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Research paper

Synchrotron threshold photoelectron photoion coincidence spectroscopy of radicals produced in a pyrolysis source: The methyl radical

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ABSTRACT

We present here a flash pyrolysis source coupled with a threshold photoelectron photoion coincidence (TPEPICO) spectrometer and vacuum ultraviolet synchrotron radiation to investigate the spectroscopy and photochemistry of free radicals. The radicals are produced from pyrolysis in a heated silicon carbide tube, and the TPEPICO scheme provides a strategy to obtain pure spectra of the radicals without contamination from other byproducts. As a representative example, the methyl radical was studied, and its threshold photoelectron spectrum shows a series of umbrella vibrational transitions. The adiabatic ionization energy of the methyl radical was determined to be 9.84 ± 0.01 eV.

1. Introduction

Free radicals, as important reactive intermediates, play an essential role in the chemical reactions of combustion, atmosphere and interstellar space and have attracted a great deal of attention in the past few decades [1–5]. Therefore, the detection and characterization of free radicals is crucial for understanding their underlying chemistry in these fields. To investigate free radicals in the laboratory, several techniques, such as electric discharge [6], photolysis [7,8] atomic fluorine abstraction [9] and flash pyrolysis [10,11], have been developed and adopted to produce free radicals. Among them, flash pyrolysis with a very simple configuration can generate free radicals at high concentrations and has been widely utilized in experiments [12–14].

Various experimental methods, including laser-induced fluorescence (LIF) [5], cavity ring-down spectroscopy (CRDS) [5,15], photoelectron spectroscopy (PES) [16], photoionization mass spectrometry (PIMS) [17] and photoelectron photoion coincidence spectroscopy (PEPICO) [9,14], have been employed to investigate free radicals, and significant advances have been made. Typically, spectroscopic methods require prior knowledge of the species and are usually applied for molecules that contain a few atoms. PES often uses a monochromatic light source, such as He(I) resonant light at $h\nu = 21.2$ eV, and an analyzer to measure the electron kinetic energy of target molecules [18,19]. However PES lacks the target's mass information and has its restriction in complex systems, such as free radicals. PIMS coupled with tunable vacuum ultraviolet (VUV) synchrotron radiation has been utilized with great success to identify reaction products and provides valuable insight in gas-phase reactions [4,20,21]. Building on the capabilities of PES and PIMS, PEPICO collects and analyzes both photoelectrons and photoions simultaneously and provides more information than the other techniques [22–26]. In particular, mass-selected threshold photoelectron spectroscopy (TPES) with high resolution for each species can provide structures of vibrational and excited ionic states and has been used to study radicals [9,14].

A few years ago we constructed a threshold PEPICO (TPEPICO) spectrometer with a double velocity map imaging (VMI) design at National Synchrotron Radiation Laboratory (NSRL) in Hefei, China [23,27]. The spectrometer has been operated for several

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years to probe the photoionization and dissociative photoionization of molecules [28]. Recently, to meet synchrotron users' requirements, we developed a new flash pyrolysis molecular beam source coupled with the TPEPICO spectrometer and Hefei synchrotron radiation to explore the spectroscopy and photochemistry of organic radicals in the VUV energy range. Additionally, we selected the methyl radical, the simplest alkyl radical, which has been well studied by PIMS, PES and PEPICO [8,11–13,29–31], produced from pyrolysis of nitromethane precursor as a representative example to characterize the generation and spectroscopy of free radicals. Some preliminary results, such as TPEPICO time-of-flight (TOF) mass spectra and the mass-selected TPES of the methyl radical in the VUV energy range, are reported and discussed in this letter.

2. Experimental methods

The experiment was performed on the Atomic and Molecular Physics beamline of NSRL, China [32]. Synchrotron photons emitted from an undulator were dispersed by a 6-m monochromator equipped with a 370 lines/mm spherical grating covering the photon energy range of 7.5–22.5 eV. A gas filter filled with rare gas (presently Ar for $h\nu < 15.5$ eV) was used to suppress the high-order harmonics emitted from the undulator. With the absorption lines of Ar in the gas filter, the absolute photon energy of the monochromator was calibrated on-line within an accuracy of ±5 meV. A photodiode (SXUV-100, IRD Inc.) located immediately behind the photoionization region was used to monitor the photon flux to normalize the signals in the photon energy scans.

A schematic diagram of the flash pyrolysis molecular beam source and TPEPICO spectrometer [23] is shown in Fig. 1. The flash pyrolysis source is home-made and was inspired by the design of Chen and co-workers [10]; this source primarily consists of an orifice nozzle (50 μm diameter), a ceramic plate and a silicon carbide (SiC) tube (1 mm inner diameter). The ceramic plate was used to insulate the nozzle from the SiC tube, both electrically and thermally. The jet of a suitable precursor seeded in rare gas in the nozzle was adiabatically expanded into the SiC tube in vacuum with a fast speed, and a continuous molecular beam was formed. Radicals were then generated from pyrolysis of the precursor molecules in the SiC tube. The SiC tube was heated resistively, and the heating length was ~2 cm, as determined by the distance between two tungsten electrodes. The two electrodes were connected to a DC power supply via a vacuum feedthrough port, and the pyrolysis power was controlled outside. After passing through the SiC tube, the gas mixture was collimated and sampled through a skimmer (1 mm diameter). Moreover, the flash pyrolysis molecular beam source was mounted on a manually controlled XYZ manipulator in the source chamber of the TPEPICO spectrometer, and its position was tuned in real-time to optimize the signals.

The TPEPICO spectrometer has previously been introduced in detail and is mainly composed of two time-of-flight analyzers for electrons and ions operated in coincidence [23]. The molecular beam, VUV synchrotron light and spectrometer axis cross each other at right angles in the photoionization region. As shown in Fig. 1, the electrons and ions produced in the photoionization region were pushed by a DC extraction field and flew apart in opposite directions. A double VMI design [27] was utilized to enhance the electrons and ions' collection efficiencies and energy resolutions. Ions were focused onto the surface of micro-channel plates (MCPs, 40 mm diameter) and mapped by a phosphor screen. A charge-coupled devices (CCD) camera was employed to record the ion images in TPEPICO imaging experiments. The mass resolution of the TPEPICO spectrometer [23] is $M/\Delta M = 900$ (full width at half maximum, FWHM), with an extraction electric field of 14 V cm^{-1}. The electron detector consists of two MCPs in a chevron configuration as well as a plate anode to collect electron signals. A mask with a small central hole located at the front of the electron MCPs was used to collect zero kinetic energy electrons (threshold electrons), which were velocity focused into the hole, as shown

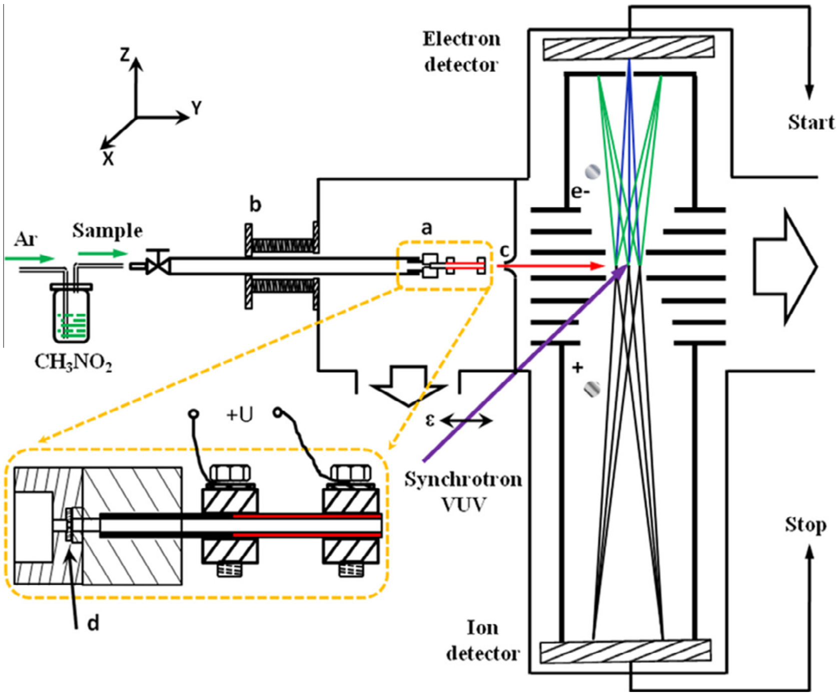

Fig. 1. Schematic diagram of the flash pyrolysis molecular beam source and threshold photoelectron photoion coincidence (TPEPICO) spectrometer used to investigate VUV photoionization of free radicals. The trajectories of the threshold electrons, energetic electrons and ions are depicted as blue, green and black lines, respectively. a: Flash pyrolysis molecular beam source with a resistively heated silicon carbide tube is shown in red; b: XYZ manipulator; c: skimmer; d: orifice nozzle.