

## Identify New Products of Crossed Molecular Beam Reactions Using Synchrotron Radiation

### Beamline

21A1 Chemical Dynamics beamline

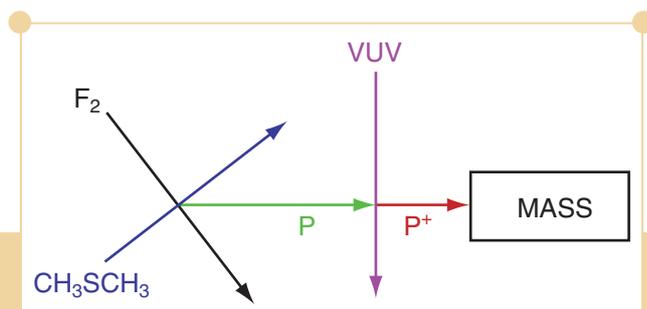
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The crossed molecular beam method has been very powerful to study dynamics of elementary reactions by measuring mass-resolved product velocity and angular distributions. However, crossed molecular beam experiments often encounter a serious background problem. Although triple differential pumping in the detection chamber has significantly reduced effusive gases from the scattering chamber, the background may be still high for a reaction which has a small reaction cross section. The major background is from elastic and inelastic scattering of impurity in the molecular beam. Especially in electron impact ionization detection, dissociative ionization is often extensive, which spreads the background into a wide mass range. Here we like to demonstrate that photoionization detection scheme can reduce dissociative ionization processes very efficiently and therefore reduces possible background sources. Furthermore, photoionization spectroscopy of the product can offer important information, such as ionization potential and appearance energy of ion fragmentation, which are often different for various isomers. Unambiguous determination of the chemical identities of the products can be made by comparing observed quantities with accurate energetics from either thermodynamics cycles or high level *ab initio* calculations. In fact, this method has been applied to photodissociation reactions to distinguish product isomers. It is much more challenging for crossed molecular beam reactions due to small number density of the products. The high photon flux of  $10^{16}$  photon/sec provided by the U9 undulator is really a great help to observe the weak signals.

One interesting example is a molecule-molecule reaction which usually has a quite small reaction cross section. Thus, the vast majority of crossed molecular beam studies involve at least one radical reactant to ensure a significant percentage of reactive events under the single collision condition. Molecular beam studies on reactions between two stable species are really sparse, although they can be important and interesting. To gain some ideas, a comparison of rate constants of a few selected reactions is listed in Table 1. We chose the reaction between fluorine molecule and dimethyl sulfide ( $F_2 + CH_3SCH_3$ ). Despite of the closed shell nature of both reactants, significant signals were observed under the

crossed molecular beam condition. Nascent products were detected by VUV photoionization and also by electron impact ionization. Figure 1 shows the schematic configuration of the crossed molecular beam experiment using photoionization detection.  $F_2$  molecular beam was produced by expanding

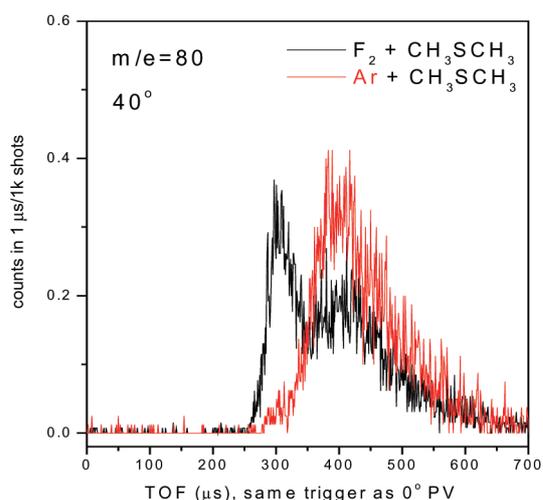


**Fig. 1:** Scheme of photoionization detection of crossed molecular beam product P.

**Table 1:** Kinetic rate constants of  $R_1 + R_2$  reactions to show some typical fast molecule-molecule reactions (blue), fast molecule-radical reactions (green) and very fast atomic radical-molecule reactions (red).  $k(T) = Ae^{-E_a/RT}$ . Units:  $\text{cm}^3\text{molecule}^{-1}\text{sec}^{-1}$  and kcal/mol. Data are from <http://kinetics.nist.gov>

$R_1$	$R_2$	$A$	$E_a$	$k(298\text{K})$
$F_2$	NO	$7 \times 10^{-13}$	2.3	$1 \times 10^{-14}$
	$H_2S$			$< 6 \times 10^{-16}$
	$C_2H_4$	$8 \times 10^{-14}$	4.6	$4 \times 10^{-17}$
$F_2$	$CH_3$	$7 \times 10^{-12}$	1	$1.3 \times 10^{-12}$
	H	$5 \times 10^{-11}$	2.1	$1\sim 4 \times 10^{-12}$
$O(^1D)$	$N_2O$	$1\sim 2 \times 10^{-10}$	$< 0$	$1\sim 2 \times 10^{-10}$
	$CH_4$	$1\sim 3 \times 10^{-10}$	$< 0$	$1\sim 3 \times 10^{-10}$
	$C_3H_8$	$6\sim 10 \times 10^{-10}$	$< 0$	$6\sim 10 \times 10^{-10}$
	$SiH_4$	$3 \times 10^{-10}$	$< 0$	$3 \times 10^{-10}$

$F_2/He/Ne$  gas mixture through a fast pulsed valve (Even-Lavie valve, high rep-rate model, Tel Aviv University, Israel). Various Ne concentrations from 0 to 90% with  $F_2$  concentrations from 5 to 10% were used to tune the molecular beam speeds. Dimethyl sulfide (DMS) molecular beam was produced by expanding 20% DMS/He gas mixture through a similar pulsed valve which was heated to  $160^\circ\text{C}$  to avoid cluster formation. Sharp edge skimmers were used to confine the angular divergence of both molecular beams to  $\pm 2^\circ$ . Two pulsed valves were synchronized to have

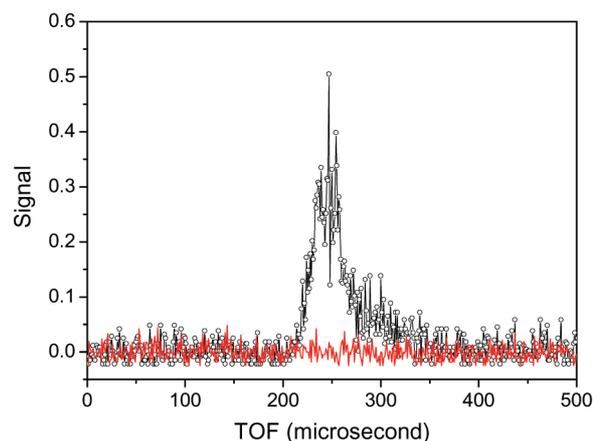


**Fig. 2:** TOF spectrum of  $m80$  product ( $CH_3SFCH_2^+$ ) from crossed beam reaction detected by electron impact ionization. Black line: signal from  $F_2 + DMS$  scattering; red line: background from  $Ar + DMS$  scattering. There is an offset in the flight time.

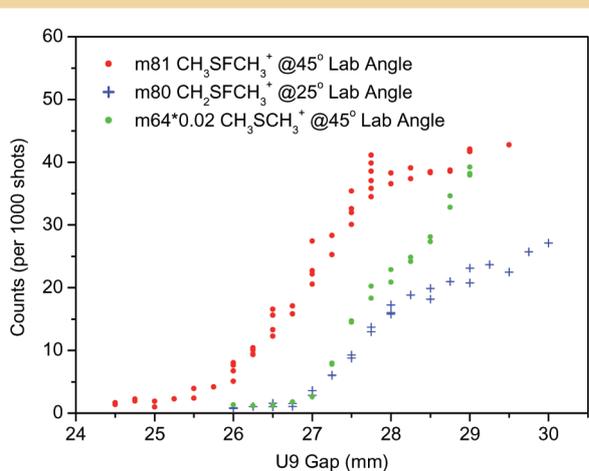
optimized overlap of the molecular beam pulses. The neutral products traveled for 10 cm and were ionized by the VUV photon beam from the synchrotron radiation. The product time of flight (TOF) was recorded by a multichannel scalar after mass selection and ion counting.

Although the reaction signals are significant, there are still many possible sources of backgrounds such as impurities in the sample. Therefore, we carried out two types of experiments to verify if the signal is true. First we carried out a scattering experiment of  $Ar + CH_3SCH_3$  as a background test. Ar atom has a similar mass to  $F_2$  molecule. When we use similar beam speeds, the Newton diagram and scattering kinematics should be similar in both cases except for the reactive scattering. Therefore the Ar scattering experiment tells us the background from impurities in the  $CH_3SCH_3$  sample. Secondly we used  $CD_3SCD_3$  reactant to double check the product masses. Figure 2 shows that significant impurity from the commercial sample interferes the reactive signal if we use electron impact ionization detection. In VUV photoionization detection, the background is negligible (see Fig. 3).

The photoionization efficiency spectra of the sulfur containing products can be measured by tuning the undulator gap to vary the photon energy. The top-up injection mode of the storage ring provides stable and higher photon flux, which really helps the data acquisition. The chemical identities of the pro-



**Fig. 3:** TOF spectrum of  $m80$  product ( $CH_3SFCH_2^+$ ) from crossed beam reaction detected by VUV photoionization. Black line: signal from  $F_2 + DMS$  scattering; red line: background from  $Ar + DMS$  scattering. Other experimental conditions were similar to those of Fig. 2. There is an offset in the flight time.



**Fig. 4:** The photoionization efficiency spectra of the mass 80 ( $\text{CH}_2\text{SFCH}_3$ ) and mass 81 ( $\text{CH}_3\text{SFCH}_3$ ) products from the  $\text{F}_2 + \text{CH}_3\text{SCH}_3$  crossed beam reaction at 9 kcal/mol collisional energy. The resolution of the synchrotron radiation photon beam is about 3% ( $\Delta E/E$ ). A spectrum of  $\text{CH}_3^{34}\text{SCH}_3$  (m64, from the non-reactive scattering) recorded under otherwise identical conditions is also shown for comparison.

ducts can be determined by comparing the observed ionization thresholds with *ab initio* calculations. Two distinct product channels were observed, one produces two molecular products,  $\text{HF} + \text{CH}_2\text{SFCH}_3$ , and the other produces two radical products,  $\text{F} + \text{CH}_3\text{SFCH}_3$ . The ionization energy of  $\text{CH}_2\text{SFCH}_3$  product is about 8.7 eV and the ionization energy of the radical product,  $\text{CH}_3\text{SFCH}_3$ , is about 7.8 eV. Typical photoionization efficiency spectra of the reaction products are shown in Fig. 4.

The yield of the radical product channel decreases very significantly when the collision energy is lowered to 6 kcal/mol, indicating a clear threshold behavior. From the product time-of-flight spectra and angular distributions, we found that the  $\text{HF} + \text{CH}_2\text{SFCH}_3$  channel has a much higher translational energy release than the  $\text{F} + \text{CH}_3\text{SFCH}_3$  channel, consistent with a typical HF elimination process. The angular distribution of  $\text{HF} + \text{CH}_2\text{SFCH}_3$  channel is strongly forward at collisional energies ranging from 4 to 11 kcal/mol, suggesting significant contributions from large impact parameters and a low reaction barrier.

It has been proposed that a charge transfer mechanism might be responsible for the reactivity between  $\text{F}_2$  and  $\text{CH}_3\text{SCH}_3$ , based on that  $\text{F}_2$  has very high electron affinity and  $\text{CH}_3\text{SCH}_3$  has low ionization energy such that the ion pair of  $[\text{CH}_3\text{SCH}_3^+][\text{F}_2^-]$  is more stable than most other combinations. This mechanism sounds reasonable but might be oversimplified. We are doing high level *ab initio* calculations to find the reaction paths. To investigate more about the reactivity between these two closed shell species, we have carried out a beam-cell attenuation measurement, which provides the absolute scattering cross section between  $\text{F}_2$  and  $\text{CH}_3\text{SCH}_3$ , which

consists of both reactive scattering and non-reactive scattering. The ratio between them was obtained in the crossed molecular beam experiment. So the absolute reaction cross section can be deduced.

Closed shell molecules are usually far less reactive than radicals. Investigation of the reaction dynamics between two stable species is really sparse. It often takes a significant amount of energy to promote reaction between two closed shell molecules, but the  $\text{F}_2 + \text{DMS}$  reaction may be one of the exceptions. Using the crossed molecular beam technique, translational energy dependence of reactivity can be studied explicitly. This work investigated a new type of reaction, in which significant reactivity between two closed shell molecules was observed under near ambient conditions. The results are definitive and intriguing. Together with future efforts of theoretical calculations, we should be able to learn more about the mechanism of this interesting reaction.

### Experimental Station

Chemical Dynamics end station

### Publications

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- L. R. McCunn, K. C. Lau, M. J. Krisch, L. J. Butler, J.-W. Tsung, and J. J. Lin, *J. Phys. Chem. A* **110**, 1625 (2006).
- Y.-Y. Ji, P. Bobadova-Parvanova, C. Larson, P. C. Samartzis, K. Morokuma, J. J. Lin, T.-T. Ching, C. Chaudhuri, S.-H. Lee, and A. M. Wodtke, *J. Chem. Phys.* (2006), accepted.

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