Direct Signature of Light-Induced Conical Intersections

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Direct Signature of Light-Induced Conical Intersections

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Synopsis By analyzing the photodissociation process of the D_2^+ molecule, we found a robust effect in the angular distribution of the photofragments which serves as a direct signature of the light-induced conical intersection (LICI) providing undoubted evidence for its existence.

Nonadiabatic effects are ubiquitous in physics, chemistry and biology. They are strongly amplied by conical intersections (CIs) which are degeneracies between electronic states of triatomic or larger molecules. A few years ago it has been revealed that CIs in molecular systems can be formed both by running and standing laser light even in diatomics. In this situation the rotational degree of freedom comes into play and serves as a proper second degree of freedom so as to form the branching space where the degeneracy is lifted. It has been demonstrated in several former theoretical works that due to the prevailing strong nonadiabatic couplings, the LICIs have strong impact on the dynamical properties of molecular systems. Recently, we have made an attempt to provide and analyze a physical event which may serve as an undoubted evidence of the LICI, giving a direct observable signature of the presence of this intersection [1].

It is known in the field of nonadiabatic molecular dynamics that due to the extreme breakdown of the Born-Oppenheimer approximation, conical intersections are responsible for ultrafast radiationless processes, typically on the femtosecond time scale. They provide pathways for extremely fast population transfer between electronic states. This latter effect is probably the most important inherent feature of the CIs. Nevertheless, until now one could not find an unambiguous experimentally measurably quantity which reflects directly this population transfer between electronic states for a LICI.

Recently a physical process has been found, where an ultrafast population transfer takes place between the electronic states of a diatomic molecule, providing direct evidence for the existence of the LICI. The photodissociation dynamics of the D_2^+ molecule serves as a show case physical example. We used the exact time dependent Hamiltonian and calculated the dissociation rate which provides a direct and experimentally measurable impact of the LICI. One and two dimensional calculations (1d, 2d) have been performed. In the 1d calculations the Hamiltonian depends only parametrically on the rotational degree of freedom (θ), therefore the LICI is not taken into account. The structure and magnitude of the 2d ($\nu = 5$) dissociation rates close to $\theta = \pi/2$ undoubtedly demonstrate the strong nonadiabatic effects due to the presence of the LICI.

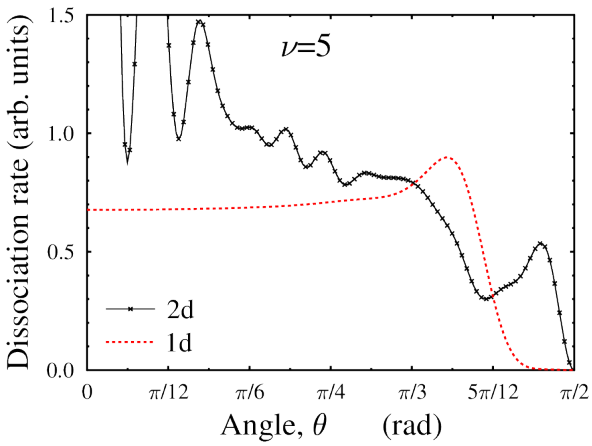

Figure 1. Fragment angular distributions of the dissociating D_2^+ molecule for initial vibrational states $\nu = 5$. Curves are presented both for one dimensional (1d) and for two dimensional (2d) cases. The applied field intensity is $1 \times 10^{14}\, W/cm^2$.

References

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