

# Photoionization and Photoelectron Studies of Radicals and Other Transient Species in Gas Phase

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## INTRODUCTION

In order to extend the clearly demonstrated experimental capabilities of the 9.0.2 Beamline and further exploit its outstanding potential, we have recently embarked upon a program aiming to study free radicals and other transient gas-phase species.

Free radicals can be loosely described as molecular fragments that are detached from some molecular precursor via bond breakage. Most of these species are open-shell and highly reactive, frequently approaching collisional half-life periods. Free radicals play an important part in the mechanism of many chemical reactions, particularly those that are relevant to combustion and atmospheric chemistry. Hence, understanding radicals and knowing their properties is a *condicio sine qua non* for constructing plausible reaction mechanisms and building realistic models of chemical processes. Radicals and other transient species that are of particular interest to us are those that are intimately connected to various energy-producing and other technologically relevant processes, with particular emphasis on species related to combustion processes, subsequent atmospheric chemistry, or are of fundamental academic interest.

Photoionization mass spectrometry and its variants (such as ZEKE, MATI, PFI, PEPICO, etc.) are a powerful tool for the study of species in gas phase, producing a plethora of fundamental spectroscopic information, such as various molecular and energetic constants, photoion yield curves (which have to be known if one desires to develop efficient diagnostics for real-life systems), details on electronic and geometric structure, as well as a variety of dynamical information, which includes insights on unimolecular decomposition of molecular ions, intramolecular energy transfer, autoionization phenomena, etc.

An additional and important intrinsic benefit of photoionization studies emanates from the fact that these measurements are capable of providing accurate and reliable thermochemical information, such as bond dissociation energies or, equivalently, enthalpies of formation of both radicals and stable species. Most often, the desired thermochemical information is obtained from a series of measurements performed on a radical or some other transient species, coupled to measurements on one or more suitably chosen stable precursors.

Measurements on free radicals tend to pose quite formidable experimental challenges. The primary reason for this is the high reactivity and consequent ephemeral nature of these species, resulting in relatively low number densities that can be achieved in practice. This directly translates into low-intensity experimental signals. It is precisely this aspect that can be quite successfully overcome by using the outstanding brightness of the ALS.

## EXPERIMENTAL PROGRESS

The prerequisite for studies of radicals is the successful construction and implementation of a broad variety of *in situ* sources that can produce these ephemeral species in sufficient number densities.

Among the multitude of sources of radicals that we are planning to develop and install, the first one selected for actual implementation was laser photodissociation at Endstation 2. The primary challenge here was to develop a continuous or quasi-continuous source of transient species, while using the available pulsed laser source of moderately high repetition rate (100-300 Hz). An additional requirement, which greatly simplifies the extraction of thermochemically meaningful values, was to produce radicals whose internal energy content is rather accurately known. An obvious way to achieve the latter is to allow complete collisional relaxation of the excess energy initially carried away by the nascent radicals during the photodissociation step, and hence produce an effusing stream of transient species that are reasonably well equilibrated at a known temperature. The third requirement was that the source construction had to accommodate the constraints imposed by the geometrical complexities of the current apparatus. All three goals were achieved by devising a relatively simple T-shaped source design that was previously developed and tested at Argonne National Laboratory. These preliminary tests have shown that the effusing stream of radicals is pseudo-continuous, and that, when combined with appropriate timing sequences, the source is capable of producing radicals that are well equilibrated at the temperature of the wall of the source. While studies at Endstation 2 have been so far performed with the source kept at 300 K, the design has provisions for the addition of thermal jackets, which allow temperatures ranging from the condensation temperature of the precursor compound to 1200 K.

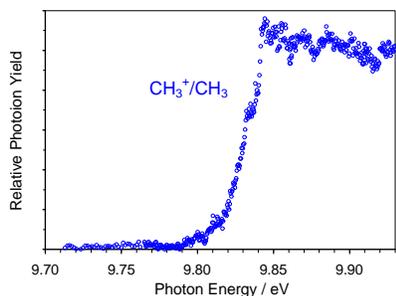


Figure 1. Photoion yield curve of methyl radical equilibrated at 300 K, obtained during tests on ES 2

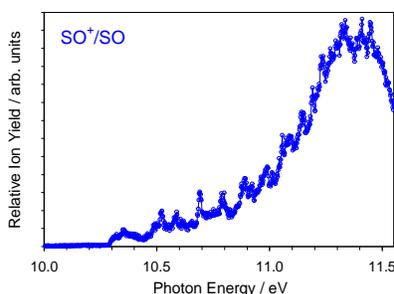


Figure 2. Photoion yield curve of SO radical equilibrated at 300 K, obtained during tests on ES 2

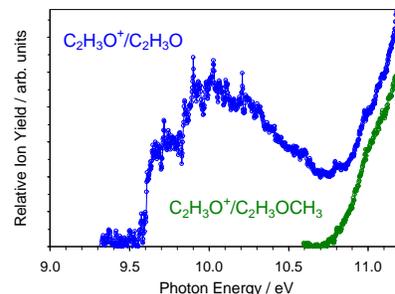


Figure 3. Exploratory scan of the photoion yield curve of vinyloxy radical obtained on ES 2

Initial tests of this source on Endstation 2 were performed on  $\text{CH}_3$  generated by photodissociation from two precursors: methyl iodide and acetone. Methyl radical was selected for two reasons: its photoion yield curve is already quite well known,<sup>1, 2</sup> and, since it is not as extremely reactive as some other radicals, it can be produced *in situ* with relatively high yields.<sup>2</sup> The test runs have produced a quite satisfactory spectrum (see Figure 1) and also allowed us to explore various timing sequences required for data collection and fine-tune them. The second part of these tests was carried out on SO obtained by laser photolysis of  $\text{SO}_2$  (see Figure 2). The idea behind exploring SO, which has also previously known photoelectron and photoionization spectra,<sup>3, 4</sup> was to test the PFI technique, since the selected production method provides a window in the appropriate energy domain that is relatively free of other possible contaminants. While the

tests have demonstrated that the radical source and the timing sequences are correct, it also suggested that the silicon carbide grating that was in use at the time on the Eagle monochromator had insufficient reflectivity in the low energy range, where most radicals of interest have ionization onsets. After a new MgF<sub>2</sub> coated grating was installed, we started exploring vinyoxy radical (see Fig. 3) and produced its first photoionization spectrum.

Even more recently, we have implemented the same source on Endstation 3. The idea here was to trade resolution for even higher light intensity. In spite of the fact that the 3-m monochromator was not yet fully commissioned at the time, we were able to conduct performance checks of this source, again using CH<sub>3</sub> as a test case. These were extremely encouraging, suggesting that a good future strategy would be to use Endstation 3 to obtain overview spectra of radicals, and Endstation 2 to perform high-resolution studies of selected spectral regions.

## FUTURE PLANS

The initial tests of the laser photodissociation source indicate the great potential of Beamline 9.0.2 for photoionization and photoelectron studies of radicals, as well as the complementarity of the two Endstations that were tested. The immediate plans are to start utilizing this source in earnest, and in fact, we have begun exploratory studies of HOCO and C<sub>2</sub>H<sub>3</sub>. Both of these radicals have very unfavorable Franck-Condon factors for photoionization, which frustrates the unambiguous determination of their adiabatic ionization energies in conventional laboratories.

In parallel we intend to further expand the number of sources available for this program, such as a second laser photodissociation source that exploits the cooling capabilities of jet expansion, producing radicals that are quite cold rotationally and at least partly vibrationally relaxed. While this is a pulsed source, and hence suffer from a non-unity duty cycle, it will be extremely suitable for study of radicals that are easily destroyed via heterogeneous decomposition involving walls. Other sources that are planned include *in situ* abstraction reactions with H, F, or Cl atoms, which are produced in a microwave discharge. This particular CW source has been developed and very successfully used over the past fifteen years at Argonne national Laboratory, and has been shown to be a clean source of a very large variety of radicals. With minor modifications, this source can also be used for direct generation of certain radicals in the microwave discharge. The full future complement of sources of radicals and metastable species available at this beamline will include pyrolysis and corona discharge sources, both effusive and coupled to expansion from a nozzle, as well as a high-temperature effusive source, based on a modified Knudsen cell.

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