Experimental evidence of light induced conical intersections in dissociation of diatomic Molecules

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Abstract: We present evidence for the effect of light induced conical intersections in strong field photodissociation of H_2^+, manifested in angular distribution modulations that result from the topological singularity induced by intense laser pulses.

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Conical intersections (CI) facilitate ultrafast and efficient non-radiative energy transfer between electronic states, and play an important role in molecular dynamics [1] of large molecules. At the CI, the adiabatic potential surfaces become degenerate, which results in a strong non-adiabatic coupling between electronic and rovibrational states. An important consequence of CI is the existence of a geometric or Berry's phase [2], which can cause interferences for parts of a wavepacket that traverses around it. CI cannot exist for free diatomic molecules as they require at least two degrees of freedom. Additionally, CI are very challenging to measure and control, as their positions and characteristics are inherent to the specific molecular system. Recently, it was predicted [3] that light induced conical intersections (LICI) can be realized for diatomic molecules, where the internuclear distance r and the angle of the molecular axis with respect to the laser polarization θ provide the required degrees of freedom. In theoretical studies that followed, it was shown that the realization of such LICI will have a strong impact on diatomic molecular dynamics [3,4]. In this study, we show experimental evidence for the LICI phenomenon in a diatomic molecules undergoing dissociation.

Strong-field interaction with matter can be described with the Floquet formalism. For diatomic molecules, this is expressed by shifting an excited potential curve down by $\hbar\omega$, where ω is the frequency of the laser. The new "dressed" diabatic potential curves cross at some internuclear separation where the two states are resonantly coupled by the laser field. The LICI is defined at this crossing point when the angle of the polarization of the laser with respect to the molecular axis is $\theta = \pi/2$. For other angles, this crossing becomes avoided, a gap opens between the two curves and the dynamics is adiabatic. The higher the laser intensity, the narrower the LICI cone is, reflecting a more abrupt transition from adiabatic to non-adiabatic dynamics.

We'll examine the influence a LICI has on the angular distributions of H_2^+ photodissociation. In H_2^+ only the $1s\sigma_g$ and $2p\sigma_u$ potential curves need to be considered for the field intensity discussed, and this simplicity helps disentangle the effect the LICI has from other processes. We analyzed the angular distributions of fragments rising from photodissociation of H_2^+ by a transform limited 30 fs pulses at 795 nm with a peak intensity of 2×10^{13} W/cm^2. The molecular ions were produced in a Nielsen source by ionizing H_2, and had a Franck-Condon distribution of vibrational states. Additional details on the experimental setup can be found here [5,6]. We concentrate on angular distributions at specific kinetic energy releases (KER) from rovibrational states that were in the vicinity of the LICI. In Fig 1(a), we show the measured angular distributions taken from narrow (20 meV) KER slices that correspond to vibration levels $v = 7, 8, 9$. We observe distinct interference features at 30°-60°, that stand in contrast to the typical smooth $cos^{2n}(\theta)$ type distribution strong field dissociation generates [5]. We believe the reason this has not been observed in previous experiments is related to the demanding resolutions needed in angle and energy, as bigger bin sizes for the KER or the angle coordinate will obscure the modulation observed. We also notice a flattening of the distribution toward 0°. This is explained as saturation of the probability amplitude for near resonant levels, as also reported here [6].

In order to follow how the LICI contributes to the interference features on the angular distributions, we have numerically solved the time-dependent Schrödinger equation both for nuclear and rotational degrees of freedom. Starting with an initial pure rovibrational state (v, j), we propagated it as it interacted with the laser and we calculated its dissociation probability, namely, $P(\theta, t) = \int_0^\infty |\psi(r,\theta,t)|^2 W(r) dr$, by projecting the part of the dissociating wavefunction onto an absorbing boundary along the spatial axis, $W(r)$. Fig 1 (f-g) shows the distinct interference patterns in $P(\theta, t)$ for several initial rovibration states ($v = 7, 8, 9$, $j = 0$). We shall now discuss the source of these interferences.
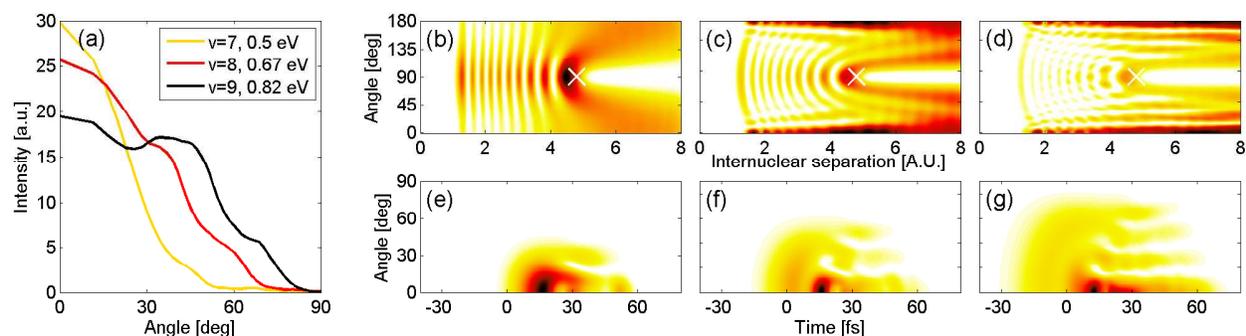
Fig. 1. (a) Measured dissociation yield vs angle of H_2^+. Different kinetic energy release values reveal modulations at different angles. Evolution of the calculated probability density initialized with $v = 9$ at (b) $t = -20$fs, (c) $t = 0$fs, and (d) $t = 15$fs. Peak intensity of pulse happens at $t = 0$fs and $\times$ marks the position of the LICI. (e-g) Calculated disassociation probability as function of time and angle for molecules that were initialized in the (e) $v = 7$, (f) $v = 8$ and (g) $v = 9$ vibrational eigen-states, in the ground rotational state $j = 0$.

As the laser field grows, molecules dissociate by a typical adiabatic dissociation or dynamically align via non-resonant Raman transitions that broaden the rotational distribution. In addition, molecules are affected by the LICI, and non-adiabatic energy transfer to different rovibrational states happens. Consequently, there can be more than a single quantum path for which the wavefunction ends up in the same state. Paths related to the LICI contribute a phase factor that may result in interference. In a sense, the LICI operates as a quantum-point scatterer, spreading parts of the wavefunction across spatio-angular phase space and creating interferences in both the nuclear and rotation degrees of freedom. This view is supported when we examine how the wavefunction propagates during the laser pulse, as shown in Fig 1 (b-d). We start with an initial state $v = 9$, where the spatial wavefunction is evenly distributed over all angles (not shown). However, 20 fs before the pulse peaks (Fig 1b) we see that the part of the population that was initially aligned with the laser (close to $0°$ or $180°$, has already started to dissociate, while parts closer to $\theta = \pi/2$ have accumulated, and later, when the pulse peaks (Fig 1c) they scatter off the LICI. This creates a spatio-angular interference pattern, that bends around the LICI. This bending is just the superposition of the outgoing and the scattered parts of the wavefunction. Some 15 fs past the peak, the wavefunction propagates almost freely, as the potential surfaces flatten, and the modulations in the angular distribution of the dissociating wavefunction are established (Fig 1d).

Our calculation also shows how the LICI affects different initial states. For example, in $v = 7$ only high rotational states have apparent overlap in position with the LICI. Since these states are most efficiently populated when the pulse peaks via Raman transitions, the non-adiabatic dynamics happens only for a limited duration and the interference obtained is rather limited. However for $v = 9$, which is closest to resonance with the laser field, already at the leading edge of the pulse the LICI prevails, and a richer angular interference pattern appears.

In conclusion, LICI are integral in any resonant strong field-matter interaction. It's controllability makes it attractive for novel spectroscopy techniques and research in quantum control, as recently shown in polyatomic systems [7]. The authors would like acknowledge V. S. Prabhudesai, U. Lev, D. Zajfman and Y. Silberberg for collaborating on the original experiment from which the data was extracted. This research is supported through Stanford PULSE Institute, SLAC National Accelerator Lab by the U.S. Department of Energy, Office of Basic Energy Sciences.

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