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ScienceDirect
Journal of Electron Spectroscopy and Related Phenomena 156–158 (2007) 86–91
JOURNAL OF ELECTRON SPECTROSCOPY and Related Phenomena
www.elsevier.com/locate/elspec

Design and performance of an (e, e+ion) spectrometer for studies of fragmentation of dipole and non-dipole states of gaseous molecules

Glyn Cooper, Jacob Stewart-Ornstein, Adam P. Hitchcock *

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

Abstract

An (e, e+ion) spectrometer has been constructed that has the capability to measure time-of-flight (TOF) mass spectra of gases in coincidence with energy selected inelastically scattered electrons, as a function of impact energy, electron energy loss and electron scattering angle. Relative to earlier dipole-regime implementations of the (e, e+ion) technique, this spectrometer can be used to study molecular fragmentation under both dipole and non-dipole electronic excitation and ionization conditions. The spectrometer uses a position-sensitive electron detector and a TOF tube positioned at 90° with respect to the electron impact and scattering plane. The TOF design makes it possible either to extract all ions from the interaction region, or to discriminate preferentially for ions that have kinetic energy along the axis of the TOF tube, thus allowing one to collect spectra with maximum efficiency, or to study the dynamics of the production of the molecular and fragment ions. The design and construction of the spectrometer is described, along with preliminary results for ionization in the S 2p excitation and ionization region of SF_6.

Keywords: Time-of-flight mass spectrometer; Electron impact; Gas phase; SF_6; Electron-ion coincidence

1. Introduction

The electronic excitation of atoms and molecules above 6 eV [1] plays an essential role in many fundamental and technologically important processes, e.g. auroras and plasma-induced etching of materials. Ionic fragmentation of inner shell excited and ionized molecules is an expanding field of study [2] which yields information about ionization dynamics and possible selective X-ray photochemistry. Such data are of fundamental interest and help interpret photon stimulated ionic desorption from surfaces, which is critical to practical X-ray photochemistry and lithography. Lab based fragmentation studies are a time honoured component of this field. For example, Eland and co-workers have pioneered photoelectron-photoion (PEPICO), photoelectron-fluorescence (PEFCO), velocity imaging photoelectron (VIPCO), and electron time-of-flight (ETOF) spectroscopy using lab-based systems [3]. Bonham used non-coincidence electron impact mass spectrometry to study cross sections for dipole and non-dipole electron impact induced fragmentation of molecules [4–7], and ion–ion coincidence in the dissociative multiple ionization and fragmentation of molecules (without tagging the excitation electron) following pulsed electron ionization [8,9].

Electron energy loss spectroscopy, under varying experimental conditions of electron impact energy, energy loss and scattering angle, has the ability to excite not only the electric dipole-allowed transitions probed by light, but also electric quadrupole (and other higher-order electric multipole transitions) and spin-exchange excitations. For the past ∼12 years a program of variable angle (non-dipole) electron energy loss spectroscopy has been carried out at McMaster University [10–12] (in collaboration with researchers from Rio de Janeiro) using a unique, home-built spectrometer. Studies include high-resolution non-dipole inner shell spectroscopy (100 meV) [11] and variable impact energy, variable scattering angle studies of inner shell excitation intensities, resulting in quantitative generalized oscillator strengths [10,12]. In a parallel research program, a time-of-flight (TOF) mass spectrometer has been used, in conjunction with synchrotron radiation as the excitation source, to study core-excited molecules [2]. The energy dependence of photofragmentation processes of molecules provides detailed information on chemical bonding, photoioinzation dynamics and site and/or state selective fragmentation. State-selective photochemistry can be used to control chemical reactions and may be useful for making new materials or devices. For example, photofragmentation studies of SPF_3 [13] showed that loss of all

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* Corresponding author. Tel.: +1 905 525 9104x24749; fax: +1 905 521 2773.
E-mail address: aph@mcmaster.ca (A.P. Hitchcock).

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doi:10.1016/j.elspec.2006.11.058

three fluorine atoms to produce SP^+ occurs predominantly with P 2p excitation, and not at all with S 2p excitation or ionization. In contrast, the S=P bond is much more readily broken with S 2p excitation, as evidenced by the production of PF_3^+, PF_3^{++} and the (S^+, PF_3^+) ion pair signals only following S 2p excitation. Studies of the polarization, angle, and kinetic energy aspects reveal details of the photo-fragmentation mechanism. If bond breaking in an energetic ionic fragmentation occurs before rotational randomization of molecular orientation, then the direction of preferential ion emission is determined by the transition symmetry. In SPF_3 [13], when the TOF detector is aligned perpendicular to the electric vector of the light the P $1s \rightarrow e^*$ transition dominates the S^+ partial ion yield spectrum, whereas when the TOF detector is rotated 90° to place it parallel to the electric vector, the P $1s \rightarrow 14a_1{}^*$ transition becomes the strongest.

The construction of the (e, e+ion) equipment described in this work is intended to extend the previous synchrotron (which are intrinsically dipole experiments) and dipole (e, e+ion) measurements [14–16] into the non-dipole regime. This is the first (e, e+ion) coincidence spectrometer capable of detecting TOF coincidence mass spectra at specifically selected non-zero electron scattering angles. The present paper describes the construction of the TOF tube and the operation of the resultant (e, e+ion) coincidence spectrometer, followed by some early results on the dipole and non-dipole fragmentation of SF_6. The results presented here are preliminary, and are intended to illustrate the current performance of the instrument and discuss our current instrumental challenges, rather than to document the expected fully optimized performance.

2. Experimental

The electron spectrometer portion of the apparatus is the McMaster Variable Angle, High Resolution Electron Spectrometer (McVAHRES). This instrument has been described in detail in previous publications [17,18], including installation and performance of the position sensitive parallel electron detection system [19]. An ion TOF tube was added to this instrument in the vertical direction, orthogonal to the scattering plane of electron beam and the electron spectrometer. This necessitated construction of a new collision region and the TOF tube itself, along with implementation of the associated steady state voltages and detector and coincidence electronics for operation of the spectrometer in the (e, e+ion) coincidence mode. Schematic views of the resulting non-dipole (e, e+ion) spectrometer, both from the side and top, are shown in Fig. 1. The experimental geometry consisting of an electron scattering plane, detection of scattered electrons at varying angles, and the perpendicular TOF-tube and ion detector, can be seen clearly. The spectrometer incorporates both a direct and a monochromated electron beam source, but for the present experiments, only the direct electron gun was used. Energy resolution for the electron spectrometer is typically ∼0.7 eV using electron beam from the direct (unmonochromated) electron gun, while ∼50 meV resolution has been achieved using the monochromated electron source. The effective acceptance angle of the electron analyzer varies with scattering angle from ∼1° at scattering angles ≤4° to ∼0.2° for scattering angles ≥80°, as documented in Ref. [19]. This very small angular acceptance limits the overall efficiency of the (e, e+ion) system. Changes to the electron optics to increase the acceptance angle are planned.

In basic form, the coincidence detection is started by detection of an energy loss electron at the position-sensitive electron detector, followed (usually some microseconds later) by detection of one or more positive ions by the ion detector. The detector is a Burle Instruments model APTOF40 with “fast” channel plates. Coincidence detection is provided by a multi-stop time-to-digital-converter (TDC) (Ortec model 9308), the signals for which are fast pulses taken from the back of the rear channel plate of the electron detector, and from the solid anode of the ion detector. These fast pulses are amplified (Ortec VT120A) and conditioned by constant fraction discriminator units (Ortec model 473A) before being fed to the TDC. The originating position of the detected electron (and hence its energy loss) can be obtained from a position sensitive detector (PSD, Quantar model

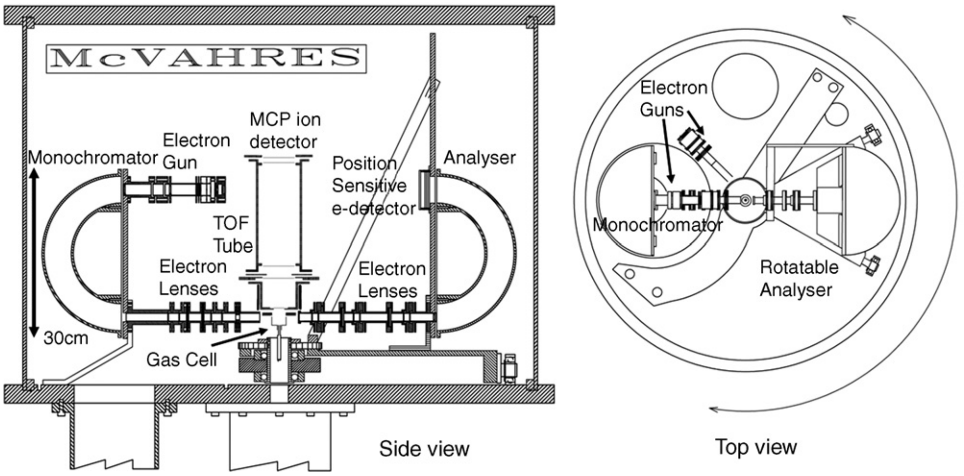

Fig. 1. Overview diagram of the McVahres spectrometer, showing side view (left hand side) and top view (right hand side). The experimental geometry can be clearly seen. For the present experiments, the non-monochromated electron gun source was used.