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Water vapor electron scattering cross-section measurements using a hydrophobic ionic liquid

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ABSTRACT

The interface of ionic liquid (IL) 1-ethyl-3-methylimidazolium-bis-(trifluoromethylsulfonyl)-imide, [EMIM][Tf₂N], was examined in the presence of water vapor using lab-based ambient pressure X-ray photoelectron spectroscopy (APXPS) with a monochromatic Al K α X-ray source. Room temperature water vapor exposures to [EMIM][Tf₂N] ranged from 10⁻⁶ to 2.0 Torr with no evidence of water uptake at the IL-vapor interface. The hydrophobic nature of [EMIM][Tf₂N] allowed for measuring the attenuation of F 1s, O 1s, N 1s, C 1s and S 2p APXPS peaks as a function of pressure, allowing for the determination of the electron scattering cross-section (σ_e) of gas phase water. The elemental diversity of [EMIM][Tf₂N] allowed for the extraction of σ_e over a 520 eV kinetic energy range in the absence of a variable energy X-ray source. Herein we show that lab-based APXPS in combination with an elementally diverse, unreactive substrate is an effective tool for the determination of electron scattering cross sections for gas phase species.

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1. Introduction

Electron collisions with gas phase molecules play an important role in applied science such as physics and chemistry of planetary atmospheres [1] and studies of radiation induced damage in biological specimen [2]. The strength of electron-molecule interactions can be assessed by inelastic electron scattering cross section (σ_e) measurements which highlights the importance of understanding and quantifying those interactions particularly with relevant gases [3]. Experimental measurements of σ_e as a function of kinetic energy (KE) have been determined predominantly through use of primary electron beam collision studies up to ~20 keV [1,4–8]. Synchrotron-based ambient pressure X-ray photoelectron spectroscopy (APXPS) was utilized to measure σ_e for water vapor in the KE range of 100–700 eV using the C1s signal of a hydrophobic highly oriented pyrolytic graphite (HOPG) surface [9]. The results were comparable with previous studies [4] in the same KE range, establishing synchrotron-based APXPS as a viable measurement technique in calculating σ_e utilizing a variable X-ray energy source to generate variable KE photoelectrons. Herein we utilize for the first time lab-based APXPS to determine σ_e for water vapor. Lab-based APXPS utilizes a constant X-ray energy source. Thus, in order

to assess σ_e as a function of KE a chemically diverse, hydrophobic substrate is needed to provide numerous elements over a wide range of KEs. For the experiments described herein we utilize an elementally diverse ionic liquid substrate.

Ionic liquids (ILs) are defined as salts with a melting point of 100 °C or less and have a negligible vapor pressure. For imidazolium based ILs the anion is primarily what determines the hydrophobicity versus hydrophilicity of the IL [10,11]. The bis(trifluoromethylsulfonyl)imide, or [Tf₂N⁻], anion is one of the most hydrophobic ILs [11]. Imidazolium-based [Tf₂N⁻] ILs have been well characterized by ultra-high vacuum (UHV) XPS which highlight the properties of the IL-vacuum interface [12–33]. For the study herein we utilized 1-ethyl-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][Tf₂N], to determine σ_e of gas phase water. This study takes advantage of the hydrophobicity and elemental diversity of [EMIM][Tf₂N] to examine the electron scattering cross-section of water vapor in the KE range of 794 eV to 1313 eV using lab-based APXPS.

2. Experimental details

[EMIM][Tf₂N] (Iolitech, 99%) was stored in a vacuum desiccator and used without any further purification. [EMIM][Tf₂N] has a melting point [34] of -15 °C and a density [35] of 1.52 g cm⁻³ at room temperature. For APXPS experiments, a droplet of IL ~5 mm dia. and <1 mm thick was deposited onto a polycrystalline Au foil (Alfa

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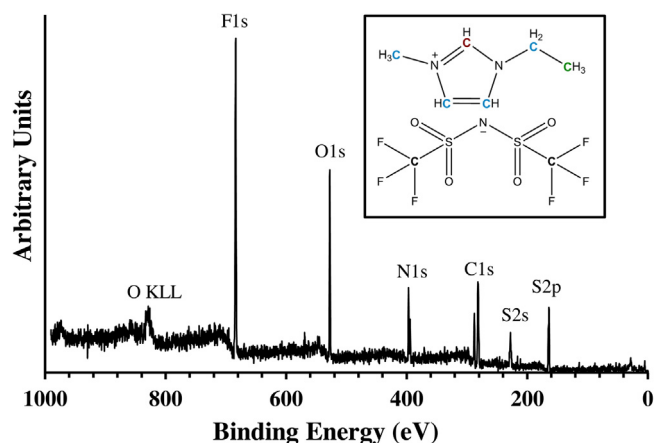


Fig. 1. Survey spectrum of [EMIM][Tf₂N] under vacuum.

Aesar, 0.25 mm thickness, 99.9975% purity) that was pre-cleaned with acetone and 18.2 M Ω water. The sample was introduced into the APXPS analysis chamber and pumped for two days reaching a base pressure of 4.5×10^{-8} Torr prior to the start of experiments.

The IL-gas interface was probed using a lab-based APXPS system with a HIPPI-2 photoelectron analyzer (Scienta, R4000) and a monochromatic Al K α X-ray source (Scienta, MX 650) operated at 20 mA and 10 kV. Additional instrument details have been published previously [36]. All spectra were collected utilizing a 0.5 mm aperture in the transmission lens mode and a collection angle of 22 $^\circ$ from the sample normal. A survey spectrum was collected at 200 eV pass energy while F 1s, C 1s, N 1s, O 1s and S 2p spectra were at 50 eV pass energy. Water vapor was introduced into the APXPS analysis chamber through a variable leak valve connected to a water bulb containing 18.2 M Ω water. Prior to the start of the APXPS studies the water bulb was freeze-degassed three times. The experiment was conducted in the water vapor pressure range of 10^{-6} to 2.0 Torr at room temperature.

XPS spectra were fit using peak fitting software (CasaXPS v2.3.16) with 70%–30% Gaussian-Lorentzian peaks and a linear

background subtraction. Binding energies (BEs) were referenced to the cation C 1s alkyl chain component (C_{alkyl}) at 285.0 eV, similar to previous UHV XPS IL studies [24,25,30]. The full width at half maximum (FWHM) of the C 1s imidazolium peaks were constrained to within a 0.06 eV window while leaving the BEs unconstrained. For S 2p spectra the S 2p(1/2) spin was constrained to the known separation of 1.18 eV [37] from the S 2p(3/2) spin. All other peaks (F 1s, N 1s, O 1s) were unconstrained.

The measured electron KEs for C 1s C_{alkyl} species were ~ 1197 eV, corresponding to an inelastic mean free path (λ) of 3.5 nm calculated using the Gries predictive formula from NIST software [38]. Defining the sampling depth to be $3\lambda\cos(22^\circ)$, corresponding to 95% of the XPS signal [39], we estimate it to be 9.8 nm for [EMIM][Tf₂N]. The thickness of one monolayer (ML) of IL is calculated [40] using $\rho^{-1/3}$, where ρ is the bulk density. Thus, for [EMIM][Tf₂N] 1 ML is calculated to be 0.75 nm which gives a probing depth of 9.8 nm/0.75 nm = 13 ML for [EMIM][Tf₂N] C 1s spectra with a KE of ~ 1197 eV. Similar calculations for elements S, N, O and F yield a probing depth range of ~ 9 –14 ML with a KE range of 794 eV (F 1s) to 1313 eV (S 2p) for the experiments performed herein with [EMIM][Tf₂N].

3. Results and discussion

The IL was initially characterized prior to the start of water vapor exposures with a broad survey spectrum (Fig. 1) at a base pressure of 4×10^{-8} Torr. The surface of [EMIM][Tf₂N] contains the expected elemental makeup of F, O, N, C and S as seen in the molecular structure in Fig. 1. No other elements were observed, indicating the absence of any detectible impurity at the IL interface. Fig. 2 shows representative F 1s, S 2p, N 1s, C 1s and O 1s spectra taken under vacuum (bottom spectra). The F 1s vacuum spectrum shows one symmetric peak with a BE of 688.4 eV for the fluorine present in the [Tf₂N⁻] anion. The sulfur present in the anion shows an expected doublet with an S 2p(3/2) BE of 168.5 eV. N 1s shows two resolved peaks, one associated with nitrogen in the [EMIM⁺] cation at 401.6 eV and the other with the anion at 399.0 eV. The two peaks are present in a 2:1 cation-to-anion ratio consistent with [EMIM][Tf₂N] stoichiometry. The C 1s spectrum shows four distinct

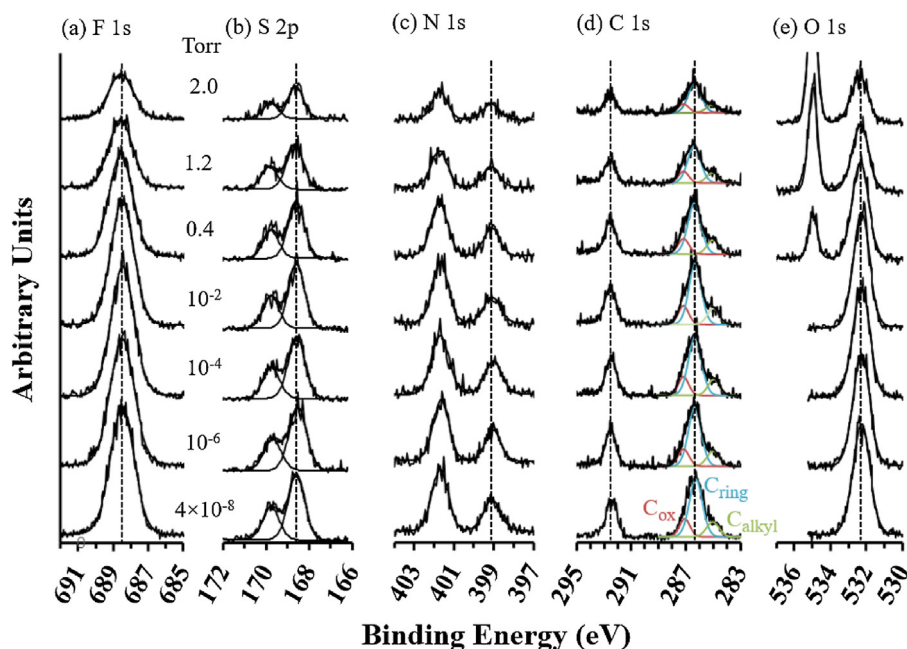


Fig. 2. APXPS spectra of [EMIM][Tf₂N] as a function of increasing water vapor pressure in the (a) F 1s, (b) S 2p, (c) N 1s, (d) C 1s, (e) O 1s regions. Bottom spectra taken prior to the introduction of water vapor.

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