

**ELECTRONIC EXCITATIONS BY ADSORBATE MOTION ON METAL SURFACES:
BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION IN SURFACE CHEMISTRY**

Alec M. Wodtke, Russell Cooper, Igor Rahinov, Zhi-sheng Li, Daniel J. Auerbach

Department of Chemistry and Biochemistry, University of California Santa Barbara

ABSTRACT

Developing a predictive understanding of surface chemistry based on the first principles of Physics must include possible breakdown of the Born-Oppenheimer approximation. Reaching this goal means progressing beyond what is now possible for gas-phase bimolecular reactive encounters. This represents one of the most important challenges to current research in chemical physics; since, to the extent that the Born-Oppenheimer approximation breaks down, we have no predictive theory of surface chemistry. This means we are working in an exciting environment where new phenomena might be discovered through experiments and inspire new theoretical developments. This lecture will present recent experimental results from our group that bears on this topic. For example, when molecules with low levels of vibrational excitation collide with metal surfaces, vibrational coupling to electron-hole pairs is not found to be strong unless incidence energies are high. However, there is accumulating evidence that coupling of large amplitude molecular vibration to metallic-electron degrees-of-freedom can be strong and becomes more important at reduced incidence translational energies. This can occur due to charge transfer between the surface and the molecule and the high kinetic energies associated with bond compression/formation. This implies theoretical approaches relying on the Born-Oppenheimer approximation may not accurately reflect the nature of transition-state traversal in reactions at metal surfaces. In related work, we have been looking at the energy transfer processes between molecules and surfaces that enable molecular trapping, the first elementary step in “Langmuir-Hinshelwood” reactions. We find remarkably large amounts of translational energy can be channelled to a metal surface and are able to look at this for different quantum-state to state scattering channels. While our results require additional theoretical comparisons, it appears that phonon coupling may not be sufficient to explain these experimental observations.

RELATED REFERENCES

- [1] A. M. Wodtke, D. Matsiev, D. J. Auerbach, *Prog. Surf. Sci.* **83**, 167 (2008).
- [2] Q. Ran, D. Matsiev, D. J. Auerbach, A. M. Wodtke, *Phys. Rev. Lett.* **98**, (2007).
- [3] Q. Ran, D. Matsiev, D. J. Auerbach, A. M. Wodtke, *Nucl. Instrum. Methods Phys. Res., Sect. B* **258**, 1 (2007).
- [4] N. H. Nahler, J. D. White, J. Larue, D. J. Auerbach, A. M. Wodtke, *Science* **321**, 1191 (2008).
- [5] J. D. White, J. Chen, D. Matsiev, D. J. Auerbach, A. M. Wodtke, *Nature* **433**, 503 (2005).
- [6] I. Rahinov *et al.*, *J. Chem. Phys.* **129**, 214708 (2008).
- [7] N. Shenvi, S. Roy, J. C. Tully, *Journal of Chemical Physics* **130**, 12 (2009).