Atomic and molecular interactions constitute a many-body quantum problem governed fundamentally only by the Coulomb forces between many electrons and nuclei. While simple to state, computers are simply not fast enough to solve this problem by brute force, except for the simplest examples. Combining the Born-Oppenheimer Approximation (BOA) with Density Functional Theory (DFT), however, allows theoretical simulations of extraordinarily complex chemical systems including molecular interactions at solid metal surfaces, the physical basis of surface chemistry. This lecture describes experiments demonstrating the limits of the BOA/DFT approximation as it relates to molecules interacting with solid metal surfaces. One of the most powerful experimental tools at our disposal is a form of double resonance spectroscopy, which allows us to define the quantum state of the molecule both before and after the collision with the surface, providing a complete picture of the resulting energy conversion processes. With such data, we are able to emphasize quantitative measurements that can be directly compared to first principles theories that go beyond the Born-Oppenheimer approximation. One important outcome of this work is the realization that Born-Oppenheimer breakdown can be induced by simple charge transfer reactions that are common in surface chemistry.  

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