Photoinitiated Processes in Small Hydrides

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This grant was in effect for a quite long time: 1984-2008. This period saw a broad range of research activities transpire in my group, and these enlisted the participation of many students, postdoctorals, and visitors. The earliest participants have since enjoyed full careers: faculty members here and abroad, government laboratories, successful entrepreneurs, and so on. Some have even retired! Consequently, during the past few months I have repeatedly asked myself: how can a coherent, readable report be prepared that covers so long a period of time and so varied a collection of projects? On the one hand, the work has *evolved* — a sensible progression of experimental techniques and strategies, as well as a parallel deepening of our theoretical understanding. On the other hand, there is a distinctiveness to many of the projects that enables them to be arranged into groups.

In the end a compromise was struck. Areas and topics that received the most focused attention are identified. Our main contributions and how they relate to the field of chemical dynamics, in general, are organized according to these groups. Publications are listed but not explained *per se*, as this would produce a manifestly unreadable document. They are all available in PDF format upon request. Following this, brief synopses are presented for each of the groupings — getting straight to the point, but with the wisdom of hindsight.

Publications (chronological order)[‡]

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2. The photolytic production of C₂H: collisional quenching of A²Π → X²Σ infrared emission and the removal of excited C₂H, F. Shokoohi, T.A. Watson, H. Reisler, F. Kong, A.M. Renlund, and C. Wittig, *J. Phys. Chem.* **90**, 5695 (1986).
3. High resolution kinetic energy distributions via Doppler shift measurements, Z. Xu, B. Koplitz, S. Buelow, D. Baugh, and C. Wittig, *Chem. Phys. Lett.* **127**, 534 (1986).
4. Kinetic and internal energy distributions via velocity aligned Doppler spectroscopy: 193 nm photodissociation of H₂S and HBr, Z. Xu, B. Koplitz, and C. Wittig, *J. Chem. Phys.* **87**, 1062 (1987).
5. Product energy distributions from the 193 nm photodissociation of NH₃, B. Koplitz, Z. Xu, and C. Wittig, *Chem. Phys. Lett.* **137**, 505 (1987).
6. Determining reaction pathways and spin-orbit populations in the photodissociation of HBr and HI using velocity-aligned Doppler spectroscopy, Z. Xu, B. Koplitz, and C. Wittig, *J. Phys. Chem.* **92**, 5518 (1988).
7. Acetylene C-H bond dissociation energy using 193.3 nm photolysis and sub-Doppler resolution H atom spectroscopy: 127 ± 1.5 kcal mol⁻¹, J. Segall, R. Lavi, Y. Wen, and C. Wittig, *J. Phys. Chem.* **93**, 7287 (1989).
8. Velocity-aligned Doppler spectroscopy, Z. Xu, B. Koplitz and C. Wittig, *J. Chem. Phys.* **90**, 2692 (1989).
9. H + CO₂ → OH + CO: yield versus HI photolysis wavelength and OH rotational distributions under single collision conditions and with CO₂-HI complexes, Y. Chen, G. Hoffmann, D. Oh, and C. Wittig, *Chem. Phys. Lett.* **159**, 426 (1989).
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12. Infrared spectroscopy of CO₂-D(H)Br: molecular structure and its reliability, Y. P. Zeng, S. W. Sharpe, S. K. Shin, C. Wittig, and R.A. Beaudet, *J. Chem. Phys.* **97**, 5392 (1992).
13. Vibrationally resolved translational energy release spectra from the ultraviolet photodissociation of methyl mercaptan, J. Segall, Y. Wen, R. Singer, M. Dulligan, and C. Wittig, *J. Chem. Phys.* **99**, 6600 (1993).

14. Reactions of hot deuterium atoms with OCS in the gas phase and in OCS-DI complexes, E. Böhmer, K. Mikhaylichenko, and C. Wittig, *J. Chem. Phys.* **99**, 6545 (1993).
15. Evidence for a cage effect in the UV photolysis of HBr in Ar-HBr: theoretical and experimental results, J. Segall, Y. Wen, R. Singer, C. Wittig, A. Garcia-Vela and R. B. Gerber, *Chem. Phys. Lett.* **207**, 504 (1993).
16. Photoinitiated processes in complexes: subpicosecond studies of CO₂-HI and stereospecificity in Ar-HX, C. Jaques, L. Valachovic, S. Ionov, E. Böhmer, Y. Wen, J. Segall and C. Wittig, *J. Chem. Soc. Faraday Transactions II* **89**, 1419 (1993).
17. Photodissociation of methanol at 193.3 nm: translational energy release spectra, Y. Wen, J. Segall, M. Dulligan, and C. Wittig, *J. Chem. Phys.* **101**, 5665 (1994).
18. HNCO + $h\nu$ (193.3 nm) $\rightarrow$ H + NCO: center-of-mass translational energy distribution, reaction dynamics, and D₀(H-NCO), J. Zhang, M. Dulligan, and C. Wittig, *J. Phys. Chem.* **99**, 7446 (1995).
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21. An experimental study of HF photodissociation: spin-orbit branching ratio and infrared alignment, J. Zhang, C. W. Riehn, M. Dulligan, and C. Wittig, *J. Chem. Phys.* **104**, 7027 (1996).
22. Vibronic interaction in NO₃ from the ²E' origin to the NO + O₂ channel, L. R. Valachovic, C. Riehn, K. Mikhaylichenko, and C. Wittig, *Chem. Phys. Lett.* **258**, 644 (1996).
23. Photodissociation of HCl at 193.3 nm: spin-orbit branching ratio, J. Zhang, M. Dulligan, and C. Wittig, *J. Chem. Phys.* **107**, 1403 (1997).
24. HCO rotational excitation in the photoinitiated unimolecular decomposition of H₂CO, M. J. Dulligan, M. F. Tuchler, J. Zhang, A. Kolessov, and C. Wittig, *Chem. Phys. Lett.* **276**, 84 (1997).
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28. Photoinitiated H_2CO unimolecular decomposition: accessing $\text{H} + \text{HCO}$ products via S_0 and T_1 pathways, L. R. Valachovic, M. F. Tuchler, M. Dulligan, Th. Droz-Georget, M. Zyrianov, H. Reisler, and C. Wittig, *J. Chem. Phys.* **112**, 2752 (2000).
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30. Intracuster superelastic scattering via sequential photodissociation in small HI clusters, D. Chastaing, J. Underwood, and C. Wittig, *J. Chem. Phys.* **119**, 928-938 (2003).
31. Two-photon photodissociation of H_2O via the B state, J. Underwood and C. Wittig, *Chem. Phys. Lett.* **386**, 190-195 (2004).
32. On the UV photodissociation of H_2Te , A. B. Alekseyev, H. P. Lieberman, and C. Wittig, *J. Chem. Phys.* **121**, 9389 (2004).
33. Heavy hydrides: H_2Te ultraviolet photochemistry, J. Underwood, D. Chastaing, S. Lee, and C. Wittig, *J. Chem. Phys.* **123**, 84312 (2005).
34. The Landau-Zener formula, C. Wittig, *J. Phys. Chem. B* **109**, 8428 (2005).
35. AsH_2 ultraviolet photochemistry, L. A. Smith-Freeman, W. H. Schroeder, and C. Wittig, *J. Phys. Chem. A* **113**, 2158-2164 (2009).

‡ In addition to these publications, a number of book chapters and review articles have been written, acknowledging DOE support. Unfortunately, I have not been able to access these articles online in order to download them. I do not think anything important is lost, as the above list tells the story insofar as what we have been working on.

Velocity-aligned Doppler spectroscopy

This method was invented and refined in my group in the mid-1980's under DOE sponsorship. It exploits the fact that, in the absence of collisions, fragment species that fly out of the path of a probe laser beam go undetected. Those species whose velocities lie parallel to the probe radiation wave vector give clear spectral signatures of their velocities via their Doppler shifts, i.e., because the spectra are not confounded by *projections* onto the axis. Namely, when a particle's velocity is not aligned with the probe laser wave vector the particle is "removed" from the field of view. Thus, the term: *velocity-aligned Doppler spectroscopy* was introduced. This method served us well for a number of years, and it was used to examine a number of interesting molecular systems. It eventually gave way to high-*n* Rydberg time-of-flight (HRTOF) spectroscopy, which is used in my lab to this very day. This was a smooth transition in which two postdocs from my group traveled to Germany to obtain details from an associate of mine (Karl Welge), who had initiated its use in molecular science. The scientific topics explored were centered on intramolecular and photodissociation dynamics of small polyatomic molecules and radicals, as discussed below.

Publications: 3-8.

Photoinitiated reactions in weakly bound complexes

This method was invented in my group in the late-1980's under NSF and DOE sponsorship. It was the first demonstration of entrance channel control of photoinitiated bimolecular processes (reactive and inelastic) in which the controlling fields are those of the van der Waals forces that bind the binary complex, i.e., rather than using an external (laboratory) field. I received the Herbert P. Broida Prize of the American Physical Society for this work in 1993, and I was named the Bourke Lecturer in the United Kingdom (and received the Bourke medal) in 2000, also for this work. We applied the method to several small prototypical molecular systems, most notably the $\text{H} + \text{CO}_2$ reaction (mainly using $\text{CO}_2\text{-HI}$ and $\text{CO}_2\text{-HBr}$ complexes to initiate the bimolecular reaction: $\text{H} + \text{CO}_2 \rightarrow \text{OH} + \text{CO}$), which is one of the most important combustion reactions, as well as its isoelectronic counterpart: $\text{H} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{OH}$, by using $\text{N}_2\text{O-HI}$ and $\text{N}_2\text{O-HBr}$ precursors. In addition, in the late 1990's my group carried out a *tour de force* experiment in which HCl dimer was excited via an overtone transition and the dimers thus tagged were photodissociated: $\text{HCl-HCl} + h\nu_{\text{IR}} \rightarrow (\text{HCl})^+-\text{HCl} + h\nu_{\text{UV}} \rightarrow \text{H} + \text{Cl-HCl}$. Our work on photoinitiated processes in weakly bound complexes spawned a large number of complementary studies worldwide, many of which continue to this day, e.g., experimental and theoretical studies of so-called entrance channel complexes.

Publications: 9, 10, 12, 14-16, 20, 25, 26, 30

Photodissociation dynamics using high- n Rydberg time-of-flight spectroscopy

My group has been interested in the intramolecular and photodissociation dynamics of small molecules for a long time. Our work began with photoinitiated unimolecular reactions and direct photodissociation, albeit with the latter often occurring on multiple potential energy surfaces. This evolved to more complex systems. During the past few years the scientific focus has been centered on curve crossings and non-adiabatic transitions. These are challenging, state-of-the-art problems that are germane to many scientific areas that go way beyond photoinitiated processes. The diagnostic tools that we have enlisted include laser induced fluorescence, multiphoton ionization, diode laser spectroscopy, velocity-aligned Doppler spectroscopy (VADS), and high- n Rydberg time-of-flight (HRTOF) spectroscopy. As mentioned earlier, Karl Welge (Bielefeld, Germany) developed the HRTOF method. It was introduced to our laboratory in the early 1990's — a natural follow-on to the VADS technique. Throughout the years, we evolved the HRTOF technique to a high technical level, and it remains the main diagnostic for much of our work. It turns out to be the method-of-choice for many of the systems of interest, i.e., those in which an H atom "messenger" is imprinted with information about the distribution of excitations in its partner product.

Publications: 11, 13, 15, 17-21, 23-26, 28-33, 34.

Unimolecular decomposition

My group has made a number of seminal contributions (in both experiment and theory) toward our understanding of the unimolecular decomposition of small polyatomic molecules. Our DOE-sponsored projects in this area have focused on the development of a microscopic understanding of reactions that transpire via loose transition states, as well as the competitions that take place between reaction pathways that proceed via loose and tight transition states. Candidate molecules were NCNO, NO₂, NO₃, and H₂CO, each serving as a valuable prototype. The cases of NCNO, NO₂, and H₂CO are, by now, well established, so let me comment here about photoinitiated unimolecular reactions of NO₃. We worked out the competition between the channels: NO + O₂ and NO₂ + O, including tunneling at energies below the barrier to NO + O₂. In the energy regime below this barrier, excited state lifetimes are lengthened to 100's of μ s. These exceptionally long lifetimes of *molecules moving in a molecular beam* required that we chase them downstream with a photomultiplier tube in order to catch their fluorescence! This fascinating system undergoes complex chemistry and photochemistry. Moreover, it is not just a laboratory curiosity. It is the main oxidizing agent in the night sky.

Publications: 1, 22, 24, 27, 28

Bimolecular reactions and energy transfer

This was a main thrust area in my group for many years, mainly the 1980's and early 1990's. In addition to the work on photoinitiated reactions in weakly bound complexes, where many such processes were examined, a number of studies were carried out in which radicals like C_2H were prepared photolytically in a range of excited states. Reactive and energy transfer processes were examined. We also examined: $H + CO_2 \rightarrow OH + CO$ under gas phase single-collision conditions and compared results to those obtained using weakly bound precursor conditions.

Publications: 2, 9, 10, 14, 16, 20, 25, 26, 30, 34

Heavy atom hydrides: relativistic effects and novel potential curves

This work has two sides to it. (1) The heavy atom hydrides that we examined provide an opportunity to prepare slow H atoms with continuously tunable velocity. This is achieved by varying the photodissociation photon energy. Specifically, strong spin-orbit interaction results in flat potential curves in the vertical excitation region, enabling us to access low product H atom translational energies. (2) The relativistic quantum mechanics of these systems is fascinating and intellectually stimulating (and, with enough effort, rewarding). Certainly it pushed me into areas of relativistic physics that five years ago I could not imagine myself entering. We laid the groundwork for the next generation experiments and calculations on these systems. For example, the Group-V hydride progression: NH_3 , PH_3 , AsH_3 , SbH_3 , and BiH_3 would constitute a textbook case in electronic structure, molecular properties, and intramolecular and dissociation dynamics, specifically, how these change in going between nonrelativistic and relativistic regimes. The last paper we published was on AsH_3 , which lies at the interface between relativistic and nonrelativistic regimes. Unfortunately, the experiments were hard beyond belief, and without a qualitative increase in funding level, it is not expedient to pursue this work, no matter how interesting the science might be.

Publications: 29, 30, 32, 33, 35.