

CHAPTER 1

**MULTIPLE CHANNEL REACTION DYNAMICS
USING UNIVERSAL CROSSED MOLECULAR
BEAM TECHNIQUES**

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1. Introduction

During the last few decades, we have witnessed tremendous growth in chemical reaction dynamics research both experimentally and theoretically. Yet, the understanding of multiple channel dynamics still remains to be a challenging topic to both experimentalists and theoreticians. On the theoretical front, such studies are difficult because of the difficulties in the development of accurate full degree potential energy surfaces and quantitative dynamics tools. On the experimental front, the measurement of the multiple channel dynamics is also extremely difficult because of the lack of ideal experimental tools for such studies. The advent of the crossed molecular beams technique¹ has been instrumental to our understanding of the dynamics of chemical reactions over the last few decades. Important and fundamental information has been derived on: primary reaction mechanisms, product angular distributions, partitioning of reaction exothermicity between product internal and translational energy, as well as the dependence of reaction cross-section on collision energy, impact parameter and reactant orientation.^{2–5} Universal crossed molecular beams (CMB) technique⁶ developed in the 1960s by Lee and Herschbach *et al.* based on electron impact ionization have played a key role in crossed beams scattering studies of fundamental chemical reactions. The most important feature of a universal CMB instrument is its ability to measure time-of-flight (TOF) spectra of *all* chemical or photochemical reaction products as a function of laboratory recoil angle. Such experimental data can be analyzed to yield the center-of-mass frame differential scattering cross-section, or “product flux map”, a fundamental quantity that reflects the inter-atomic forces governing the reaction. Up until now, most of the universal crossed molecular beams instruments have relied on

electron bombardment ionization mass spectrometry to provide sensitive, time-resolved product detection. Using electron bombardment ionization, a product flux smaller than 10^4 molecules $\text{cm}^{-2} \text{s}^{-1}$ (0.1 molecule cm^{-3} at a velocity of 10^5 cm/s) can be detected with a time response better than 10^{-6} s. However, since such instrument depends heavily on the ultrahigh vacuum (UHV) condition in the detector, any substantial residual background at a specific mass in the ionizer would prohibit sensitive detection of signals at the specific mass. Therefore, the vacuum condition in a UHV electron impact ionization detector is essential in this technique. The development of modern ultrahigh vacuum technology has provided us many powerful tools to improve the vacuum condition. In addition, quadrupole mass spectroscopic methods can also be significantly improved to enhance ion transmission efficiency for certain range of mass ions. In this chapter, we will first describe a significantly improved crossed molecular beam apparatus based on modern vacuum technologies and its applications in the crossed molecular beams studies of multiple channel dynamics of chemical reactions and complicated photochemistry processes.

Despite the success of universal electron impact ionization detection in the studies of molecular reaction dynamics, the electron bombardment ionization technique does have several disadvantages. First and foremost, electron bombardment ionization often results in fragmentation as well as ionization of the neutral reaction product. In this case, the reaction product is not detected with a mass-to-charge ratio (m/z) equal to the mass of the neutral. This can greatly complicate the identification of reaction products particularly when several reaction channels occur simultaneously. Second, electron bombardment ionization, which requires a hot filament ($T_{\text{filament}} = 2000\text{--}3000$ K), increases the background partial pressure of many species present in the detector chamber increasing the background upon which the signal must be detected. Third, electron bombardment's universality, its chief advantage, is also one of its biggest disadvantages. As an example, it is nearly impossible to construct a high vacuum chamber out of stainless steel and lower the CO partial pressure below 10^{-13} torr, while 10^{-13} torr background is difficult at best for sensitive detection of any species at $m/z = 28$ from crossed beam experiments. Indeed detection of ions with $m/z = 29$ or 27 is likely to be impossible because of mass leakage. Similar arguments hold for detection of products at $m/z = 1, 2, 15, 16, 18$ and 44 , due to trace backgrounds of H_2 , CH_4 and CO_2 . In a similar vein, the operation of the molecular beam sources gives rise to an increase in the partial pressures of molecules which, when dissociatively ionized, can

produce background at the m/z -value of the detected product. Finally, electron bombardments sensitivity and time resolution are also limited by space charge effects. At the highest electron currents, the ionizing electron beam “repels itself”, increasing its volume and lowering the electron flux available for product detection. Furthermore, ionization of products to positive ions at the highest electron flux makes ion extraction to the mass spectrometer impossible on the μs time-scale, since the electron cloud shields the positive ions from the extraction voltages.

Because of the problems associated with electron impact ionization, other detection methods are certainly desirable to overcome these disadvantages. VUV photo-ionization is certainly the best candidate to overcome all of these problems. First, when the wavelength is tuned below the dissociative ionization potential of a molecule it is a “soft” (non-dissociative) ionization method. Reaction products of mass m will be detected as ions of the same mass. Second, photo-ionization does not generate significant amounts of heat ($\sim 20\text{ mW}$ in comparison to 20 W for electron bombardment). Thus it can be employed in concert with cryogenic pumping methods. In this way the ionization region itself may be cooled with liquid Helium, further suppressing the partial pressure of many background gases. Third, photo-ionization can be universal *and* selective, since the wavelength of the light may be tuned. For example, the wavelength tunability can be used to suppress background due to the most common residual gases, CO (I.P. = 14.01 eV), CH_4 (I.P. = 12.51 eV), H_2O (I.P. = 12.61 eV), H_2 (I.P. = 15.43 eV). The tunability may also be employed to detect products with different amounts of internal energy since the ionization threshold of a molecule depends on its energy content. Finally, photo-ionization is not subject to space charge effects, since photons are not charged. Therefore, light can be focused much more tightly than can electrons. Consequently, one can produce a very small ionization volume which provide high time resolution for TOF measurements. Furthermore, there is no fundamental physical limit to the ionization efficiency. As greater and greater VUV flux becomes available, higher and higher detection sensitivity (until unity detection efficiency) can be achieved.

Despite its clear desirability, vacuum ultraviolet (VUV) photo-ionization has not been implemented in a universal crossed molecular beams apparatus previously since table top VUV light sources (which rely on non-linear frequency conversion of pulsed laser light) can not offer the $\sim 10^{16}$ photons/s flux needed for crossed molecular beams experiments and also are very hard

to tune. Recently, however, VUV synchrotron radiations at third generation synchrotron radiation sources are becoming more available. VUV synchrotron radiation based molecular beam apparatus⁷ has been established for chemical dynamics researches⁸ at the Advanced Light Source (ALS), a recently developed third generation synchrotron radiation source, in the Lawrence Berkeley National Laboratory. In this chapter we would also like to describe the design and the performance of a new crossed molecular beams endstation (an improved version over the ALS apparatus) which utilizes the synchrotron radiation source at the SRRC Light Source in Taiwan as the ionizing light source.

2. Improved Universal Molecular Beam Technique Based on Electron Impact Ionization

Mass spectrometric detection based on electron impact ionization is universal, it could not, however, necessarily detect all significant reaction products simply because of its limited detection efficiency and detector backgrounds. Therefore, in a sense, mass spectrometric detection is not a truly universal method for chemical reaction dynamics studies, especially for crossed molecular beams studies with very small scattering signals. For a typical electron impact ionizer used in our laboratory, the emission current I_e is about 1 mA ($\sim 1 \times 10^{16}$ electrons) and the ionization length l is about 1 cm, the ionization rate for a reaction product M in the ionizer, $M + e^- \rightarrow M^+ + 2e^-$, is

$$\frac{dM^+}{dt} = \sigma I_e [M^+]$$

Therefore, the probability of a molecule in the ionizer gets ionized in a one second duration is,

$$P_i = \sigma I_e = 10^{-16} \times 10^{16} = 1,$$

in which ionization cross section is typically considered to be $1 \times 10^{-16} \text{ cm}^2$. However, for a molecular product flying through the ionizer, the residential time is only about l/v , where v is the flying speed of the product molecule and l is the ionization length. The ionization probability for a typical reaction product with a flying speed of 1000 m/s is about 10^{-5} . Therefore, only one product molecule among a hundred thousand molecules flying through the detector gets ionized. This is not a very good efficiency considering there are not many product molecules to begin with. Another limiting factor in the detection efficiency is the ion transmission efficiency of the quadrupole assembly. It is known that the acceptance radius for an ion transmitting