

Light-induced nonadiabatic phenomena in diatomics with strongly coupled electronic states

András Csehi^{1,2}, Gábor J. Halász³, Lorenz S. Cederbaum⁴, Ágnes Vibók^{1,2}

¹Department of Theoretical Physics, University of Debrecen, H-4002 Debrecen, PO Box 400, Hungary

²ELI-ALPS, ELI-HU Non-Profit Ltd, H-6720 Szeged, Dugonics tér 13, Hungary

³Department of Information Technology, University of Debrecen, H-4002 Debrecen, PO Box 400, Hungary

⁴Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, H-69120, Germany

E-mail: vibok@phys.unideb.hu

Nonadiabatic effects play a very important role in chemical processes and their dynamical control. These effects arise due to avoided crossings or conical intersections which are present either naturally in field-free space or are induced by a classical electric laser field in a molecular system. Recently, it was demonstrated that nonadiabatic effects can also be created in an optical cavity by forming avoided curve crossings in diatomics^[1]. Due to the coupling of the quantized radiation field of the cavity to the electronic degrees of freedom of the molecule, a strong mixing between the nuclear and electronic degrees of freedom appears. We show here the equivalence of using the cavity's quantized radiation field and the classical

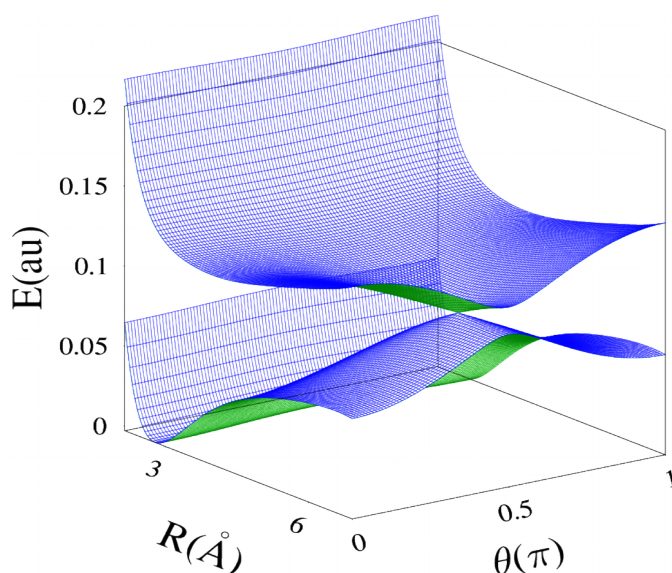


Figure 1. Light-induced potential energy surfaces as a function of the interatomic distance R and the angle θ between the molecular axis and the laser polarization direction. The applied energies and intensity of the laser pulse are $\hbar\omega_L=0.815\text{eV}$ and $I=10^{13}\text{ W/cm}^2$, respectively.

laser field as usually done for molecules. This is demonstrated for the specific molecule NaI which exhibits a pronounced natural (intrinsic) avoided crossing which competes with the avoided crossing induced by the field. Furthermore, as it is known by now that rotating molecules exhibit light-induced conical intersections in classical laser light^[2,3], we also investigate the impact of these intersections. For NaI we undoubtedly demonstrate a significant difference between the impact of the laser-induced avoided crossing and that of the laser-induced conical intersection on the dynamics of the molecule^[4].

References:

- [1] Kowalewski, M.; Bennett, K.; Mukamel, S. Cavity Femtochemistry: Manipulating Nonadiabatic Dynamics at Avoided Crossings. *J. Phys. Chem. Lett.*, **2016**, 7, 2050-2054.
- [2] Halász, G. J.; Vibók, Á.; Cederbaum, L. S. Direct signature of light-induced conical intersections in diatomics. *J. Phys. Chem. Lett.*, **2015**, 6, 348-354.
- [3] Csehi, A.; Halász, G. J.; Cederbaum, L. S.; Vibók, Á. Towards Controlling the Dissociation Probability by Light-Induced Conical Intersections. *Faraday Discuss.* **2016**, 194, 479-493.
- [4] Csehi, A.; Halász, G. J.; Cederbaum, L. S.; Vibók, Á. Light-induced nonadiabatic phenomena in diatomics with strongly coupled electronic states. *J. Phys. Chem. Lett.* submitted for publication.