = 0.144 I_{ex} / \epsilon^2$$

where m_e is the electron mass and ϵ the photon energy ($\hbar\omega$) in eV. U does not contribute to the the end-of-pulse kinetic energy of the electron, and simply adds to the ionization potential, I_p . Therefore, the energy needed to ionize must be $I_p + U$. Accordingly, an electron which absorbs n photons must have, to satisfy energy conservation, a final end of pulse kinetic energy,

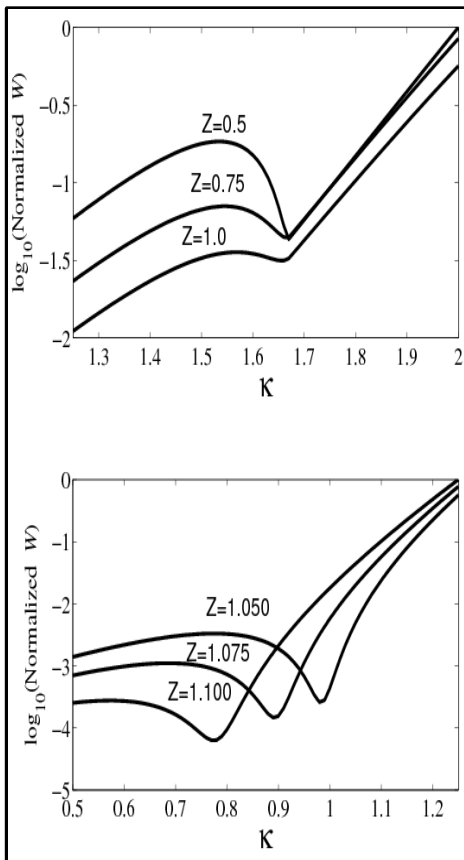
$$T = n\hbar\omega - I_p - U \geq 0.$$

As I_{ex} increases a value of I_{ex} must ultimately be reached when $n = 3$ photons are inadequate to supply $I_p + U$ and an additional photon is required to maintain $T > 0$. Hence, the lowest possible order process suddenly changes from $n = 3$ to $n = 4$ and, concurrently, the kinetic energy of the ejected electron increases by an amount equal to the energy of the 4th photon. This process continues with increasing I_{ex} until another transition is established when $n = 4$ photons become inadequate to establish $T > 0$. It is predicted that as $T \rightarrow 0$, the ionization rate will level-off. Accordingly as the n th channel approaches closing, the slope of the $\log(\text{ionization rate})$ versus $\log(I_{ex})$ should decline. Once the channel of order $n + 1$ opens (and T increases by the photon energy), this slope is expected to initially increase to $n + 1$. This is essentially the behavior in isooctane and octane.



$\log_{10}(W)$ as function of κ , where W is the normalized rate of ionization, based on Reiss's model for a $1s$ radial function with $Z = 1$, $I_p = 8.6$ eV and photon energy = 3.1 eV

Reiss in 1980 [1] derived a non-perturbative expression for the gas phase photoionization rate that explicitly exhibits its dependence on $n(\hbar\omega) - I_p - U$. The theory fails to accommodate the coulomb field and all other interactions of the ejected electron with its sibling ion, but provides an analytic and easily computed expression for non-resonant ionization. We plot the expression here where we have approximated the initial state in the theory as a Hydrogenic $1s$ function with effective nuclear charge $Z = 1$. There is a qualitative similarity between the Reiss model and our experimental data shown in slides 2 and 3. The opening of the $n = 4$ and $n = 5$ channels with their subsequent slopes of 4 and 5 in the model are similar to the $n = 4$ and $n = 5$ channel openings apparent in the experimental data. Channel openings occur at roughly the same values of κ . A Lorentz-Lorenz correction applied to the experimental irradiance, as well as uncertainties in the experimental determination of the irradiance, can explain the offset in the theoretical value of κ vis-a-vis that of the experiment.



$\log_{10}(W)$ vs. κ , where W is the normalized rate of ionization, based on Reiss's model for A) a $1s$ radial function with photon energy = 3.1 eV, $I_p = 8.6$ eV and $Z = 0.5, 0.75$ and 1.0 and B) a $3s$ radial function with photon energy = 3.1 eV, $I_p = 8.6$ eV and $Z = 1.05, 1.075$ and 1.100 .

The theory shows, as expected, a decline in slope as the transition to $n = 4$ is approached, it does not show a minimum as pronounced as that displayed in the experimental results of slide 3. However, this feature can be accommodated by the theory. To generate the theoretical plot, a simple hydrogenic $1s$ radial wavefunction was chosen to represent the ground state. Within this approximation, the parameter Z can be used to fix the diffuseness of the radial function. For a hydrogen atom embedded in a dielectric continuum of the same refractive index as isooctane, a value of $Z \approx 1/2$ would be more appropriate. Figure A on this slide compares the effects of $Z = 1, 0.75$ and 0.5 on the theoretical plots of $\log_{10}(W)$ vs κ for $I_p = 8.6$ eV and photon energy = 3.1 eV and demonstrates how increasingly deep minima can be generated using more diffuse radial functions.

The shallow minimum in the TA of isooctane at 2.5 ps, which seems to be detectable above our noise level at $\kappa = 0.9$, can also be accommodated by an appropriate choice for the momentum wavefunction, $\psi(p)$, in the theory. The insertion of nodes in the radial ground state wave function, can, under suitable conditions, generate additional minima in the ionization rate at values of κ such that $\psi(p) = 0$. Figure B shows such results using the momentum distribution function for a $3s$ radial function, with $Z = 1.05, 1.075$ and 1.100 .