# Field-modified-potential-energy-curves-control of the dissociation branching ratio in the IBr system

**C Sanz-Sanz[1]* and G A Worth[2]**

[1]Autonoma University of Madrid, Ciudad Universitaria de Cantoblanco, 28049 Madrid, Spain
[2]University College London, Gower Street, London, WC1E 6BT

**Synopsis** Strong and intemediate laser pulses can modify the potential energy curves of a system in order to guide the process through a different path. The photodissociation of IBr system occurs through an avoided crossing between two spin-orbit excited electronic states. This avoided crossing can be modified so that the dissociation branching ratio is controlled by means of the field. Preliminary dynamic results are presented in this contribution, where the system evolves in the modified potential curves.

One of the main goals in chemistry is the control of chemical reactions. Laser pulses are one of the tools that we can use to modify our system, in order to obtain a different outcome. A medium-strong laser pulse can be applied to change the shape of the potential energy surface (PES). Modern ultrafast laser pulses are on the time scale of the chemistry itself, so a precise control over the shape and delay of these pulses oers access to different portions of the PES.

The Stark effect is produced when a static eld alters molecular states. When the eld applied is time dependent the process is known as dynamic Stark effect (DSE).Of particular interest is the non-resonant dynamic Stark effect (NRDSE), in which the time dependent eld is unable to produce photon excitation. The laser pulse is used to shape the PES[1, 2]. The control of the photodissociation of IBr using NRDSE has been studied experimentally by Stolow and coworkers[3] (Fig. 1).

Non-adiabatic processes, as intersystem crossings, entail charge rearrangements that occur along a reaction path at the intersections of PES. Chemical branching ratios in non-adiabatic processes are very sensitive to the intersection geometry, and therefore the dynamic modification of these processes is an important application of the NRDSE. The photodissociation of IBr is initiated by absorption of a visible photon, exciting the system from the ground electronic state to an state which has several crossings with states that could yield the system to different dissociation channels[4]. The application of an infrared NRDSE eld can be used to modify the curve-crossing barrier (Fig. 2) at a specic time, promoting the yield of one dissociation channel over another.

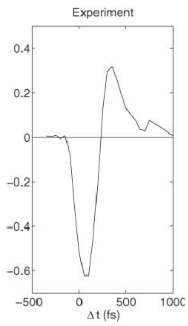


**Figure 1**. Experimental branching ratio [3]

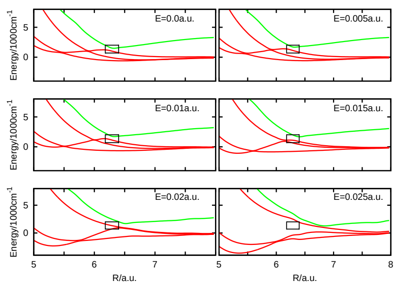


**Figure 2**. Field-modified Potential Energy Curves[2]

## References

[1] G. A. Worth, C. Sanz-Sanz, Phys. Chem. Chem. Phys., **12**, 15570 (2010).

[2] C. Sanz-Sanz and G. A. Worth, Phys. Chem. Chem. Phys. (2019) DOI:10.1039/c8cp07248e

[3] B.J. Sussman, D. Townsend, M.Y. Ivanov and A. Stolow, Science, **314**, 278 (2006).

[4] C. Sanz-Sanz, G. W. Richings and G. A. Worth, Faraday Discuss., **153**, 275 (2011).

*E-mail: cristina.sanz@uam.es