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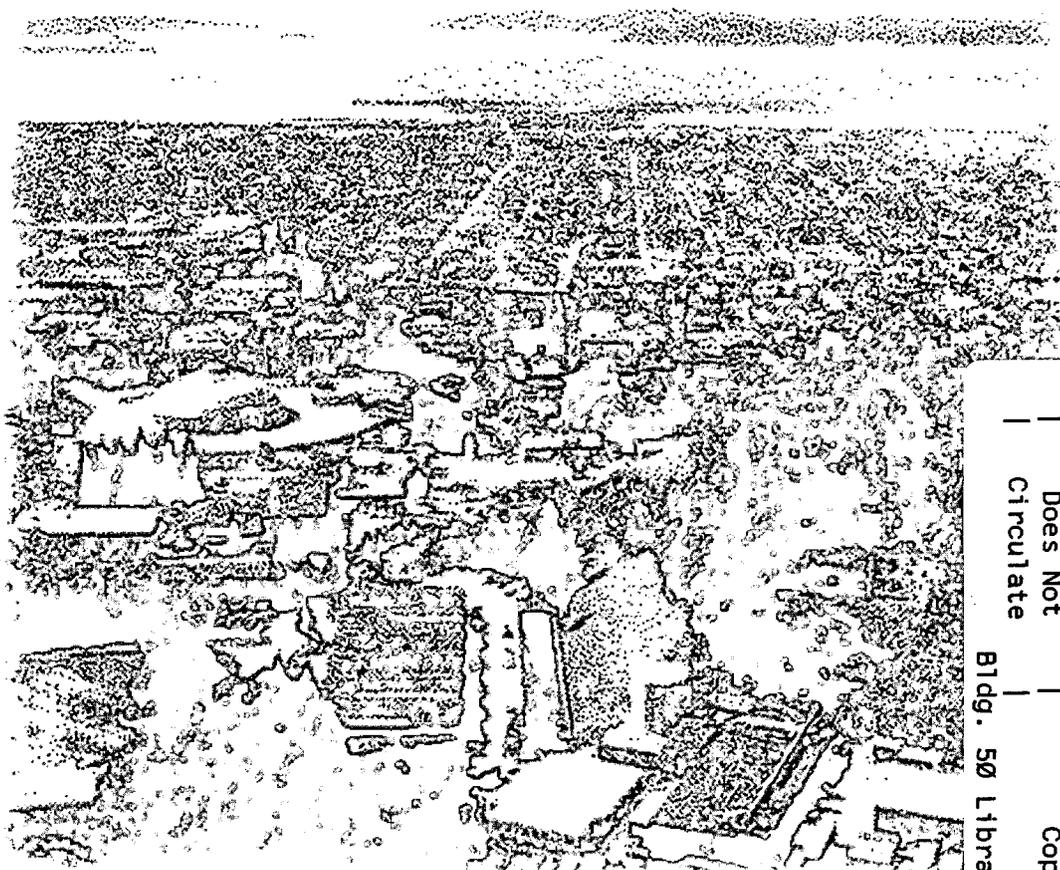


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A Crossed Molecular Beam Apparatus Using Synchrotron Radiation

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Abstract

Electron impact ionization has been the main detection tool for universal crossed molecular beam reaction and photodissociation studies for the last few decades. Yet, it has its inherent drawbacks, for example, extensive dissociative ionization, high background for certain masses and non-selective ionization. The Advanced Light Source (ALS) at Berkeley has provided us a high brightness, tunable VUV light source for clean and efficient photoionization. A dedicated Chemical Dynamics Beamline has been built at ALS as a national user facility for studies of fundamental chemical processes. High flux (10^{16} photon/s with 2% bandwidth) VUV synchrotron radiation from 5 to 30 eV can be obtained from the beamline, whose source is a five meter U10 undulator. A rotatable source crossed molecular beam apparatus has been established for unimolecular and bimolecular reactive scattering studies. Photodissociation studies were carried out using VUV synchrotron radiation as the ionization detection technique at this endstation. Results show the advantages of the apparatus using VUV ionization as the detection scheme over similar machines using electron impact as the ionization source.

(1) INTRODUCTION

The studies of bimolecular and unimolecular reactions using molecular beam techniques have greatly improved our understanding of chemical reactions.¹ The angular resolved time of flight (TOF) method for reactive scattering studies gives us the information that is needed to understand the detailed dynamics of reactive processes. Currently used universal TOF detection techniques for crossed beam reactive scattering studies are mostly associated with electron bombardment ionization. While electron bombardment ionization is the standard technique for mass spectrometric detection, it does have certain disadvantages, such as: extensive dissociative ionization, limited TOF resolution because of its finite ionization region, high background for certain masses, and certainly no selective ionization of different species.

Light, from the early flash lamp source to the modern lasers, has been widely used in the studies of chemical processes. Tunable coherent VUV light as the ionization detection tool in TOF measurements, instead of electrons, is expected to have many advantages over the widely used electron bombardment ionization method. Firstly, tunable VUV ionization can be somewhat species selective since the ionization potentials for different species are different. As a result it should be possible to eliminate the high background at mass 15(CH_3^+), 16(CH_4^+), 18 (H_2O^+), and 28(CO^+), which normally exist in the electron impact ionization detector. This is particularly important when detecting hydrocarbon radical species with IP much lower (in many cases) than those of the background molecules. Tunable VUV light will also allow us to obtain information about the internal energy of the reactive species due to the different characteristics of energy dependent ionization cross sections between "cold" and "hot" species. Secondly, soft (low energy) VUV ionization is expected to cause much less fragmentation than electron impact ionization, making the detection and analysis of multiple channel reaction processes much simpler and more straightforward. Thirdly, since undulator VUV light is focusable, the ionization region can be much smaller than a comparable electron bombardment ionizer, making both the translational energy and angular resolution much higher. Since a VUV light source has a very small heat load (~ 20 mW) in comparison to the 20 W heat load of the electron impact ionizer, the ionization region can also be easily cooled to very low temperature, making the inherent background much smaller in the detector. Lastly, much like electron impact ionization, VUV ionization is still a universal detection technique. However, in order to make the VUV ionization a standard universal detection technique for chemical

reactions, one has to meet the following two criteria: high VUV photon flux (high enough sensitivity) and wide range tunability. The two criteria together are hard to meet even by the modern state-of-art laser techniques. The recently developed third generation synchrotron radiation source at the Lawrence Berkeley National Laboratory, namely the Advanced Light Source, has provided us such a light source.

In this paper we will describe in detail the design of the crossed molecular beam machine on the ALS Chemical Dynamics Beamline, and then present our first results using synchrotron radiation to study photodissociation of methylamine and ozone using this machine.

(2) APPARATUS DESIGN

The Advanced Light Source (ALS) is one of the first low emittance, third generation synchrotron radiation facilities available.² The design of ALS is optimized for insertion devices (undulators, wigglers) which produce tunable VUV to soft X-ray radiation with much higher photon flux than bending magnets. A U8 (8cm) /U10 (10 cm) undulator has been used for the generation of VUV light. A beamline dedicated for chemical dynamics research has been constructed using the U8/U10 undulator, providing $\sim 10^{16}$ photon/s (2% bandwidth) VUV light, tunable from 5 to 30 eV.^{3,5} The higher order radiation of the light generated in the undulator is filtered out by a gas filter.⁴ The fundamental undulator radiation is then directed to the rotating source crossed molecular beam machine.

The new crossed beam apparatus is designed primarily for three types of experiments: (1) Crossed molecular beam reactive scattering studies using synchrotron radiation or electron impact ionization as the detection scheme; (2) Photodissociation studies using synchrotron radiation or electron impact ionization as the detection method. 3) Photodissociation studies using synchrotron radiation as the photolysis source and electron impact ionization as the detection light source. The main detector is, therefore, equipped with both electron impact ionization and VUV ionization detection schemes. Figure 1 shows the schematic of the crossed molecular beam apparatus. It has three main parts: the rotatable source, the main chamber and the detector. The rotating source has two source chambers, each of which has a differentially pumped region. The two molecular beam sources are fixed at 90 degrees, and the whole source chamber is rotatable from -20 to 110 degrees (total 130 degrees rotation). Each of the two main source regions is pumped by a high-throughput magnetically levitated 2000 l/s turbopump (Seiko Seiki STPH2000C). This will allow us to run the source at higher pressure than that allowed by diffusion pumps. Each of the two source differential pumping regions is pumped

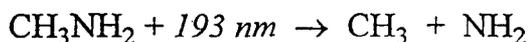
by either a 300 or 400 l/s turbopump (Seiko Seiki STP 300/400). The main chamber, which serves as the region where two molecular beams cross, is pumped by a 2000 l/s turbopump (Seiko Seiki STP2000C), which is backed by an oil free scroll pump. A base plate cooled by liquid nitrogen is also available for cryopumping of the main chamber. Normally the main chamber can be maintained at a 10^{-8} torr vacuum. In order to isolate the ionization region from the main chamber, two differential regions are present. Region I, pumped by a 300 l/s magnetically levitated turbopump (STP300), is the first differential region, can easily reach 10^{-9} torr vacuum. Region II, also pumped by a 300 l/s magnetically levitated turbopump (STP300), is the second differential region which also connects with the advanced light source. Usually, it can maintain at 10^{-10} torr vacuum. Region III is the ionization region, which includes a VUV ionizer, an electron bombardment ionizer and ion optics to transport ions. It is pumped by a 600 l/s magnetically levitated pump (STP600). This whole region is cooled to liquid nitrogen temperature, ultimate 3×10^{-11} torr vacuum can be obtained. Quadrupole (Extrel) mass selection then follows in region IV which also houses a standard Daly ion detector. This region is pumped by a 300 l/s magnetically levitated turbo pump (Seiko Seiki STP300). All four turbo pumps on the main detector are backed up by a 250 l/s magnetically levitated turbo pump (Osaka TH-250MC), which is then backed up by an oil free scroll pump. A time of flight chopper wheel is available in front of the detector for velocity measurements.

The first set of experiments carried out on the new experimental station are focused on photodissociation of molecules by an excimer laser using tunable VUV ionization detection. Only one molecular beam source is used in these experiments. An excimer laser is focused at the axis of rotation of the molecular beam source. Photodissociation products are then detected as a function of flight time and scattering angle. Preliminary results will be shown in the following section for methylamine photodissociation at 193nm and ozone photodissociation at 193 nm and 248 nm, which will show some of the advantages of the new apparatus.

(3) PRELIMINARY RESULTS

Detecting hydrocarbon radicals, especially the methyl radical, has been a difficult task for electron impact ionization detection because of extensive dissociative ionization and high background. We have investigated the photodissociation processes of methylamine at 193 nm which provides us an excellent example to show sensitive detection of methyl radical using the new machine. Tunable VUV light of 8.5 eV or higher was used in this experiment with a storage ring running at 1.0 GeV with a U8 undulator as the light source. The main dissociation

signals are found to be at $m/e=29$ (H atom loss channel likely). However, there is another minor dissociative channel



for methylamine at 193 nm photodissociation. Figure 2 shows the time of flight spectra of $m/e=15$ at $\theta=25^\circ$, and $m/e=16$ at the same angle after 4×10^5 laser shots. Eventhough this is a very minor channel (a few percent or less of the total dissociation), good signal to noise can still be obtained due to the extremely low background at both $m/e=15$ and 16. By tuning the VUV energy lower than the IP of the background species, the background can be almost eliminated. The momentum matched fits to both $m/e=15$ and $m/e=16$ at 25 degrees show clearly that the signals at $m/e=15, 16$ are from the methyl group loss channel. In comparison with results obtained using electron impact ionization detection technique,⁵ the signal-to-noise ratio at $m/e=15$ in this experiment is at least more than one order of magnitude better. Energy dependence of the total ionization cross section of photofragments can also be mapped out using the tunable VUV ionization.

Photodissociation of ozone at 248 nm has also been carried out using the full undulator light (without higher order harmonic suppression) as the detection light source, with the lowest fundamental frequency at 18 eV. In this experiment, a storage ring running at 1.5 GeV is used with a U8 undulator. Figure 3 shows the time of flight spectra of O_2 and O when ozone was photolysed at 248 nm. The data is not yet fully analyzed. Nevertheless this figure shows one of the main advantages of the new endstation: even at 18 eV, direct peak-to-peak momentum matching of the two products can be seen, with little dissociative ionization of O_2 to give mass 16 signal in the VUV ionizer. This is in contrast to the results of previous photodissociation studies of O_3 using electron impact ionization, where extensive dissociative ionization complicates the analysis.⁶ Vibrationally resolved structures in the TOF spectra of the photofragment at 248 nm have been observed. From our comparison with the photodissociation machine⁷ using electron impact ionization detection, the detection sensitivity of the new machine is at least comparable if not better.

(4) CONCLUSION

A unique chemical dynamics beamline has been established for reaction dynamics studies at the Advanced Light Source. The new crossed molecular beam apparatus is now in

full operation. Preliminary results are reported for photodissociation studies of methylamine and ozone. Experimental results show that the new experimental station using ALS VUV light as the ionization detection scheme has many advantages over similar machines using electron bombardment ionization as the detection technique.

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Figure Captions

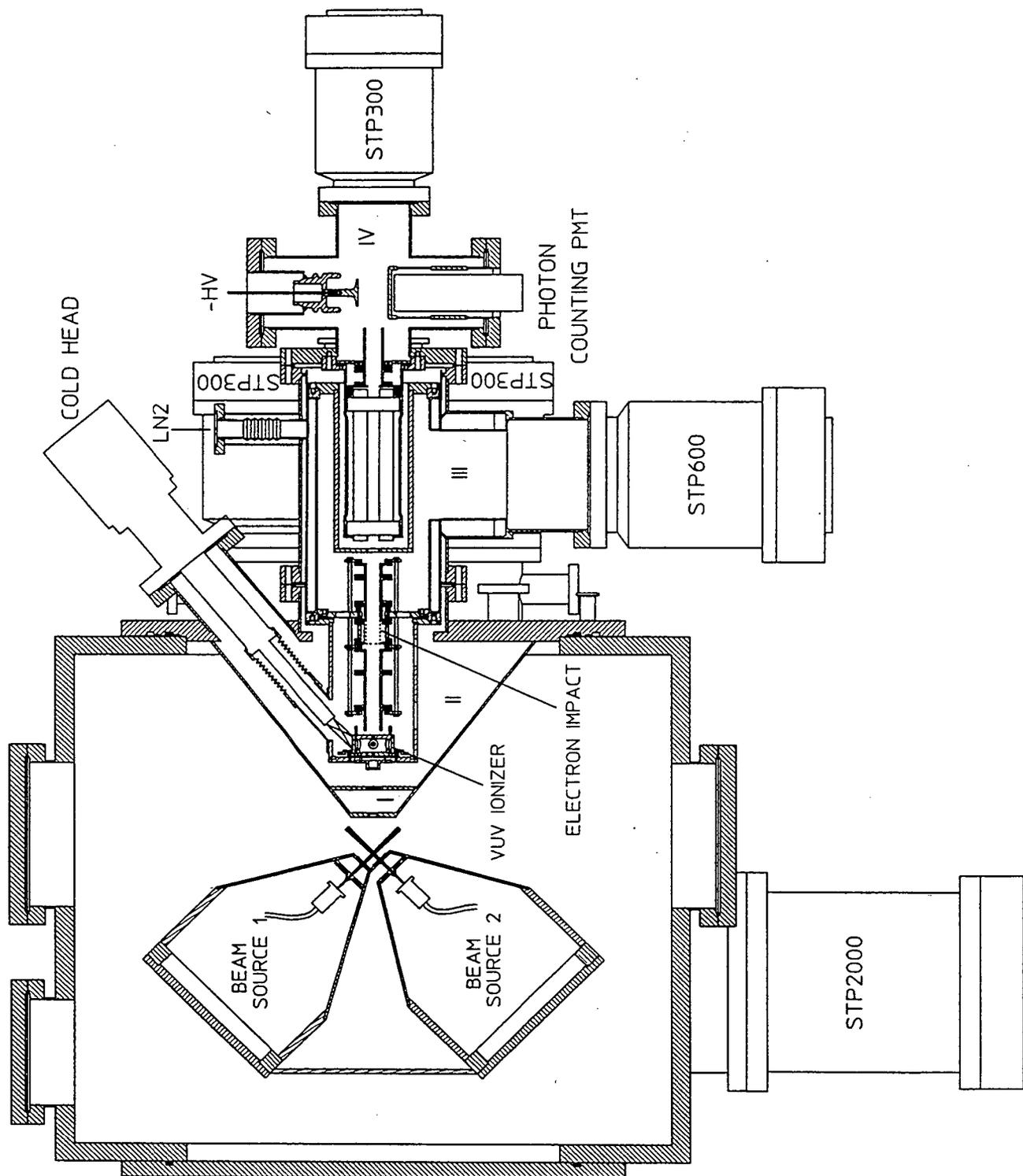
Figure 1. Schematic of the rotating source crossed molecular beam apparatus on the chemical dynamics beamline.

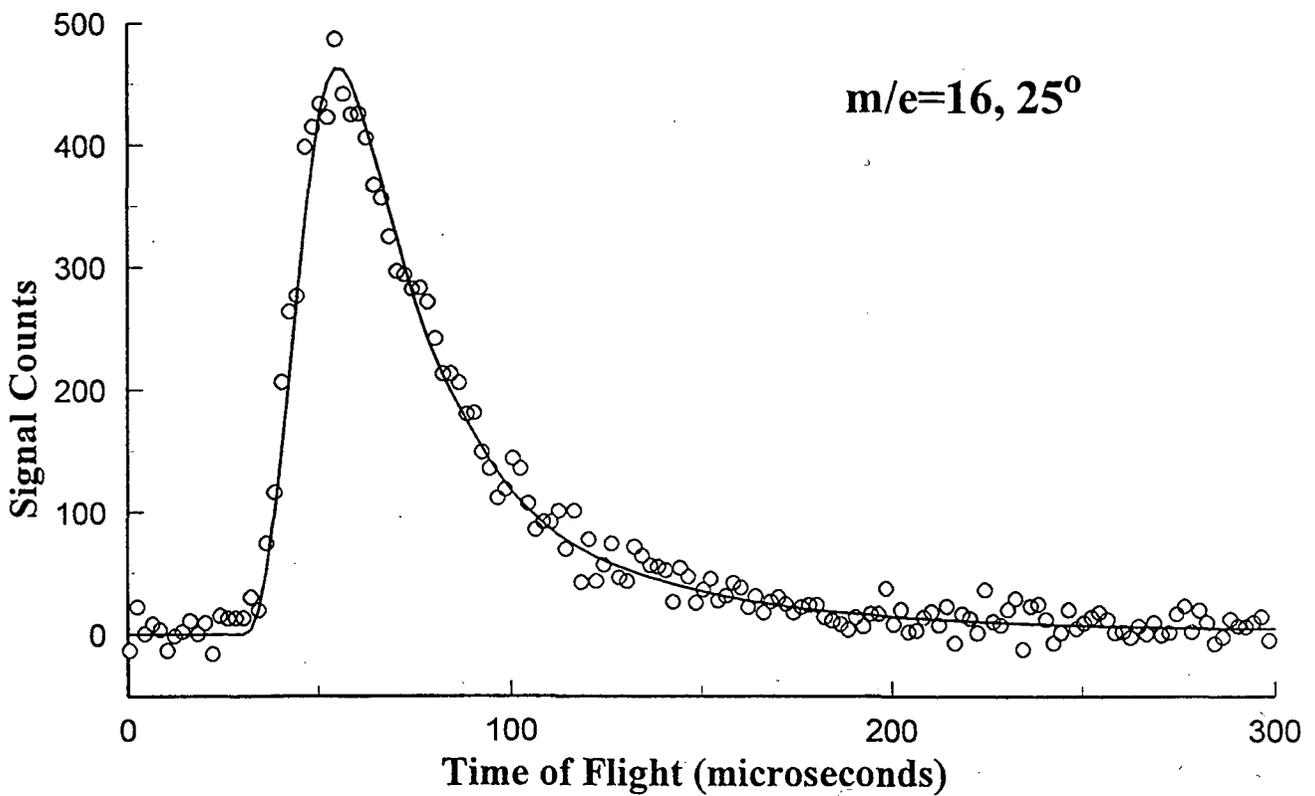
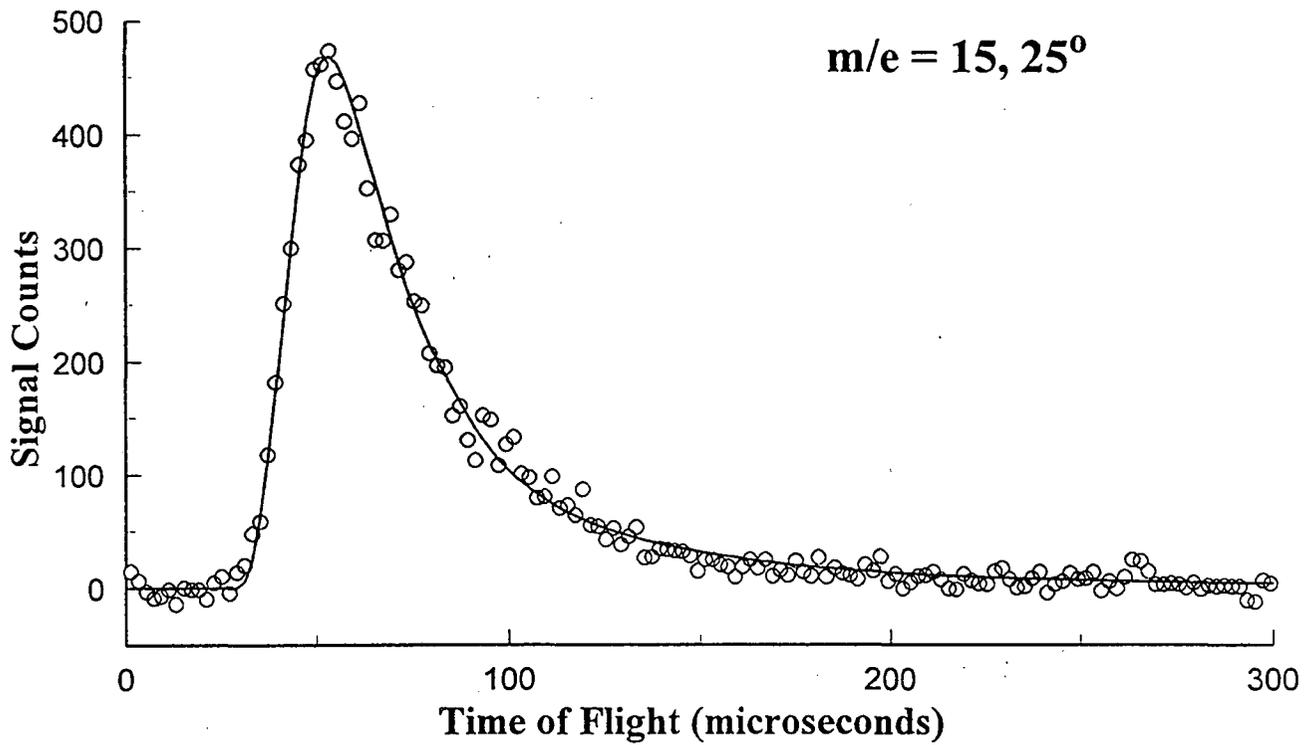
Figure 2. Time of flight spectra of photofragments at $m/e = 15, 16$ at $\theta = 25^\circ$ from photodissociation of methylamine at 193 nm. The photon ionization energy is about 13.0 eV. The open circles represent the experimental data. The solid line shows the fit to both spectra using a single translational energy probability distribution of the methyl group loss channel.

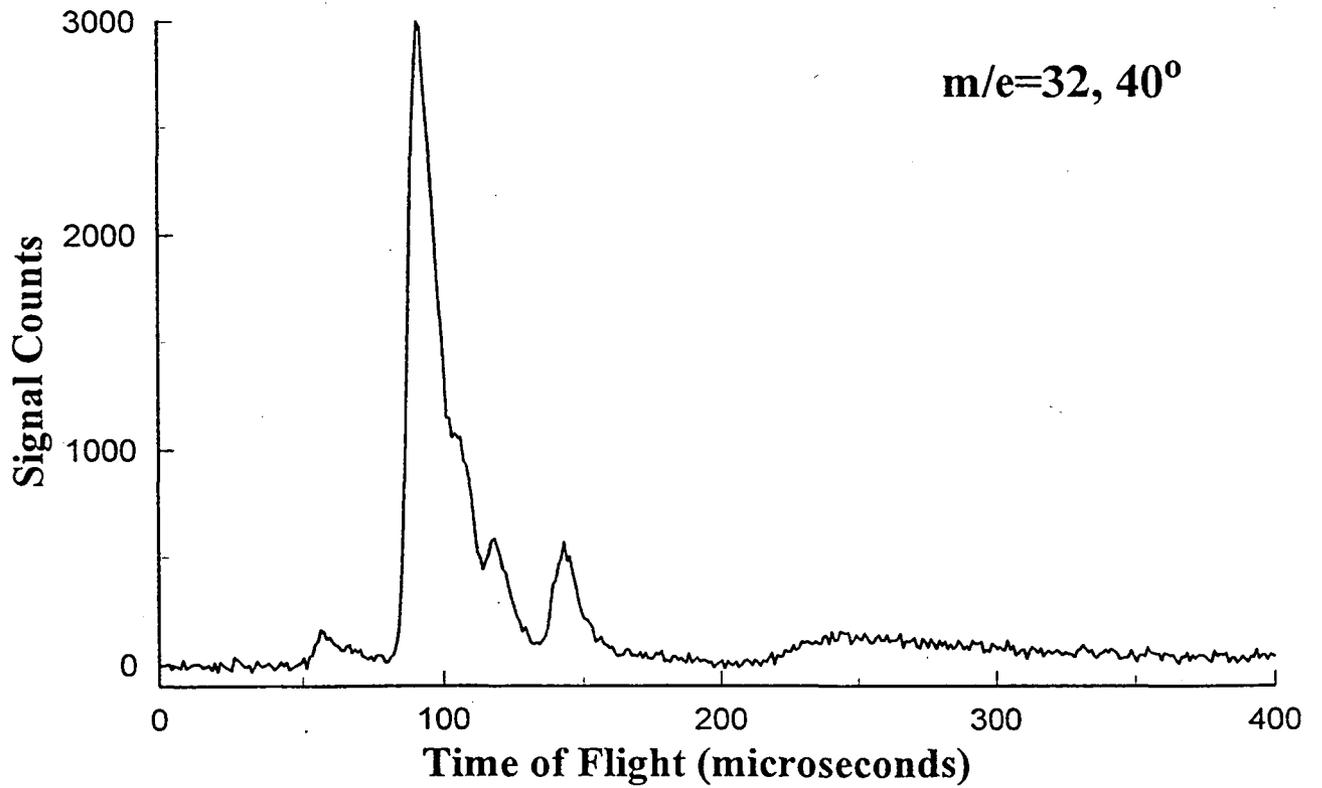
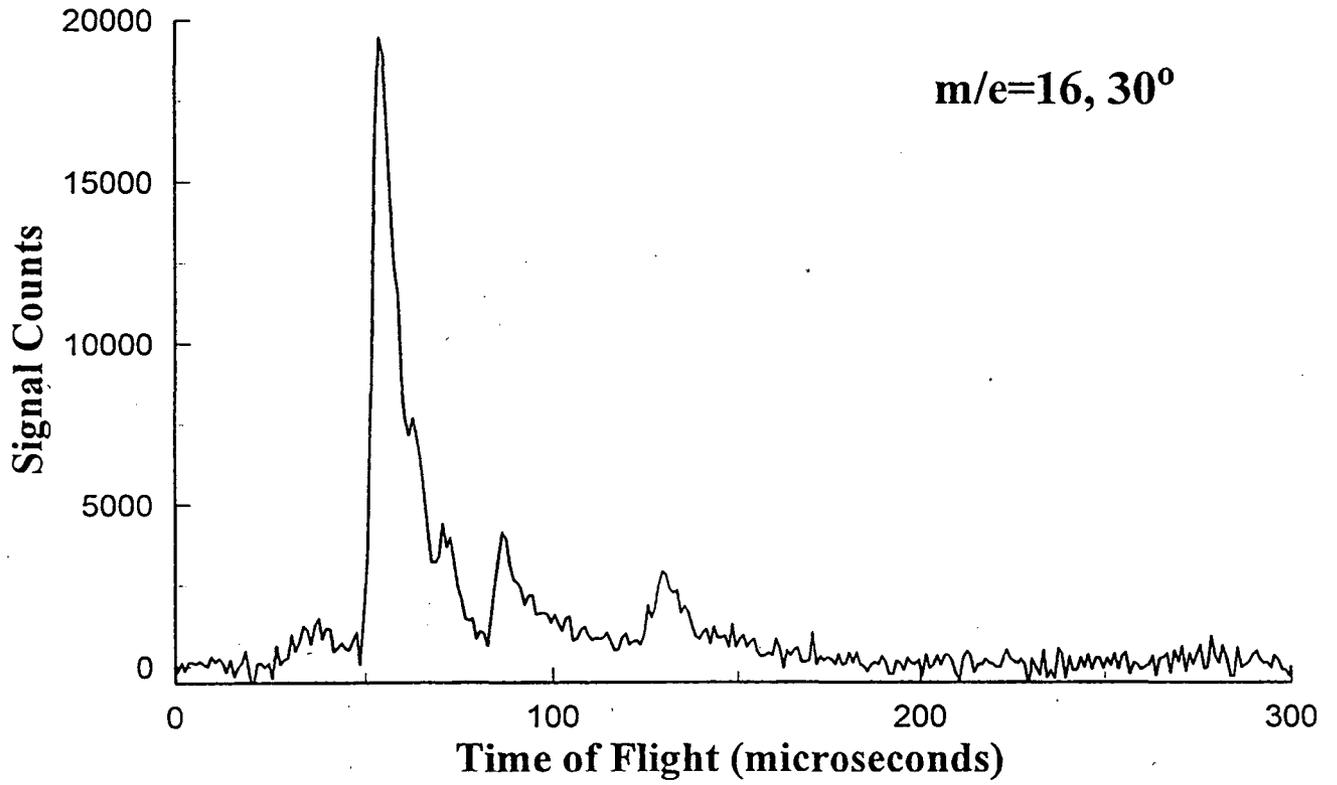
Figure 3. Time of flight spectra of $m/e = 16, 32$ from ozone photodissociation at 248 nm. It is easy to see that the six peaks on the two spectra are roughly matched up one by one.

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