ELSEVIER

Journal of Electron Spectroscopy and Related Phenomena 88–91 (1998) 71–75

JOURNAL OF
ELECTRON SPECTROSCOPY
and Related Phenomena

Ionic fragmentation of inner-shell excited molecules

Adam P. Hitchcock[a,*], John J. Neville[a], Astrid Jürgensen[b], Ronald G. Cavell[b]

[a]*BIMR, McMaster University, Hamilton, Ontario, Canada L8S 4M1*
[b]*Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2*

Abstract

The combination of tuneable synchrotron radiation and multicoincidence time-of-flight mass spectrometry is an effective means of studying the core-hole decay and fragmentation of inner-shell excited molecules. In addition to aiding spectral interpretation, partial ion and ion-pair yields enable both the more specific identification of fragmentation channels and the identification of site and/or state selective fragmentation processes. The power of photoelectron–photoion–photoion coincidence (PEPIPICO) and related techniques is illustrated using selected examples from recent high resolution spectroscopic and ionic fragmentation studies of PF_3 and SPF_3. © 1998 Elsevier Science B.V.

Keywords: Photoionization; Photofragmentation; Inner-shell excitation; Mass spectrometry; Synchrotron radiation

---

1. Introduction

The autoionization of inner-shell excited states and Auger decay of core ionized states of molecules generated by synchrotron radiation photoionization is an efficient source of multiply charged ions. The charge separation and fragmentation of these species can be studied by photoelectron–photoion–photoion coincidence (PEPIPICO) and related techniques [1]. In conjunction with photoabsorption, such studies provide detailed information on dissociation mechanisms and give insights into molecular bonding and electronic structure. The use of tuneable synchrotron radiation enables an investigation of the dependence of the fragmentation process on the X-ray energy and can reveal cases of site and/or state selective fragmentation [1–6].

In comparison with total ion yields, the consideration of partial ion yields can provide both additional insight into complex inner shell spectra and increased spectroscopic selectivity. Even greater selectivity is achieved by using multicoincidence techniques such as PEPIPICO and examining the yields of particular ion pairs. Multicoincidence techniques also allow for the more specific identification of core-hole decay and fragmentation channels. Recent results from photoionization and photofragmentation measurements of PF_3 and SPF_3 illustrate these points.

2. Experimental

Total and partial ion yield spectra were recorded using a time-of-flight (TOF) mass spectrometer operated under Wiley–McLaren [7] focussing conditions with a multi-stop time-to-digital converter (TDC) for data acquisition [8]. Mass spectra were recorded using either a photoelectron (PEPICO) or ion extraction pulse (pulse-TOF) as the TOF start signal. Tuneable monochromated synchrotron radiation was provided by beamline 9.3, the grasshopper line of the Canadian Synchrotron Radiation Facility

---

[*] Corresponding author.

PII S0368-2048(97)00120-5

(CSRF), at the Synchrotron Radiation Center (SRC). Complete pulse-TOF spectra or PEPICO along with the associated PEPIPICO spectra were saved at each photon energy. The stored spectra were analyzed off-line (background subtraction and peak integration) to derive partial ion and ion-pair yields.

The time resolution limits of the TOF mass spectrometer were investigated by using an Ortec 9308 picosecond time analyzer (pTA; 19 ps time resolution when operated with a 5 μs time span) in place of the existing Tolmar TDC (12 ns time bins). PEPIPICO measurements of PF_3 in the P 2p region have been performed using the two TDCs simultaneously. The resulting TOF spectra are compared in the upper panel of Fig. 1. The improved time resolution of the pTA has not led to the finding of any additional structure in the TOF spectra. In contrast, when the photoion–photoion coincidence (PIPICO) spectra obtained from the same data sets are compared (as is done in the lower panel of Fig. 1) the benefits of improved time resolution are evident. The differences are particularly dramatic in the case of the (F^+,PF_2^{++}) ion-pair signal, occurring at a flight time difference of between 0.7 and 0.8 μs. Possible explanations for the contrast between the PEPICO and PIPICO results include time spread introduced by the finite ionization volume of the spectrometer and the contributions of multiple fragmentation pathways to the ion signals in the PEPICO TOF spectra. The size of the ionization region would have less impact upon the PIPICO spectra because they are derived from the flight times of ions produced in the same photoionization event

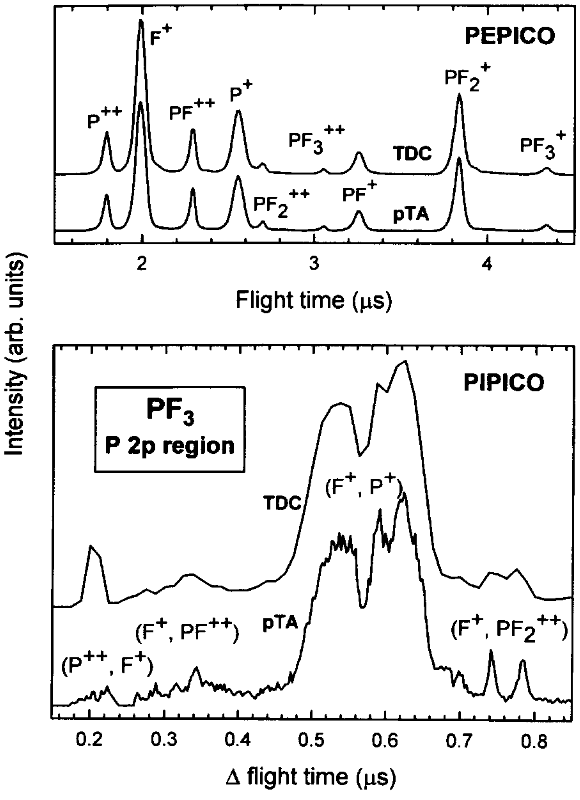

Fig. 1. TOF mass spectra recorded using a photoelectron start (PEPICO, upper panel) and photoion–photoion coincidence (PIPICO) spectra (lower panel) of P 2p excited PF_3 measured using an Ortec 9308 picosecond time analyzer (pTA) and a Tolmar time-to-digital convertor (TDC). The pTA spectra are shown with 2.5 ns time bins; the TDC spectra have 12 ns time bins. The four spectra were recorded simultaneously over an incident photon energy range of 132–142 eV.

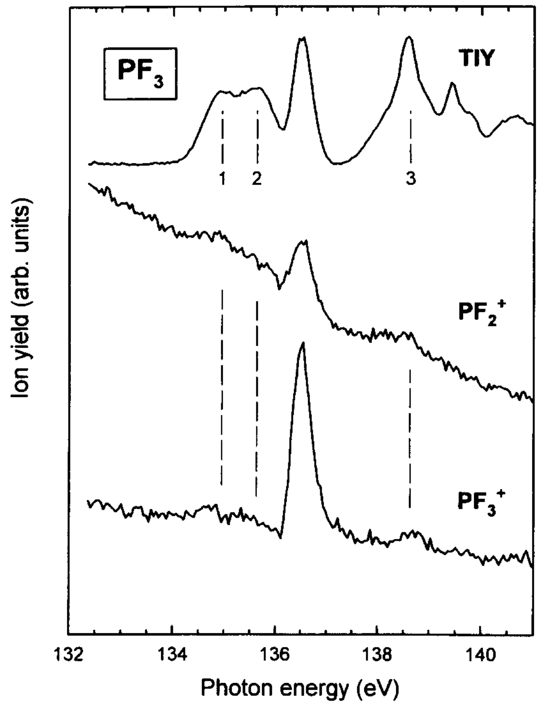

Fig. 2. Comparison of the total (TIY) and PF_3^+ and PF_2^+ partial ion yield spectra of PF_3 just below the P 2p edge. The dashed lines indicate peak positions in the TIY spectrum and have been assigned previously [9] as: (1) $2p_{3/2}$ (a_1^{-1},e) ^1E and (e^{-1},e) ^1E; (2) $2p_{1/2}$ (a_1^{-1},e) ^1E and (e^{-1}, e) ^1E; (3) $4p_z$ (a_1) Rydberg. The peak at 136.5 eV corresponds to the transition to the LS-coupled (a_1^{-1},e) $^1A_1$ state.

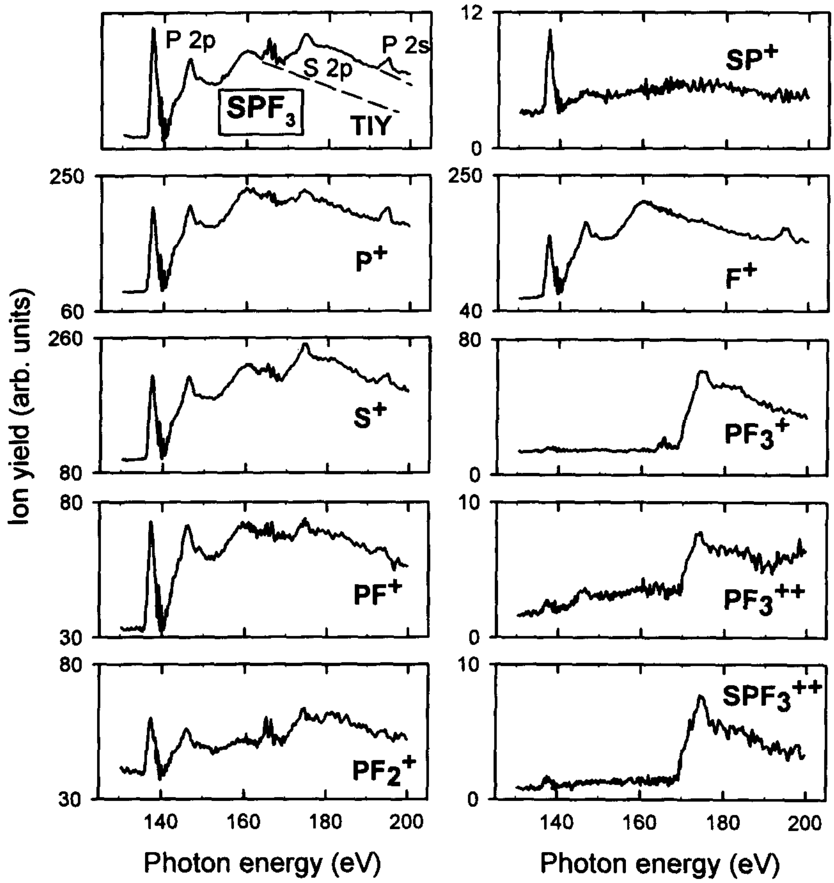

Fig. 3. Total (TIY) and partial ion yield spectra of SPF_3 in the P 2p, S 2p and P 2s regions.

and therefore in the same region of the spectrometer. Similarly, the PIPICO measurements distinguish between ions formed via fragmentation processes leading to different ion pairs and consequently having different kinetic energy distributions.

3. Results and discussion

3.1. Excitation and fragmentation of PF_3

Photoionization measurements of PF_3 in the P 2p region demonstrate clearly the utility of partial ion yield spectra for interpreting inner-shell spectroscopy and highlighting interesting spectroscopic features. This is demonstrated in Fig. 2, where the total ion yield (TIY) spectrum of PF_3 is compared with the partial yields of PF_3^+ and PF_2^+. As discussed elsewhere in greater detail [9], the 136.5 eV (e^{-1},e) $^1A_1$ state of PF_3 which dominates the PF_3^+ and PF_2^+ partial yield spectra and which lacks an obvious spin-orbit partner is best described using an LS coupling scheme. Ab initio calculations indicate that this state has a very large core-valence exchange interaction which results in the spin-orbit intensity ratio being skewed totally in favour of the $2p_{1/2}$ component [9]. Another interesting aspect of the PF_3 spectra in Fig. 2 is the difference in the energies of the P 2p discrete transitions observed between 134 and 136 eV in the PF_3^+ partial yield and TIY spectra. This suggests that the excited states of PF_3 that lead to PF_3^+ production differ from those responsible for the majority of the TIY signal in this energy region. The indicated features in the TIY spectrum have been assigned previously based upon ab initio calculations as the $2p_{3/2}$ (134.9 eV) and $2p_{1/2}$ (135.6 eV) spin-orbit

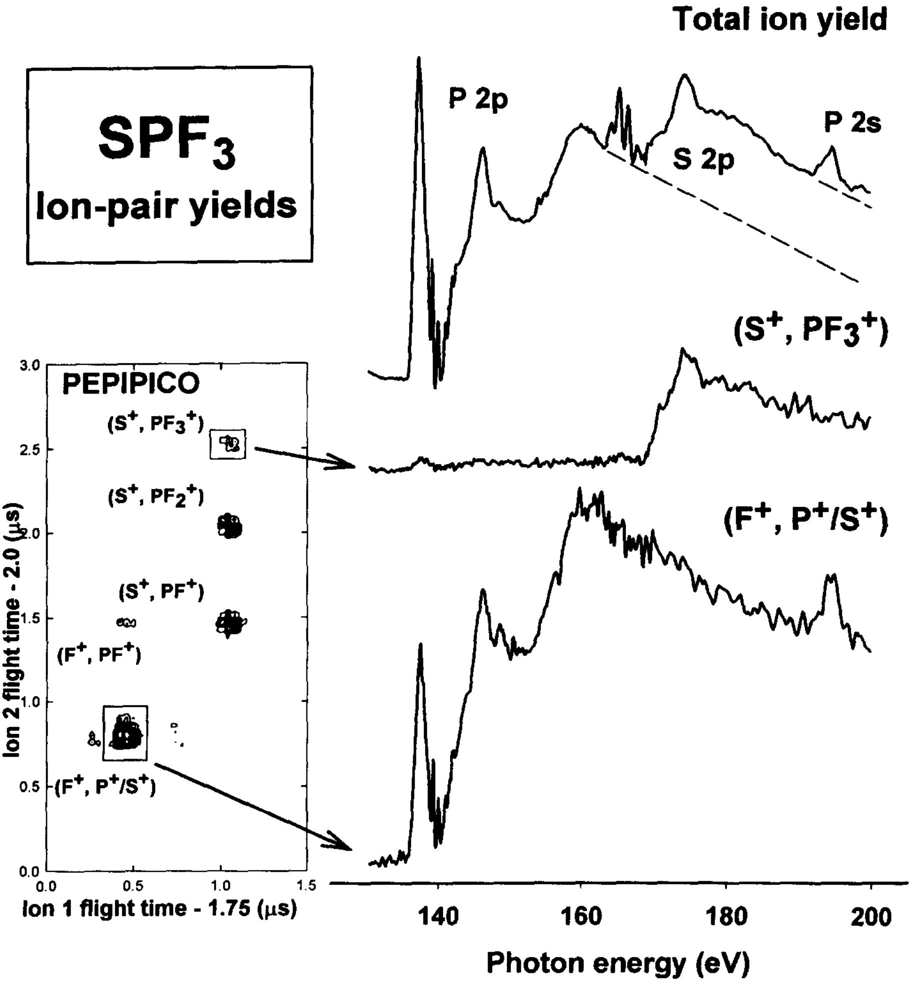

Fig. 4. PEPIPICO measurements of SPF$_3$ in the P 2p, S 2p and P 2s regions. The (S$^+$,PF$_3^+$) and (F$^+$,P$^+$/S$^+$) ion-pair yield spectra are compared with the TIY spectrum (right side). The 2D PEPIPICO map (left side) was obtained by summing data obtained at photon energies from 130 to 160 eV. The approximate regions of the PEPIPICO signal that were integrated to obtain the ion-pair yield spectra are indicated by boxes.

partners of the energetically similar (a_1^{-1},e) ^1E and (e^{-1},e) ^1E states [9].

3.2. Excitation and fragmentation of SPF$_3$

A recurring theme in the work of a number of groups exploring the decay of core excited and ionized states is the identification of state and/or site selective ionic fragmentation processes which might have potential application to X-ray selective photochemistry [1-6]. PEPICO and PEPIPICO measurements of SPF$_3$ in the P 2p and S 2p regions provide a dramatic example of such state and site selective fragmentation.

The TIY spectrum of SPF$_3$ from 130 to 200 eV photon energy, obtained in PEPICO mode using an extraction field of 400 V cm^{-1}, is compared in Fig. 3 with partial ion yield spectra of nine of the observed photoionization products. The partial ion yield spectra of several of the ions, namely P$^+$, S$^+$, PF$^+$ and PF$_2^+$, have a structure similar to that of the TIY spectrum, with the P 2p and S 2p discrete and continuum features evident in each spectrum. The notable exception is the P 2s feature at 194 eV, which is only evident in the F^+, P^+ and S^+ partial ion yields, indicating that P 2s excitation results in more extensive fragmentation of SPF_3 than does P 2p or S 2p excitation and/or ionization. In contrast, the production of several ions is specific to one edge or the other. The F^+ partial ion yield spectrum is essentially identical to the TIY up to a photon energy of 164 eV (i.e. through the P 2p region) and includes P 2s signal but is devoid of S 2p features. The reverse is true of the PF_3^+, PF_3^{++} and SPF_3^{++} partial ion yields, which 'turn on' in the S 2p continuum region, but are absent or very weak at lower photon energies. The partial ion yield of SP^+ provides a striking example of state selectivity, with significant production of this ion occurring only in the P 2p discrete transition at 137.5 eV. These results indicate that, in general, decay following P 2p excitation and ionization of SPF_3 leads primarily to fragmentation of P–F bonds, while S 2p excitation results in S–P bond cleavage.

The results of PEPIPICO measurements of core-excited SPF_3 are shown in Fig. 4. These multicoincidence measurements enable the identification of the various ions produced in the same photoionization event. The correlations between ion signals are illustrated by the 2D map on the left side of the figure, which plots the coincidence signal as a function of the flight times of the first and second ions detected. The ion pairs responsible for each feature in the map are indicated. The similar masses of P^+ and S^+ make discrimination of these ions difficult using the current instrumentation. Ion-pair yields are obtained by integrating all counts in a region of the 2D ion-correlation map associated with a particular ion pair (represented by the two boxes on the map) and monitoring that intensity as a function of photon energy, as illustrated by the (S^+,PF_3^+) and (F^+,P^+/S^+) ion-pair yields on the right side of Fig. 4. The (S^+,PF_3^+) ion-pair yield is the only one displaying the sudden onset at the S $2p^{-1}$ edge, supporting the observation made above from the partial ion-yield spectra that following S 2p ionization, significant fragmentation occurs involving S–P bond breakage without accompanying P–F bond breakage. In contrast, the (F^+,P^+/S^+) ion-pair yield spectrum is in agreement with the TIY spectrum in the P 2p region, but lacks features arising from S 2p excitation and ionization. The (F^+,P^+/S^+) ion-pair yield is also the only ion-pair yield containing the P 2s feature at 194 eV, supporting the conclusion from the partial ion yield data that P 2s excitation leads to substantial fragmentation of SPF_3.

4. Summary

Photoionization and photofragmentation studies of core excited and ionized PF_3 and SPF_3 have been performed using synchrotron radiation and time-of-flight mass spectrometry. Examples of state and site specific photoionization and photofragmentation processes are found in each molecule. Consideration of partial ion yields has led to the identification of a novel aspect of P 2p spectroscopy, namely 'LS-coupled states'.

Acknowledgements

We thank A.L.D. Kilcoyne and T. Tyliszczak for their expert work in fabricating the time-of-flight/TDC measurement system. We thank J.D. Bozek (ALS), Kim Tan (SRC) and Dieter Gravel (Osnabrück) for their assistance with the measurements. Financial support for this work was provided by NSERC (Canada). This work is based in part upon research conducted at the Synchrotron Radiation Center, University of Wisconsin—Madison, which is supported by the NSF under Award No. DMR9531009.

References

[1] I. Nenner, P. Morin, in: U. Becker, D.A. Shirley (Eds.), VUV and Soft X-Ray Photoionization, Plenum Press, New York, 1996, p. 291.
[2] D.M. Hanson, Adv. Chem. Phys. 77 (1990) 1.
[3] M. Simon, T. LeBrun, R. Martins, G.G.B. de Souza, I. Nenner, M. Lavolée, P. Morin, J. Phys. Chem. 97 (1993) 5228.
[4] H.C. Schmelz, C. Reynaud, M. Simon, I. Nenner, J. Chem. Phys. 101 (1994) 3742.
[5] N. Saito, J.D. Bozek, I.H. Suzuki, Chem. Phys. 188 (1994) 367.
[6] M. Simon, P. Morin, P. Lablanquie, M. Lavollée, K. Ueda, N. Kosugi, Chem. Phys. Lett. 238 (1995) 42.
[7] W.C. Wiley, I.H. McLaren, Rev. Sci. Instr. 26 (1955) 1150.
[8] A.P. Hitchcock, A.L.D. Kilcoyne, T. Tyliszczak, E. Rühl, J.D. Bozek, J.T. Spencer and P.A. Dowben, manuscript in preparation.
[9] N. Kosugi, R.G. Cavell, A.P. Hitchcock, Chem. Phys. Lett. 265 (1997) 490.