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A multicoincidence study of ionic fragmentation of methyl tiocyanate, CH_3SCN involving S 2p electrons.

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INTRODUCTION

Organosulfur compounds have attracted much attention and outstanding reviews covering the chemistry of thiocyanates (RSCN) and isothiocyanates (RNCS) have been reported [1],[2]. The simplest alkylated species, with R= CH_3, are very well known molecules. Much information is available for both species in their fundamental, ionic and excited electronic states, as well as concerning the study of the CH_3SCN <–> CH_3NCS isomerization equilibrium. Of particular interest for the present work, Hitchcock et al. [3] have reported the optical oscillator strengths for C 1s, N 1s and S 2p inner shell excitations in CH_3SCN derived from electron energy loss spectra. Interestingly, the S 2p region of the spectrum showed the presence of very structured transitions below the ionization potential. These sharp structures were mostly explained in terms of excitations from S 2p electrons to vacant π* and σ*CS orbitals. Here we report a study of the photon impact excitation and dissociation dynamics of CH_3SCN exited at the S 2p level by using synchrotron radiation. Within our knowledge ionic fragmentation of photon excited CH_3SCN has not been previously described.

EXPERIMENT

Synchrotron radiation was used at the Laboratorio Nacional de Luz Sincrotron (LNLS), Campinas, Sao Paulo, Brazil. Linearly polarized light monochromatized by a toroidal grating monochromator available at the TGM beam line, intersects the effusive gaseous sample inside a high vacuum chamber, with base pressure in the range 10^{-8} mbar [4]. During the experiments the pressure was maintained below $5x10^{-6}$ mbar. The ions produced by the interaction of the gaseous sample with the light beam were detected using a time-of-flight (TOF) mass spectrometer of the Wiley-Mac Laren type for both PEPICO and PEPIPICO measurements [5]. The average kinetic energy release (KER) values of the fragments were calculated from the coincidence spectra by assuming an isotropic distribution of the fragments, and that they are perfectly space focused and that the electric field applied in the extraction region is uniform [6]. The sample of CH_3SCN, was obtained from commercial sources (Aldrich). The liquid sample was purified by repeated trap-to-trap vacuum distillation. The purity of the compound in both vapor and liquid phases was checked by IR and 1H NMR spectroscopies, respectively.

RESULTS AND DISCUSSION

Neither calculated nor experimental photoabsorption spectrum for CH_3SCN in the sulfur 2p edge energy region could have been reported in the literature. The TIY spectrum of CH_3SCN, measured near the S 2p edge is shown in Figure 1. Below the S 2p threshold, the spectrum is dominated by a group of well-defined signals centered at 164.4, 165.7, 167.2 and 168.5 eV. The TIY spectrum is remarkably similar to the Inner-Shell Electron Energy Loss Spectrum (ISEELS) reported by Hitchcock et al. [3] The resolution obtained in our case allows clearly identifying weak transitions at 164.4 and 170.0 eV, reported as shoulders in the ISEELS spectrum. Following the proposed assignment for S 2p transitions for CH_3SCN, the main features in this spectra have been assigned to states associated with (S2p, π*SCN) and (S2p, σ*CS) configurations. PEPICO spectra have been recorded by setting the photon energy at the resonant values observed in the TIY spectrum. In order to identify the role of resonant Auger processes in the fragmentation, spectra were measured also at photon energy values below (typically 10 eV) and above (typically 50 eV) the ionization edge. The PEPICO spectra near the S 2p edge are shown in Figure 2. The kinetic energy release values have been determined for each ion. In the former spectrum, the ions have KER values which are relatively low, while in the 176.7 eV spectrum a broadening in the peak widths are clearly observed and all the ions shows higher KER values. From these observances, it is possible to assume that the main contribution to the PEPICO spectra below the S 2p threshold comes from the fragmentation of single charged parent ions, which are formed by one photon ioniza-

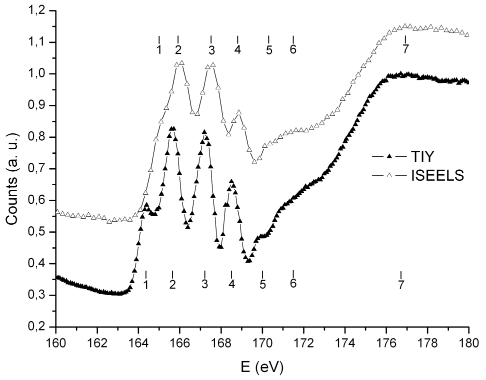

FIG. 1: TIY and ISEELS spectra of CH_3SCN in the S L region.

tion process of valence electrons. On the other hand, when the incident photon energy is increased, S 2p electronic excitation or ionization processes occurs. It is well known that the decay of such an excited species normally lead to the formation of doubly charged CH_3SCN^{+2} parent ion, for instances if a normal Auger processes take place. Moreover, the analysis of the PEPIPICO spectra results is useful for identifying two-, three- and four-body dissociation processes which especially follow Auger decay mechanisms. KER have been determined from the projection of the PEPIPICO islands in the corresponding time domain for each ion involved in the coincidence. The double coincidence branching ratio has been calculated from the PEPIPICO spectra by integrating the area of each coincidence at a given incident photon energy.

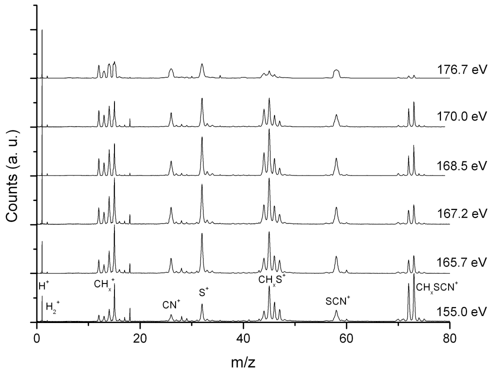

FIG. 2: PEPICO spectra of CH_3SCN in the S L region.

CONCLUSION

A detailed study of the ionic fragmentation of the CH_3SCN molecule in the gas phase following continuum valence and S 2p excitations has been performed using time-of-flight multicoincidence based techniques and synchrotron radiation as photon source. The transitions observed in the TIY spectrum around the S 2p edge shows an excellent agreement with the optical oscillator strengths derived from electron energy loss spectra recorded under electric dipole dominated conditions. The dynamic of fragmentation of charged hydrocarbon species is strongly dominated by the rupture of CH bonds. Other dissociation mechanisms were observed from the analysis of the double coincidence islands. In particular, the two body dissociation mechanism yielding CH_3^+ and SCN^+ single charged ions is observed with abundances around 10 % of the double coincidences. A similar mechanism that involves the rupture of the C-S bond dominates the dissociation of electronically excited neutral CH_3SCN. Electronic excitations to the σ*CS antibonding molecular orbital should play a key role in the dynamic of the process. Less attention have received the virtual σ*SC orbital corresponding to the thiocyanate group. Our calculations predict that both σ*SC and σ*CS MO should have influence in the electronic properties of CH_3SCN. The fragmentation of methyl thiocyanate excited at S 2p edge produces a series of ions derived from the rupture of the S-CN bond in the thiocyanate moiety.

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