

On the role of nonadiabatic electronic effects in the interactions of atoms and molecules with metal surfaces

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It is generally believed that most chemical processes can be described using the Born-Oppenheimer approximation as motion on a single electronic potential energy surface. This approximation rests on the large difference in time scale for electronic and nuclear motion and the large spacing of available electronic states. As the nuclei move, the electrons adjust adiabatically to establish the potential energy surface governing the motion. For gas phase interactions, the Born-Oppenheimer approximation is well verified and only under special conditions involving curve crossings or very high energies, are nonadiabatic processes important.

For atomic and molecular interactions with metal surface, on the other hand, there are reasons to question the applicability of the Born-Oppenheimer approximation. The continuum of electronic energy levels of the metal means that the assumption of widely spaced isolated levels that underlies the Born-Oppenheimer is not valid. Nonetheless, almost all theoretical descriptions of chemical processes on surfaces are based on this approximation and on the idea of adiabatic evolution of a single electronic energy level.

How can we tell if this approach is valid? Is the conventional wisdom leaving out a difficult to calculate but very important set of effects? Molecular beam experiments can provide answers to these questions. From these experiments, there is a growing body of indirect evidence that nonadiabatic electronic effects play an important and even dominant role in processes at metal surfaces; these include such important processes as the adsorption of hydrogen atoms, the excitation of molecular vibration and certain chemical reactions. Recently, we have also obtained direct evidence of nonadiabatic generation of electron-hole pairs in chemical processes at surfaces. Specifically, we detect and characterize electron emission from a low work function surface resulting from collisions of vibrationally excited molecules.