

**BOUND STATES AND CONTINUA UNIFIED:
FROM SPECTROSCOPY TO CHEMISTRY VIA MQDT**

Stephen C. Ross

Centre for Laser Applications and Molecular Science

Department of Physics

University of New Brunswick

P.O. Box 4400, Fredericton, NB, CANADA E3B 5A3

The study of the bound states of a molecule is often considered to be unrelated to chemical processes. However, in some of the lowest Rydberg states of H_2 the approach to the continuum is already evident in the breakdown of the Born-Oppenheimer approximation. This is due to the excitation of the electron away from the molecular core, well on its way to ionization. At higher energy, discrepancies in the photoionization spectrum of H_2 are due to competition with photodissociation. Thus the bound states, the ionization continua, and the dissociation continua are all intricately connected. In H_2 , as in many molecules, these processes are further complicated by strong electronic interaction with doubly excited valence states.

Multichannel Quantum Defect Theory (MQDT) is ideally suited to study these interactions and processes in a single unified treatment. Applying appropriate boundary conditions to the MQDT wavefunctions, we have studied both the bound states and photoionization of H_2 , and are currently working on incorporating dissociation so as to be able to study competition between ionization and dissociation. By appropriate modification of the boundary conditions, we can reverse one or the other of these processes and then study such fundamental chemical processes as dissociative recombination and associative ionization.

This talk will present a basic introduction to MQDT along with some current results.

PHOTODISSOCIATION FROM BOUND ELECTRONIC STATES

Jürgen Troe

Institut für Physikalische Chemie

Universität Göttingen

Tammannstraße 6, D-37077 Göttingen, Germany

Photodissociation processes can be "direct" from repulsive electronic states, "unimolecular" from strongly bound excited electronic states or, after internal conversion, from the electronic ground state, or "intermediate" when the lifetime is of the order of one or two vibrational periods only. By a variety of optical excitation schemes, the excited molecules can be prepared in well defined initial states; suitable detection methods for measuring the state-resolved lifetimes or their inverse, the "specific" rate constants $k(E, J, i)$ at the total energy E , angular momentum J , and (sometimes) specific initial states i , are also available. This talk describes recent experiments on "intermediate" and "unimolecular" dissociations. Among the examples are the dissociations of HCO, NO₂, H₂O₂, HONO, HOCO, and H₂CCO. When "unimolecular" behavior is realized, statistical unimolecular rate theory in the form of the statistical adiabatic channel model provides a satisfactory and complete description of the dynamics. The analysis on the basis of ab initio potentials is demonstrated in detail.