Final Report:
EACTIONS OF ATOMS AND RADICALS
IN PULSED MOLECULAR BEAMS
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The spectroscopy and photochemistry of the hydroxymethyl radical were studied following development of the needed techniques and methodologies. New transitions to the low-lying 3s and 3p(x) Rydberg electronic states were identified and characterized, and their dissociation lifetimes estimated. Three types of spectra were recorded: (a) depletion spectra; (b) H and D photofragment-yield spectra from deuterated hydroxymethyl, with H and D detected by multiphoton ionization; (c) ionization spectra from the electronically excited state. It was impossible to observe an ionization signal from the 3s state because of its short lifetime, but using depletion a broad and structureless absorption starting with a threshold at 3.21 eV was detected. Assignments of the observed Rydberg transitions are in excellent agreement with the recent *ab initio* calculations. The lifetimes of the electronic states are all less than a picosecond, with the fastest predissociation from the lowest, 3s, state. Two independent channels are observed from deuterated hydroxymethyl, one in which the O-D bond is broken, and at higher energies, a second channel appears, where the C-H bond is cleaved. No indication of isomerization to the methoxy radical is obtained. Conical intersection calculations by Hoffman and Yarkony have identified pathways for radiationless decay that play an essential role in the photodissociation. These calculations provide a qualitative

interpretation and identify efficient intersections between the $3s$ and the ground state at long O-H and C-H distances. Following $3s$ /ground state coupling, different regions on the repulsive part of the ground state potential energy surface are accessed and eventually lead to the two channels. The photochemistry on the $3p$ states is more complicated due to multiple crossings. Because of the proximity of lower Rydberg states, Franck-Condon considerations favor initial coupling between them. Two different paths, along the O-H and C-H coordinates, subsequently lead to intersections between the $3s$ and the ground state, terminating in above the two channels.

Dissociation from higher vibronic levels in the $3p(z)$ state was also examined. The D fragment's kinetic energy distributions resulting from O-D fission are broad, implying that the formaldehyde co-fragment is internally excited. In fact, when the formaldehyde fragment is born with sufficient energy, it dissociates, producing slow secondary H atoms. A similar situation exists following C-H bond fission. The internal excitation of the products can be rationalized by out-of-plane motions required to couple the upper to the lower Rydberg states, which are of different symmetry.

The precise kinetic energy distributions determined by the core-sampling time-of-flight method enable the determination of the C-H bond dissociation energy in the hydroxymethyl radical. Combining this bond energy with the known heats of formation of the fragments, the heat of formation of the product hydroxymethylene diradical is estimated experimentally for the first time.

In summary, the experiments on the photodissociation of the hydroxymethyl radical from the lowest-lying Rydberg states reveal their spectroscopy, conical intersections, and photodissociation dynamics leading to H and D products. The experimental results serve as benchmarks for theoretical studies and modeling of hydroxyalkyl radicals.

The most challenging goal during the funding period was to study the rovibrational spectroscopy and dissociation of the radical on the ground potential energy surface. To this end, rotationally-resolved spectra of the OH- and CH-stretch fundamentals were obtained, and then extended to the first OH-stretch overtone. Detection is achieved by depletion and double-resonance ionization detected IR (DRID-IR) spectroscopy. Rovibrational spectra are recorded by tuning simultaneously the IR and UV laser

frequencies and fixing their total energy at the peak of the transition to the selected vibronic level in the excited 3p(z) Rydberg state. Rotationally resolved spectra are observed up to the first overtone of the O-H stretch, indicating that intramolecular vibrational redistribution is not extensive. In the most recent experiments, the third overtone of the OH-stretch was excited, and H fragments were detected, produced apparently by tunneling below the barrier to dissociation.

Vibrationally-mediated photodissociation experiments were also carried out, in which the IR excitation is fixed on a O-H or C-H stretch vibration, and the UV laser wavelength is scanned to access excited vibrational levels on the 3p(z) Rydberg state. This allows the identification of new vibronic levels in the upper electronic state and their lifetimes. In order to assign the rovibrational spectra, *ab initio* calculations were carried out to determine rotational constants, orientations of vibrational transition dipole moments, and transition strengths.