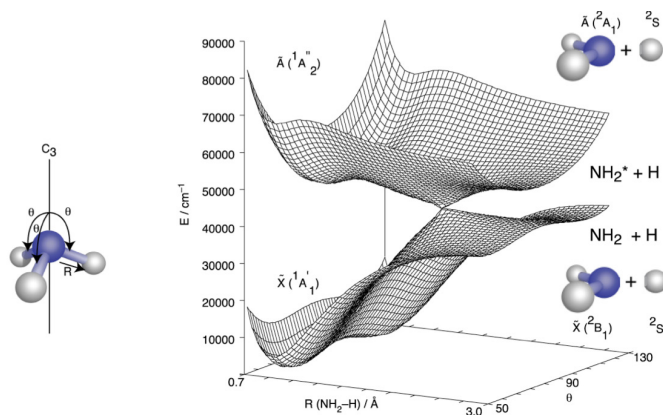


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Vibrations, Conical Intersections, and Reaction Dynamics in Gases and Liquids

Department of Physics Colloquium

Conical intersections between potential energy surfaces occur when the two electronic states become degenerate and, consequently, the Born-Oppenheimer approximation fails. Although long regarded as interesting curiosities, it is now clear that they are central to a large variety of molecular transformations. Photodissociation and photoisomerization often occur by passage of electronically excited molecules through a conical intersection, and the details of that passage control the partitioning of the products among competing pathways.

Ammonia is a prototypical molecule in which a conical intersection is important in excited-state dissociation. High resolution studies of the dissociation of isolated ammonia molecules show that excitation of selected vibrations changes the course of the dissociation dramatically, leading to the formation of electronically excited products at the expense of ground-state products. The key to this behavior is the influence of vibrational motion on passage of the system through the conical intersection.

Similar studies in solution require high time resolution rather than high spectral resolution, and it is possible to prepare vibrationally excited molecules in solution and monitor their evolution using 100-fs laser pulses. In these experiments an infrared pulse excites a vibration, an ultraviolet pulse transfers molecules to an excited state, and broadband continuum absorption monitors their evolution in the excited state. The competition between excited state vibrational relaxation and barrier crossing is the feature that determines the influence of vibrational excitation on the isomerization rate.