UNIVERSITY OF BIRMINGHAM

Memories & highlights of my early scientific career, 1975-2008 : science at 2nd generation synchrotron sources (Daresbury, UK and Bessy 1, Germany)

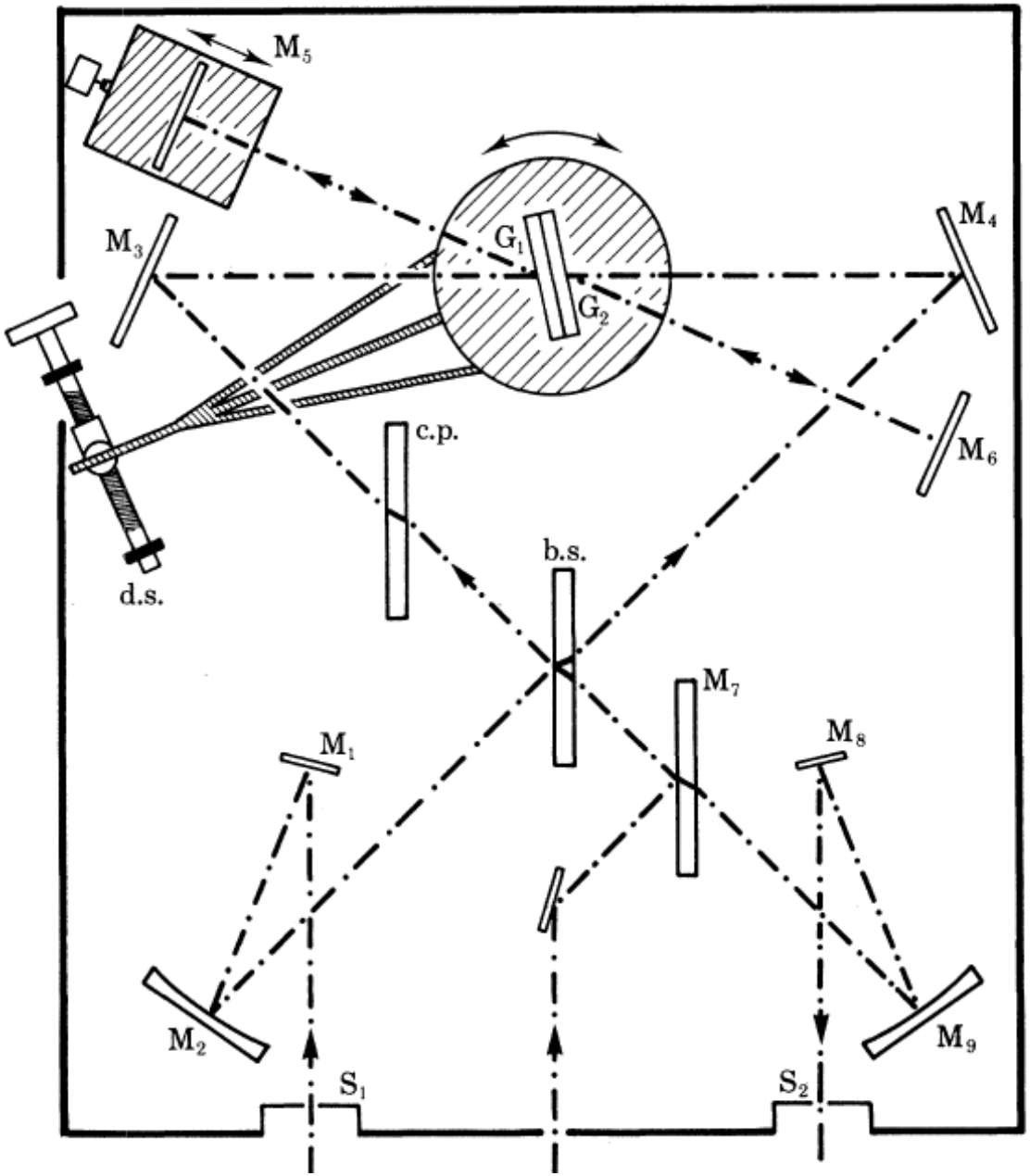
Richard Tuckett, ***University of Birmingham UK***
r.p.tuckett@bham.ac.uk

http://www.synchrotron.org.uk/index.php?option=com_content&view=article&id=114:fluorescence-experiments-on-small-molecules&catid=35:chemistry&Itemid=53

Hefei (1), October 2019

Thanks to all my research workers and collaborators

PhD, 1975-1979



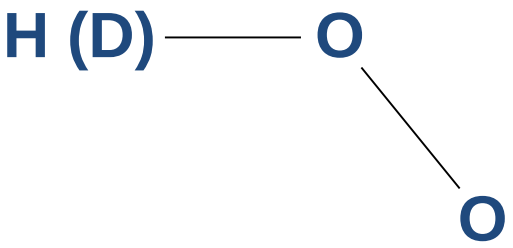
Double-pass SISAM spectrometer for the near infra-red (1–2 μm)

HO_2· free radical

$A\,^2A' \rightarrow X\,^2A''$ $\lambda_o = 1.43\ \mu m$, resolution 0.2 cm^{-1}

DO_2· free radical

$A\,^2A' \rightarrow X\,^2A''$



Geometry (two bond lengths, one bond angle) determined in both electronic states

Mol. Phys., (1979) 37, 379 & 403

PhD (1979) : O_2 $a\ ^1\Delta_g \rightarrow X\ ^3\Sigma_g^-$ (0,0) band, λ_o = 1.27 μm

Classic example of P, *Q* and *R*-branches, $\Delta B \sim 0$: resolution = 0.2 cm^{-1}

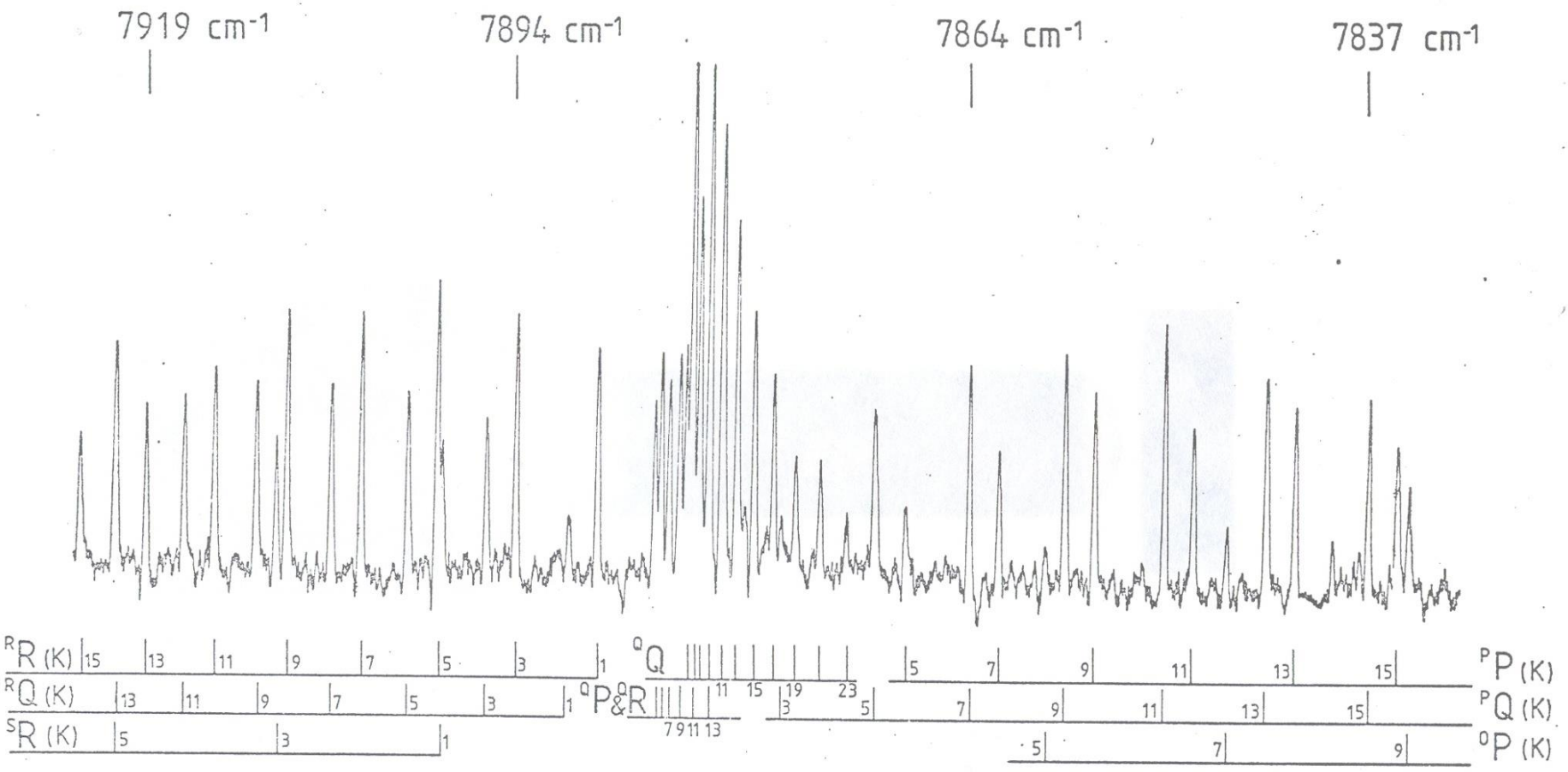
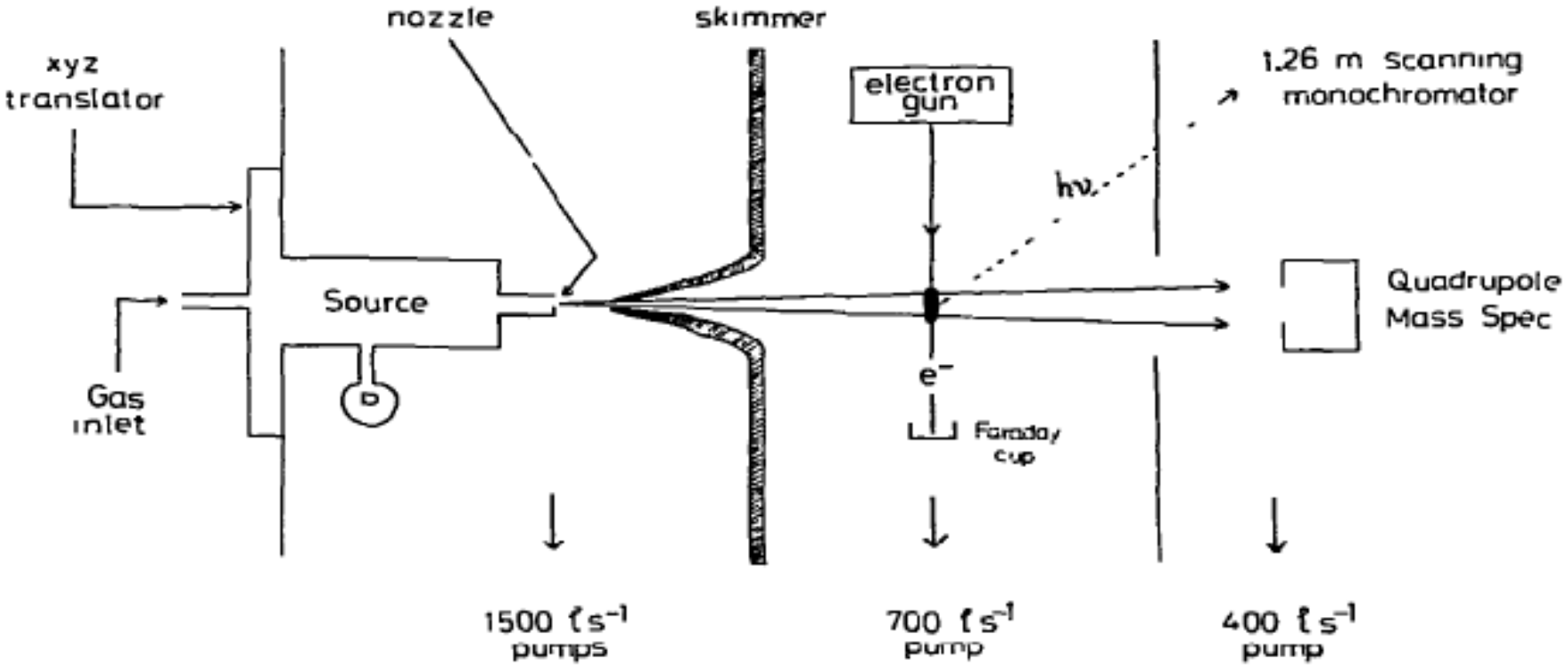


Figure 4.3 : High resolution spectrum of $O_2\ ^1\Delta_g(v = 0) \rightarrow\ ^3\Sigma_g^-(v = 0)$.

Crossed Molecular beam / Electron beam apparatus (1978–1982)
Alan Carrington (Southampton, UK)



$$AB_n + e^- \rightarrow (AB_n)^{+*} + 2e^- ;$$

$$(AB_n)^{+*} \rightarrow (AB_n)^{+} + h\nu$$

Source of rotationally-cold molecular ions. Large molecules.

Mol. Phys., (1983) 49, 475

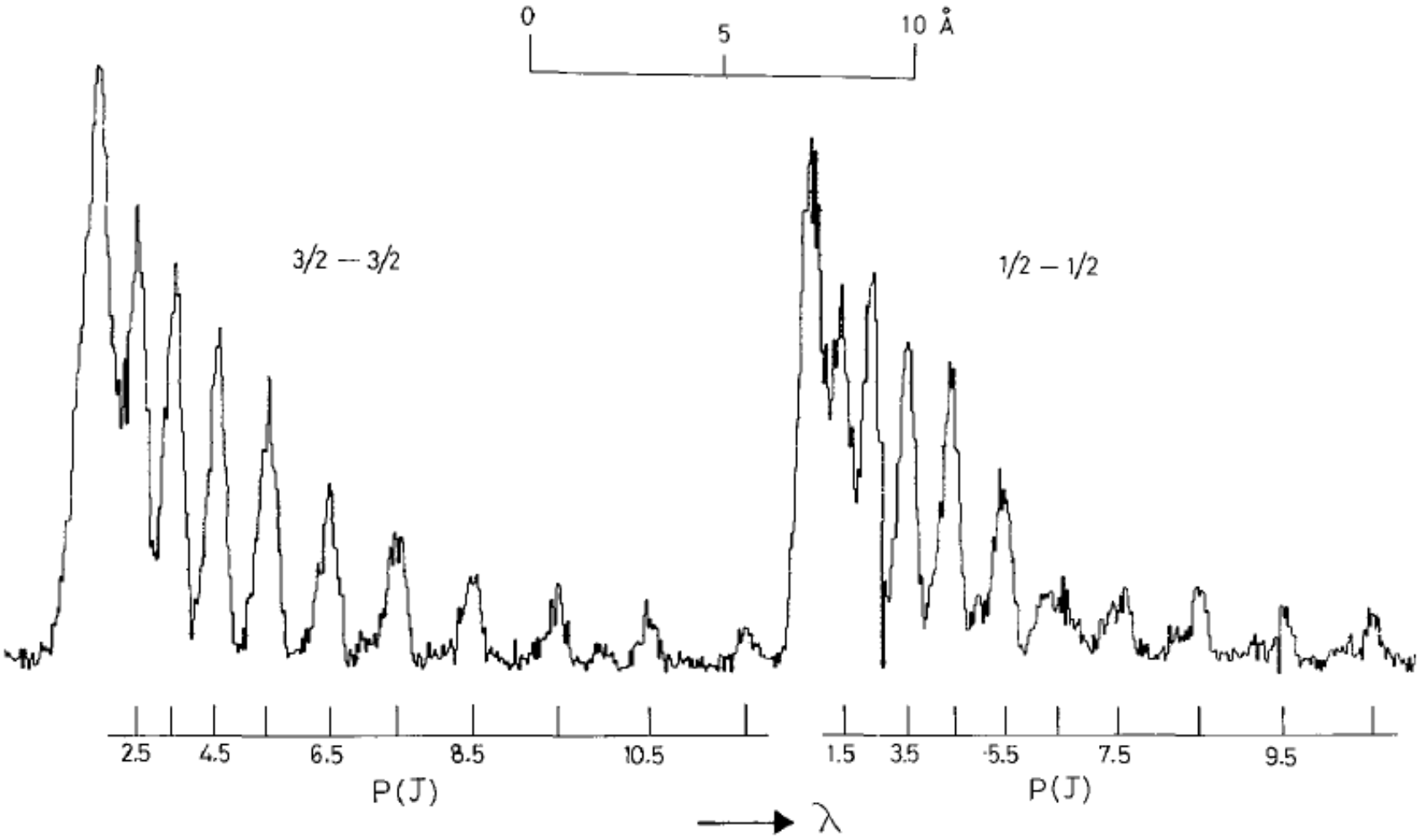
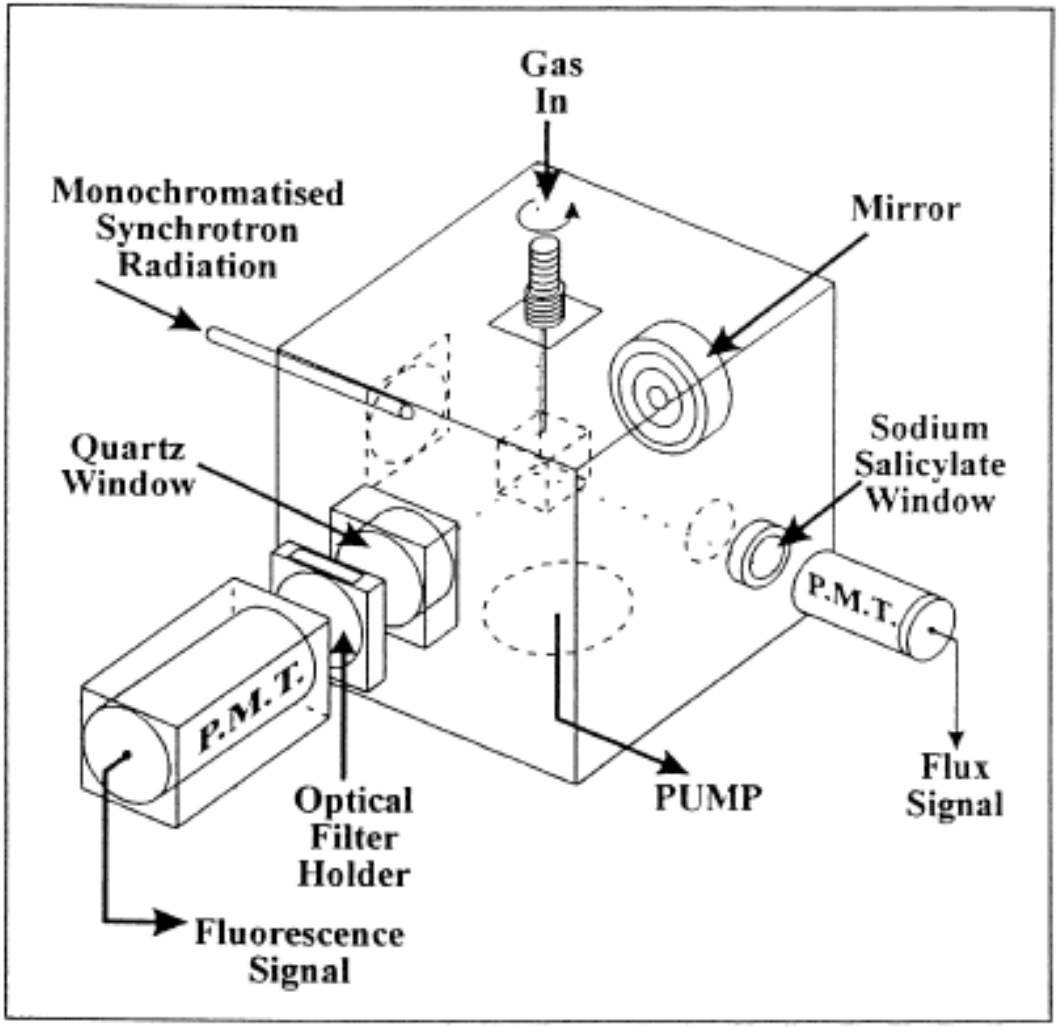


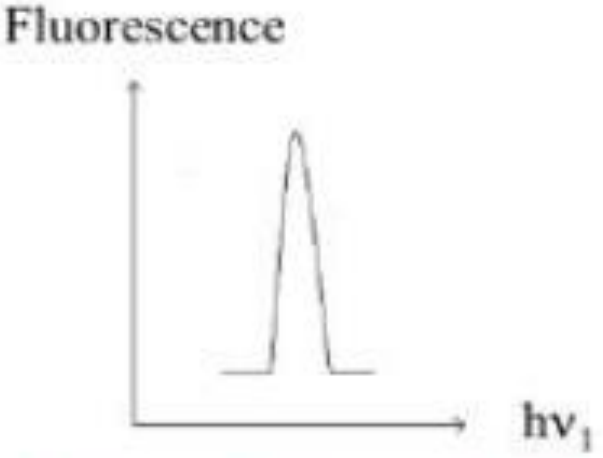
Figure 2. The (8, 3) band of F_2^+ $\tilde{A}\,^2\Pi_u \rightarrow \tilde{X}\,^2\Pi_g$ at 4560 Å, rotationally resolved. The J numberings of the two P branches are shown.

Daresbury Synchrotron Radiation Source, Cheshire (1988-2008)

First simple fluorescence excitation apparatus, Daresbury, 1988–2000



Resonant and non-resonant excitation



Resonant photon excitation

Formation of a fluorescing fragment *via* a dissociative Rydberg state of AB_n. Resonant process.

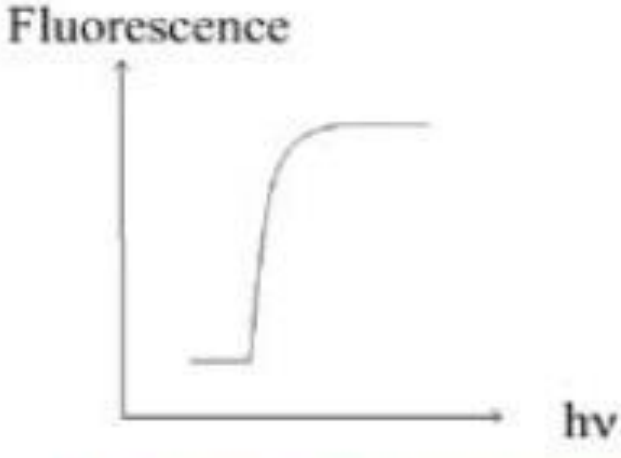
$AB_n + h\nu_1 \rightarrow AB_n^*$

$AB_n^* \rightarrow AB_{n-1}^* + B$

$AB_{n-1}^* \rightarrow AB_{n-1} + h\nu_2$

e.g. BF_2 / BF_3

BCl and BCl_2 / BCl_3



Non-resonant photon excitation

Sharp turn-on of fluorescence. Signal present for photon energies well in excess of threshold ; electron carries away excess energy. Non-resonant process ⇒ formation of excited, fluorescing electronic state of parent ion.

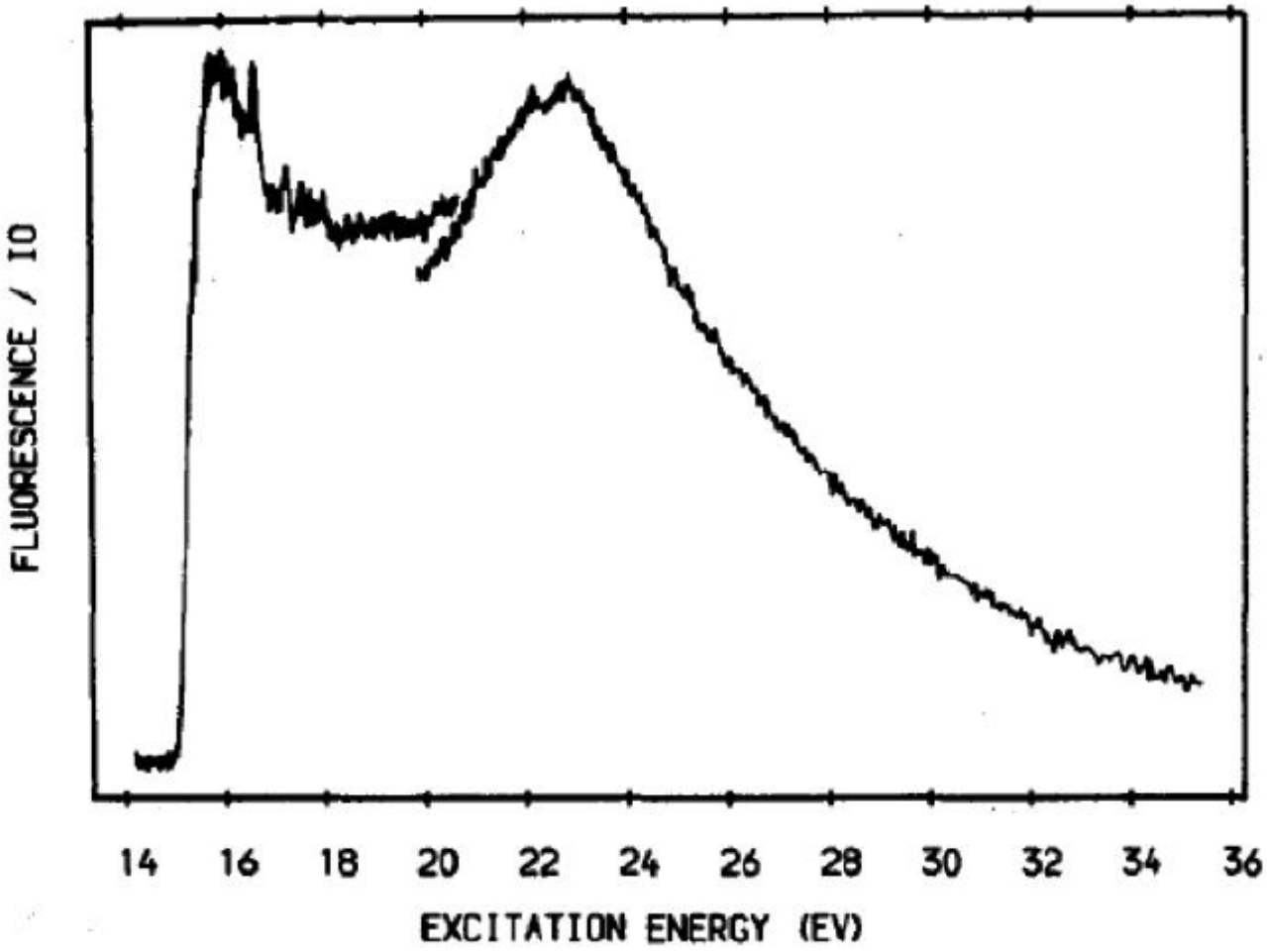
$AB_n + h\nu_1 \rightarrow (AB_n^+)^* + e^-$

$(AB_n^+)^* \rightarrow AB_n^+ + h\nu_2$

e.g. N_2^+ / N_2 ; CO_2^+ / CO_2

BCl_2^+ and BCl_3^+ / BCl_3

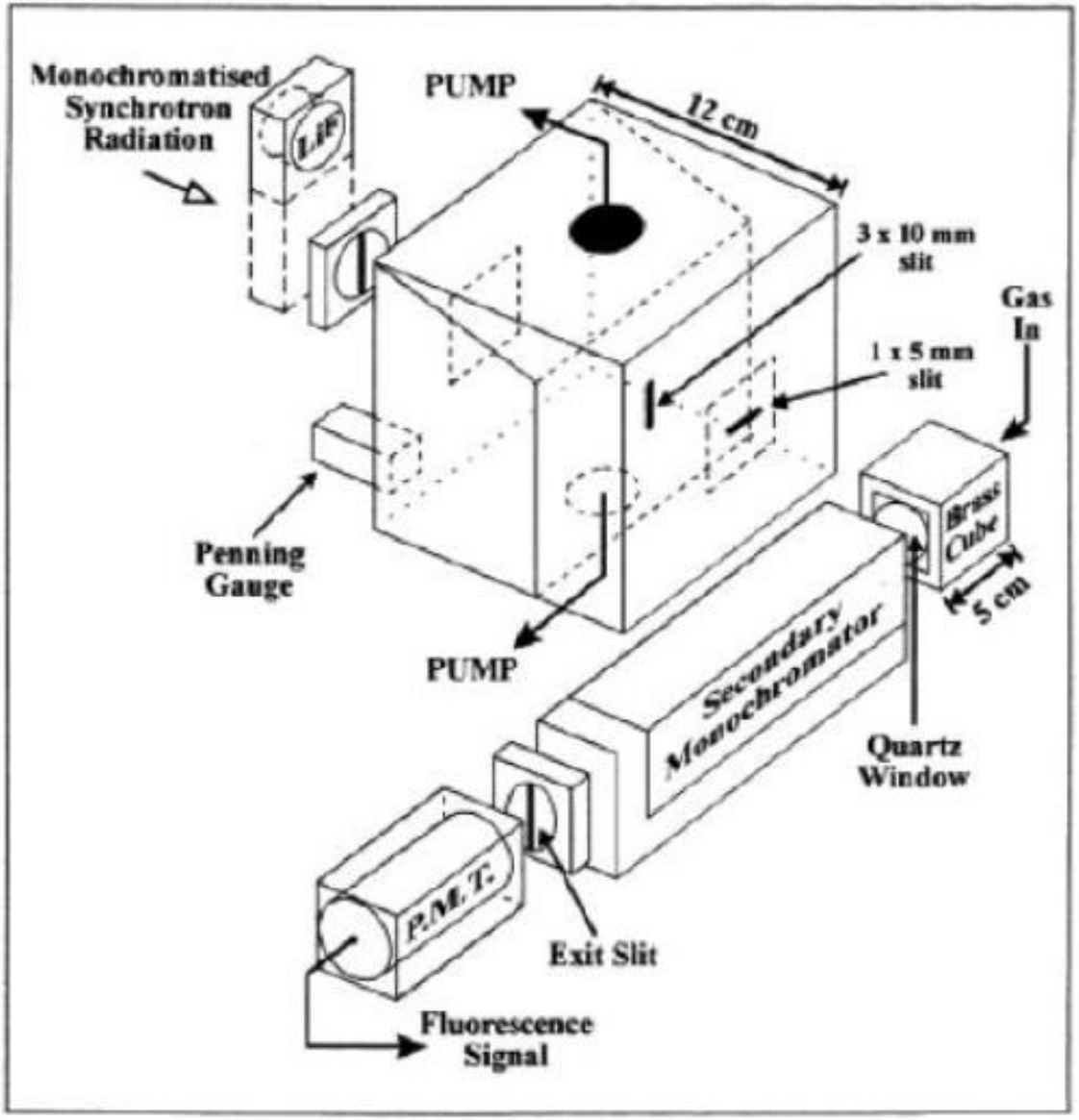
$SiCl_4$ / tunable vacuum-UV. Detect fluorescence 300–500 nm. Emitter is $SiCl_4^+$ $C\ ^2T_2$, adiabatic IE = 15.1 eV.



J. Chem. Phys., (1988) 89, 2675

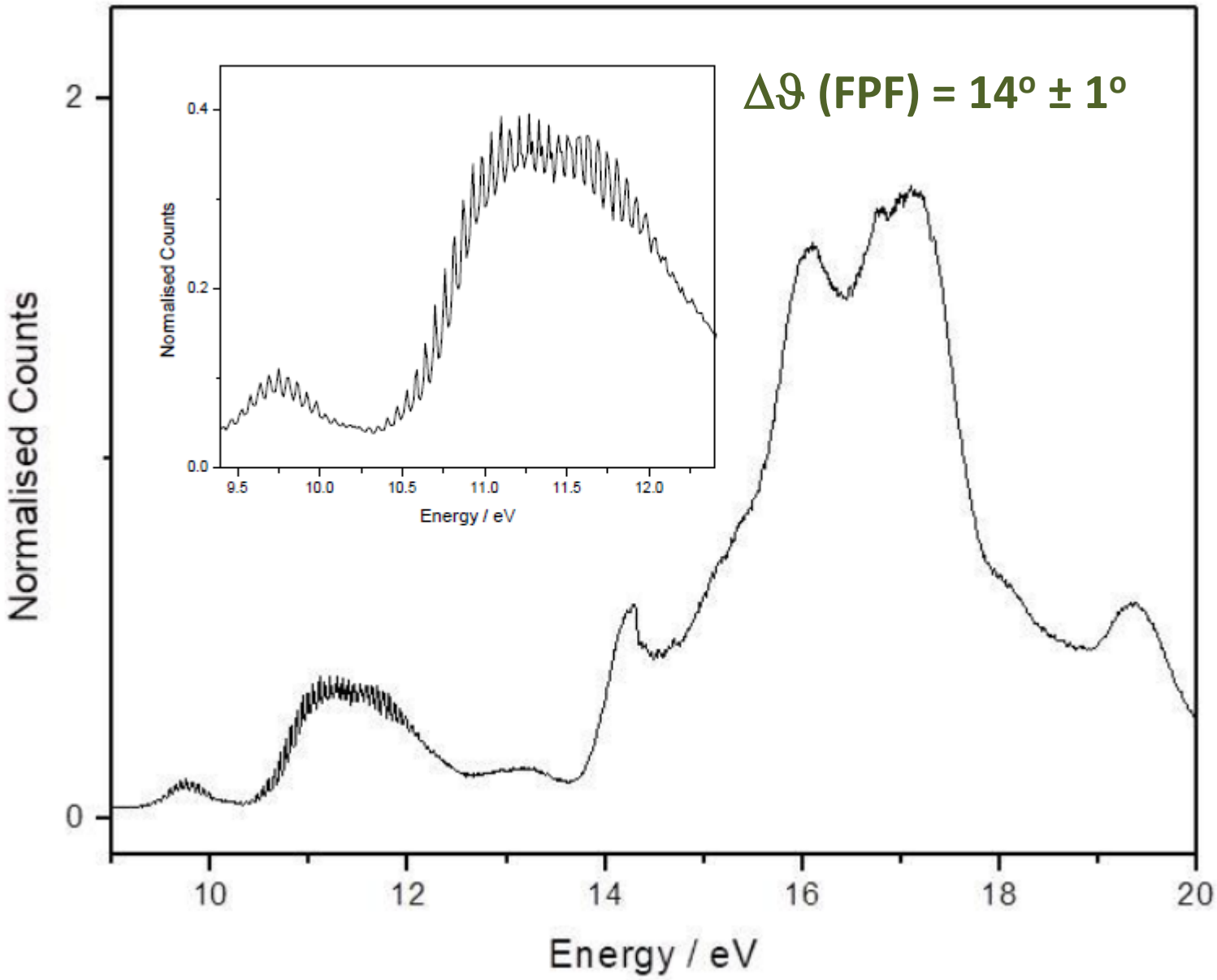
Dispersed fluorescence experiments (1) following vacuum-UV photoexcitation, Bessy 1, Berlin, Germany (Baumgärtel and Jochims), 1993–1999

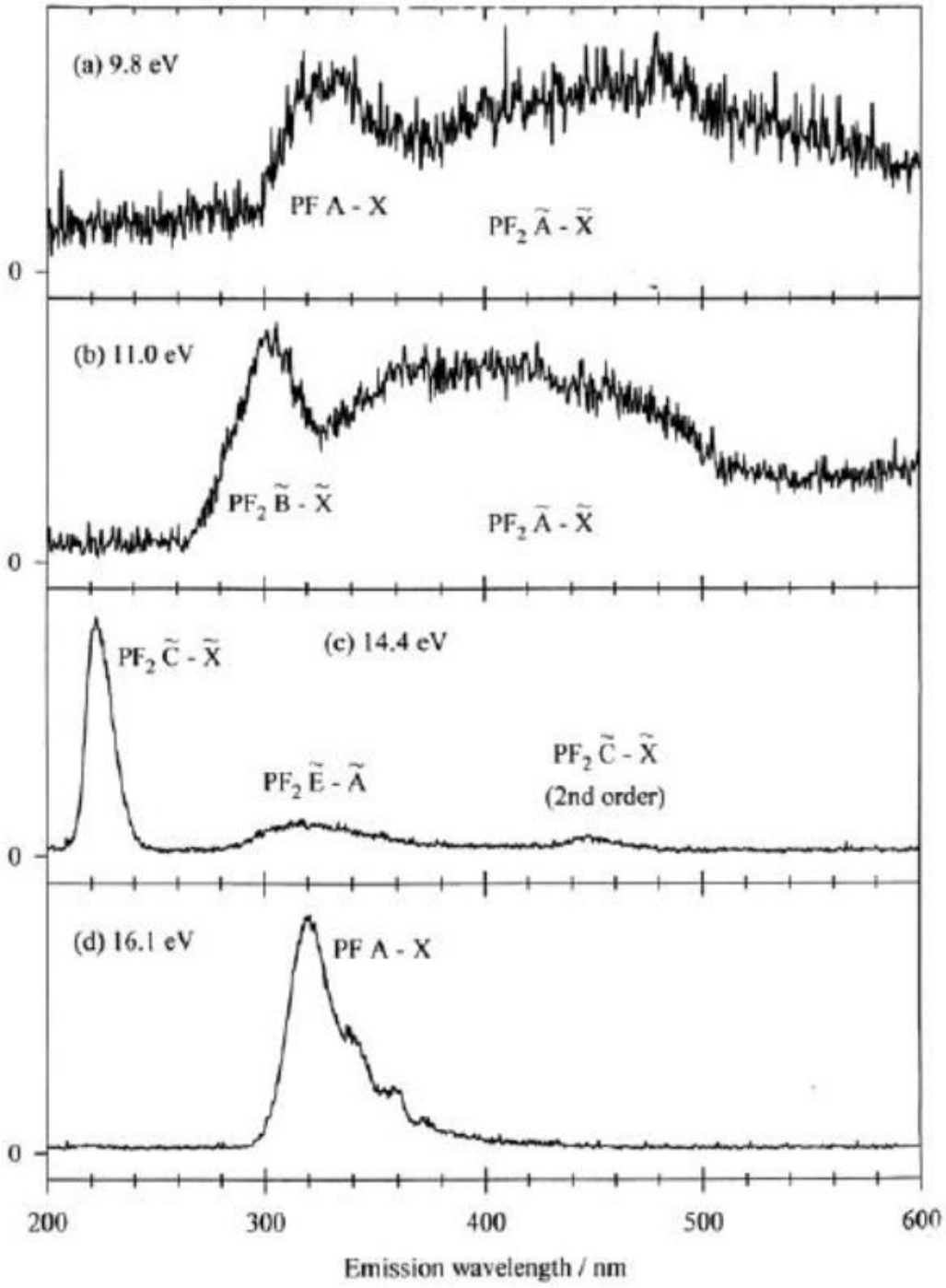
'Small is beautiful'



PF_3 / vacuum-UV excitation. Emission due to $PF_2\cdot$ or PF free radicals.

Chem Phys. Letts. (1996) 261, 486 & *J. Chem. Phys.*, (1998) 108, 857





Low resolution dispersed spectra following PF_3 vacuum-UV photoexcitation, Bessy 1 (1998)

(a) <u>9.8 eV</u> $PF_2 \cdot$ $A\ ^2A_1\ (^2\Pi) - X\ ^2B_1$

(b) <u>11.0 eV</u> $PF_2 \cdot$ $A\ ^2A_1\ (^2\Pi) - X\ ^2B_1$ and $B\ ^2B_2 - X\ ^2B_1$

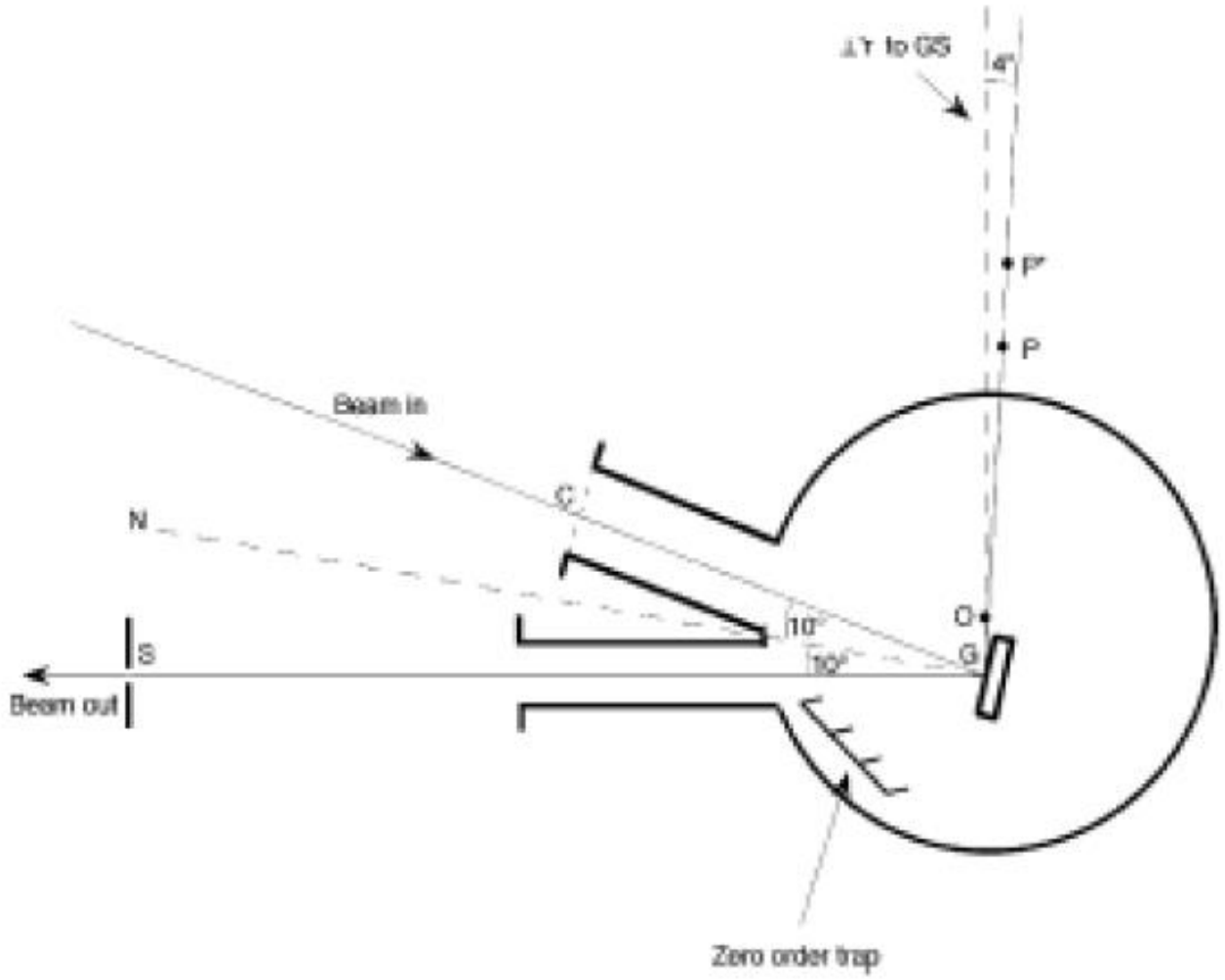
(c) <u>14.4 eV</u> $PF_2 \cdot$ $C\ ^2A_1 - X\ ^2B_1$ and $E\ ^2B_1\ (^2\Pi) - A\ ^2A_1\ (^2\Pi)$

(d) <u>16.1 eV</u> PF $A\ ^3\Pi - X\ ^3\Sigma^-$

This still remains the most extensive study of the valence spectroscopy of the $PF_2 \cdot$ free radical

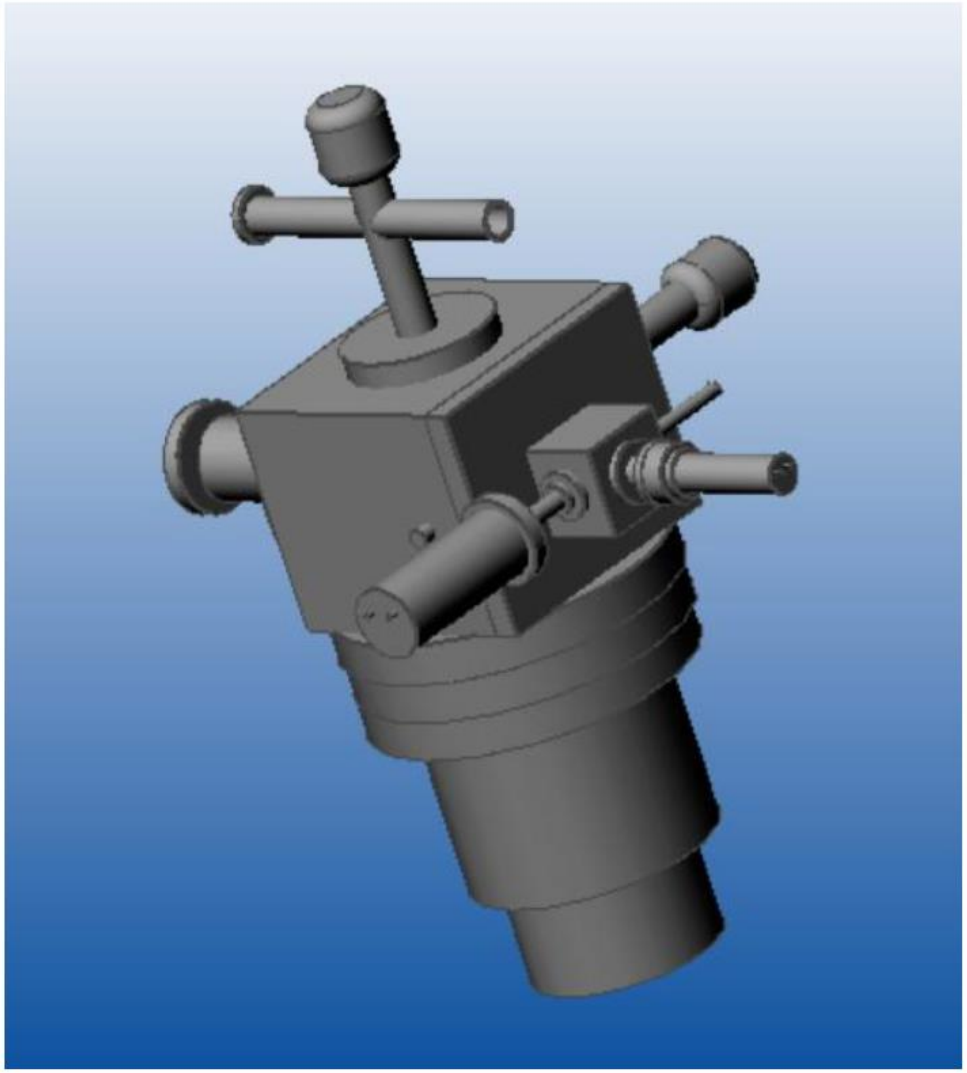
Upgrade of the 1 m Seya to a simpler 1 m Wadsworth monochromator on beamline 3.1 at Daresbury, 2001 – 2005 ***Nucl. Instr. Meth. Phys. B.,*** **(2005)** ***237****, 656*

No entrance slit, used the full horizontal aperture of the beamline.
Resolution only depended upon horizontal electron beam size in the ring, c. 0.05 nm.

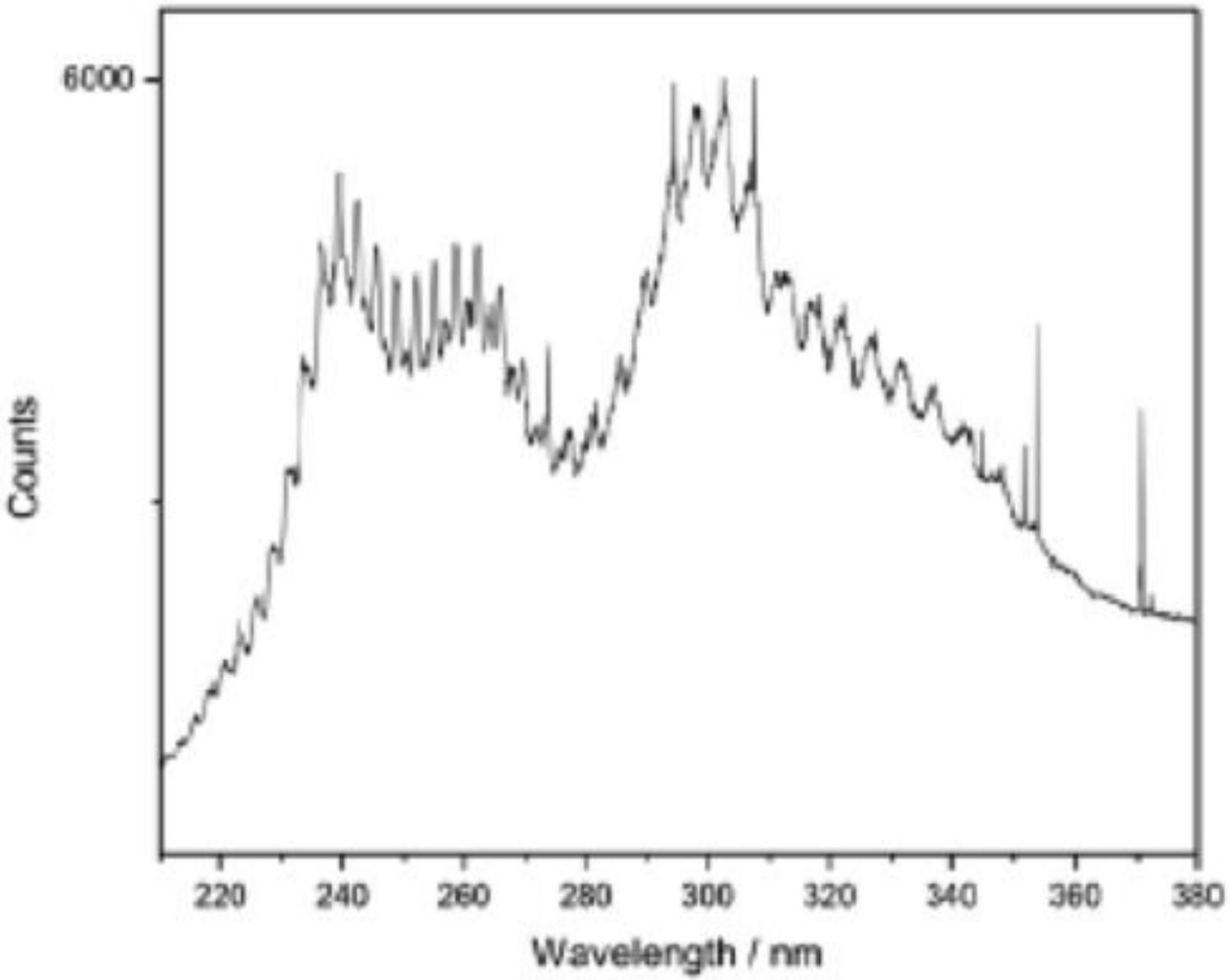


Dispersed fluorescence experiments (2) on the new upgraded beamline at Daresbury using *CCD multi-channel* fluorescence detection, 2004 – 2008.

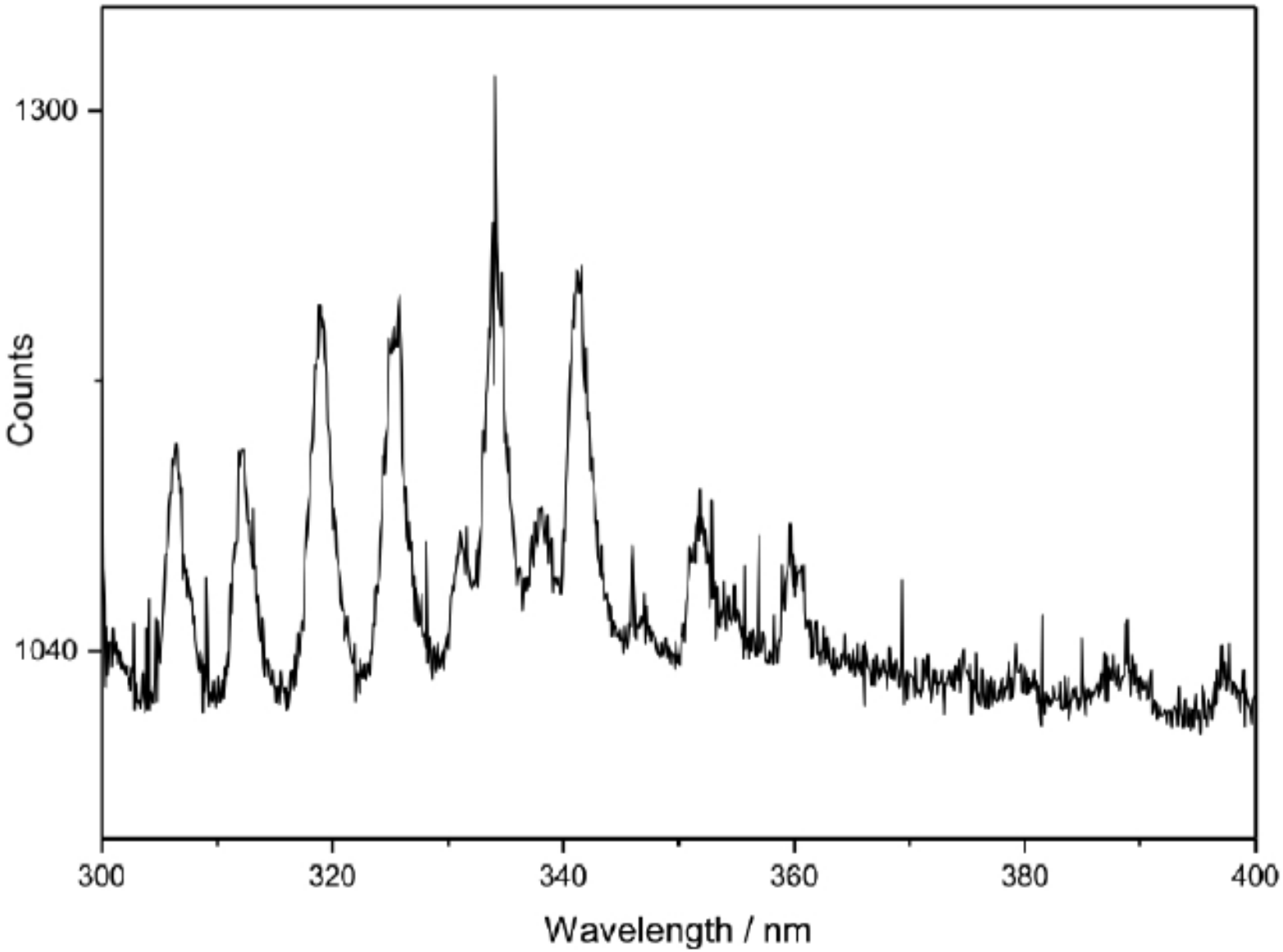
Record wide range of emitting wavelengths *simultaneously*; the Jacquinot advantage.

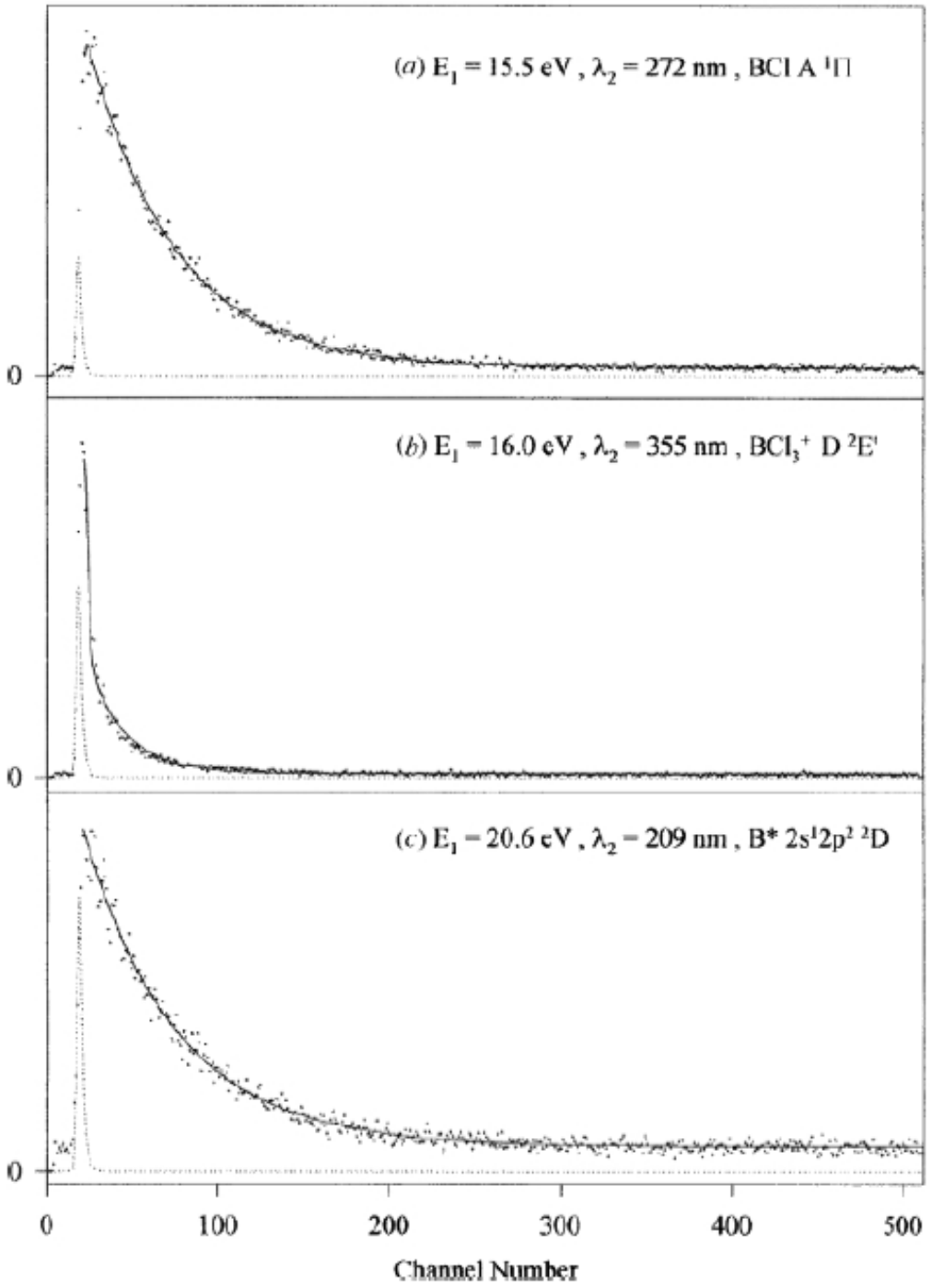


BF_3 photoexcited at $h\nu_1$ = 14.1 eV. Emission due to $BF_2\cdot$ free radical, $B\,^2A_1 - X\,^2A_1$ and $B\,^2A_1 - A\,^2B_1$ valence transitions



BCl_3 photoexcited at 17.7 eV. Emission due to BCl_2^+ cation $A - X$, vibrational progression of 650 ± 30 cm^{-1} in either excited or ground state





Single-bunch, lifetime experiments with BCl_3 conducted at Bessy 1

Both E_1 and λ_2 are defined

(a) E_1 = 15.5 eV, λ_2 = 272 nm

BCl *A* $^1\Pi$, $\tau = 20.0\ (2)$ ns

(b) E_1 = 16.0 eV, λ_2 = 355 nm

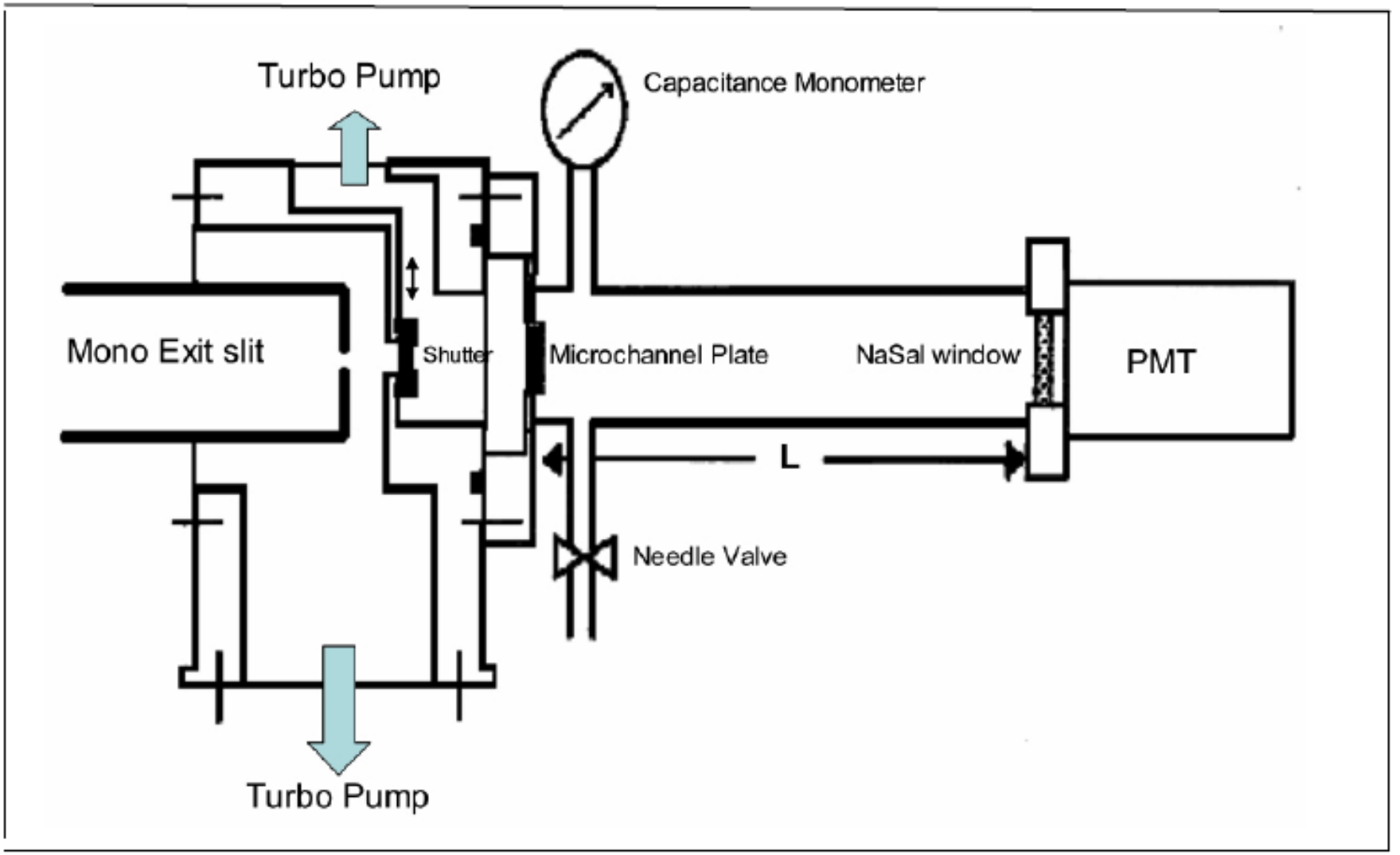
BCl_3^+ *D* $^2E'$, τ = 8.9 (2) ns

(c) E_1 = 20.6 eV, λ_2 = 209 nm

B* ($2s^1\ 2p^2$) ^2D, τ = 21.5 (6) ns

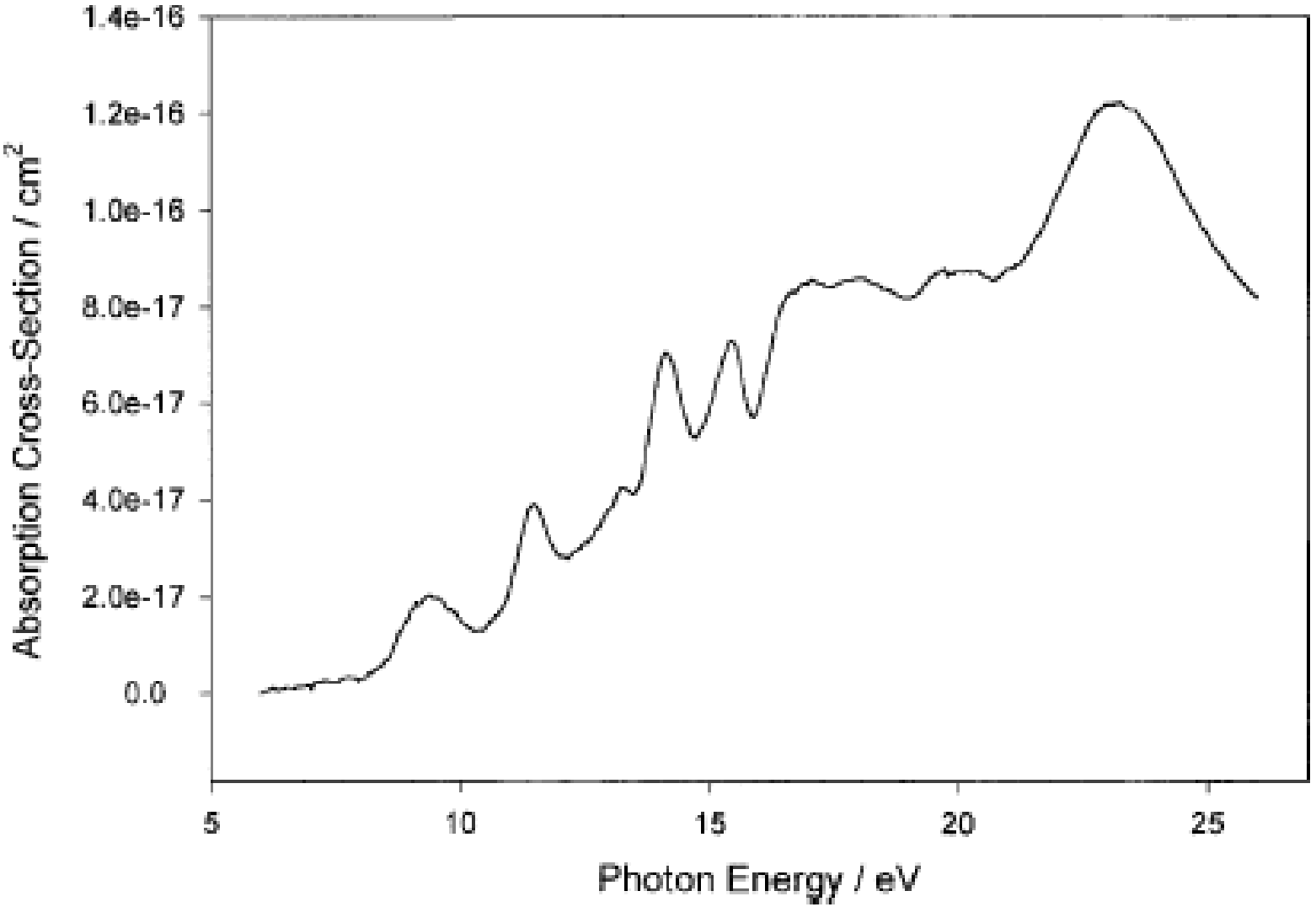
***J. Phys. B.*, (1999) 32, 2569**

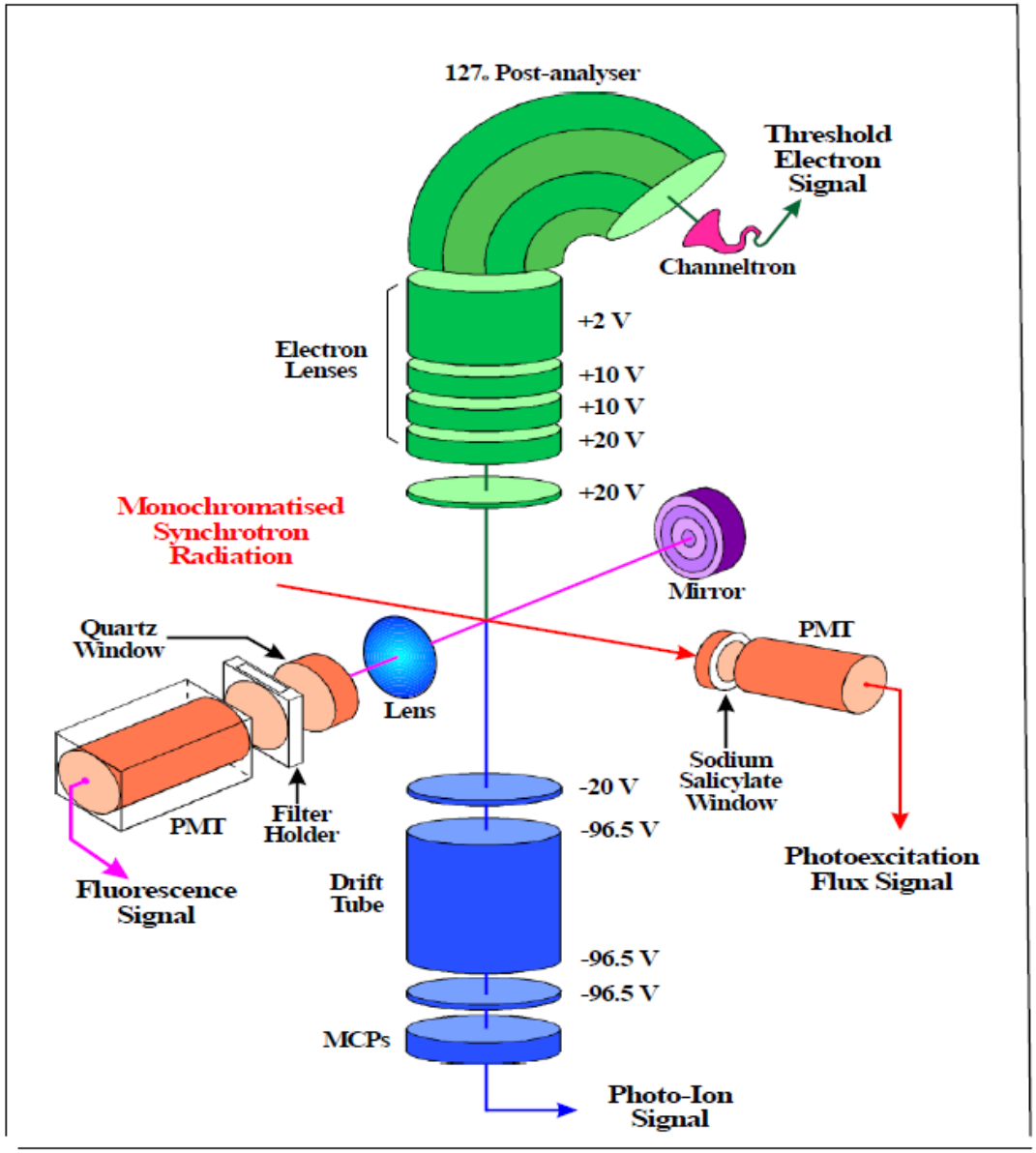
Absorption experiments, Bessy 1, for $\lambda < 105$ nm, but Beer-Lambert still applies: *absolute* values of vacuum-UV absorption cross sections are determined



Vacuum-UV absorption spectrum of SF_5CF_3 ; important to determine the lifetime of this greenhouse gas in the earth's atmosphere (τ = 800–1000 years)

***Chem. Phys. Letts.*, (2003) 367, 697**





Multi-purpose coincidence apparatus, Daresbury UK, 1993–2008

One of the early 'position-senstitive' detectors to study photofragmentation processes in polyatomic molecular ions (TPEPICO spectroscopy)

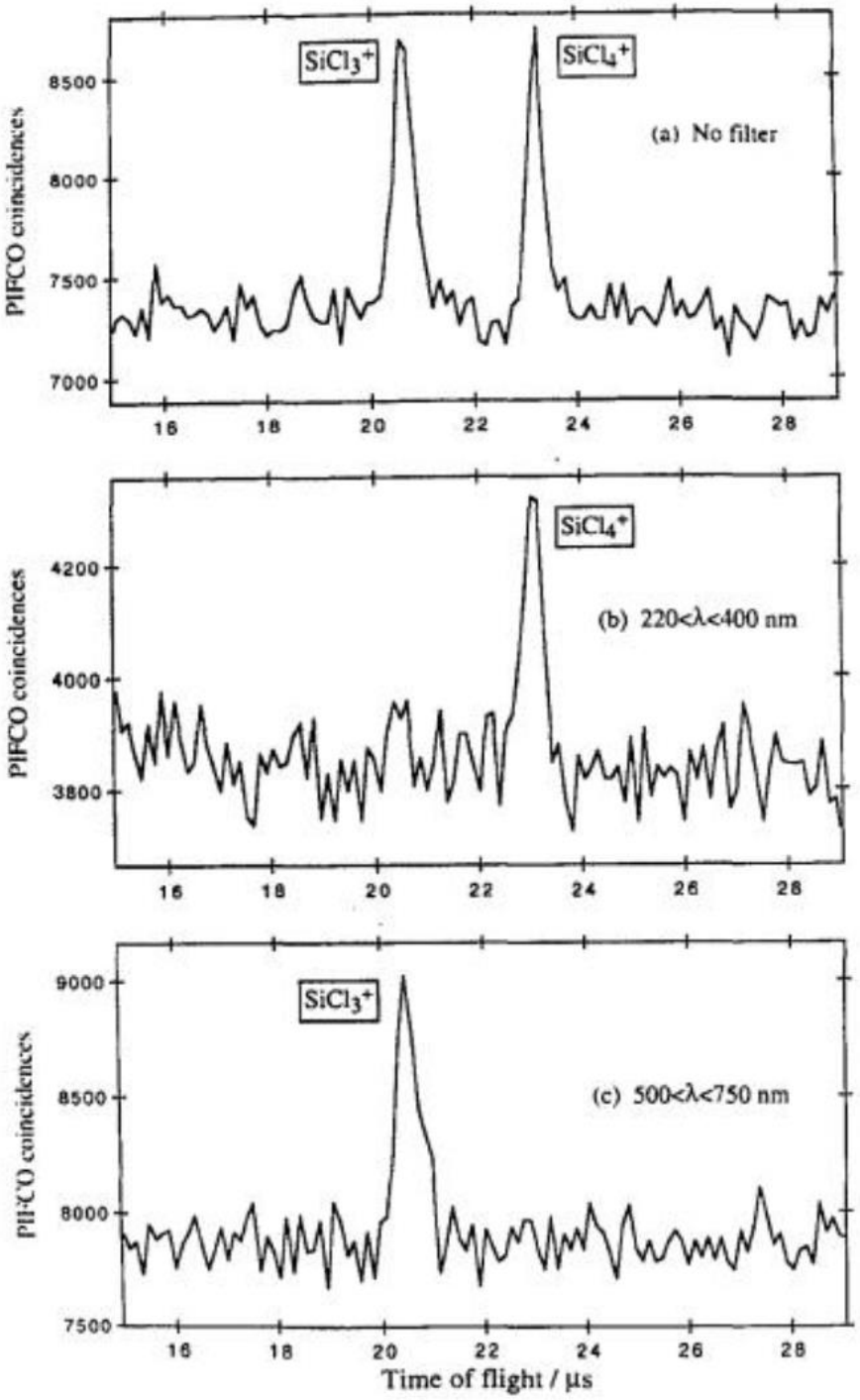
Later, was adapted to study:

PhotoIon Fluorescence Coincidence (PIFCO) spectroscopy

Threshold PhotoElectron Fluorescence Coincidence (TPEFCO) spectroscopy

***Meas. Sci. Tech.*, (1992) 3, 891**

PIFCO spectra from $SiCl_4^+$



Fluorescence from *C* $^2T_2$ state of $SiCl_4^+$ photoexcited at 15.1 eV

Unfiltered fluorescence : Coincidences observed between Photons and two Ions whose time-of-flight correspond to $SiCl_3^+$ and $SiCl_4^+$

UV fluorescence: Emission to the *X* $^2T_1$ ground state of the cation. This state is bound. Coincidences are detected between Photons and the parent ion only

Visible fluorescence : Emission to the *A* $^2T_2$ state of $SiCl_4^+$. This state is repulsive and one Si–Cl bond breaks. Coincidences are now detected between Photons and the daughter ion, $SiCl_3^+$

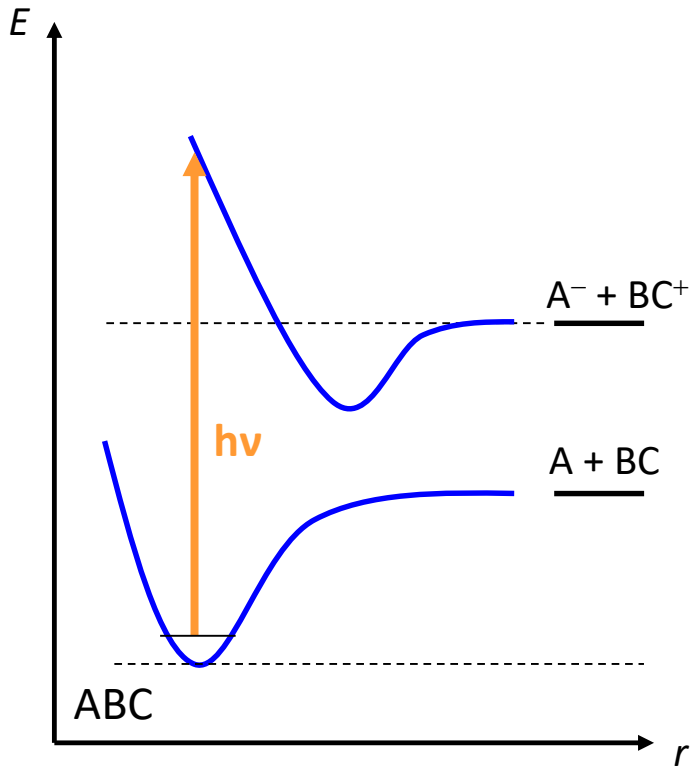
J. Chem. Phys., (1994) 101, 10559

Vacuum-UV negative photoion spectroscopy:

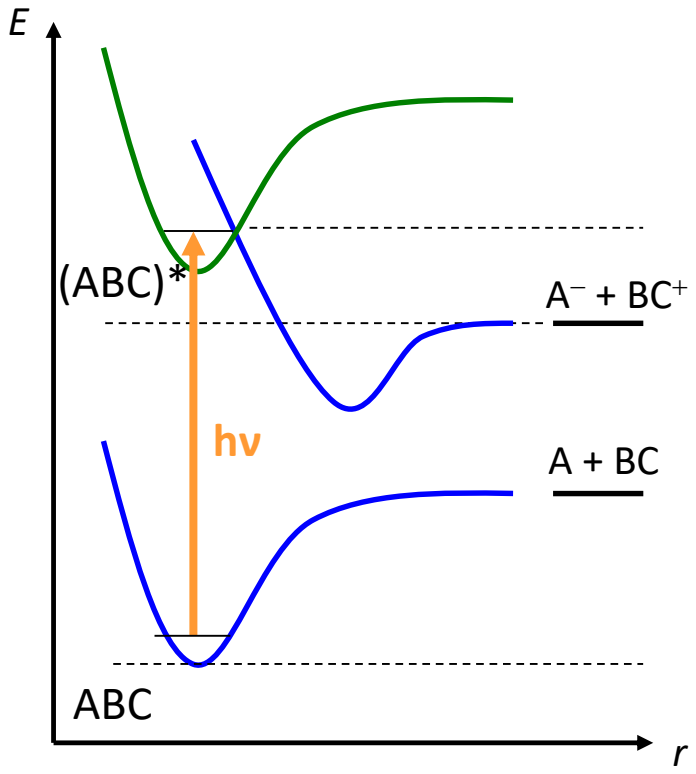
ABC + *hν* → A^- + BC^+

(Daresbury UK, 2006-2011)

Direct ion-pair formation

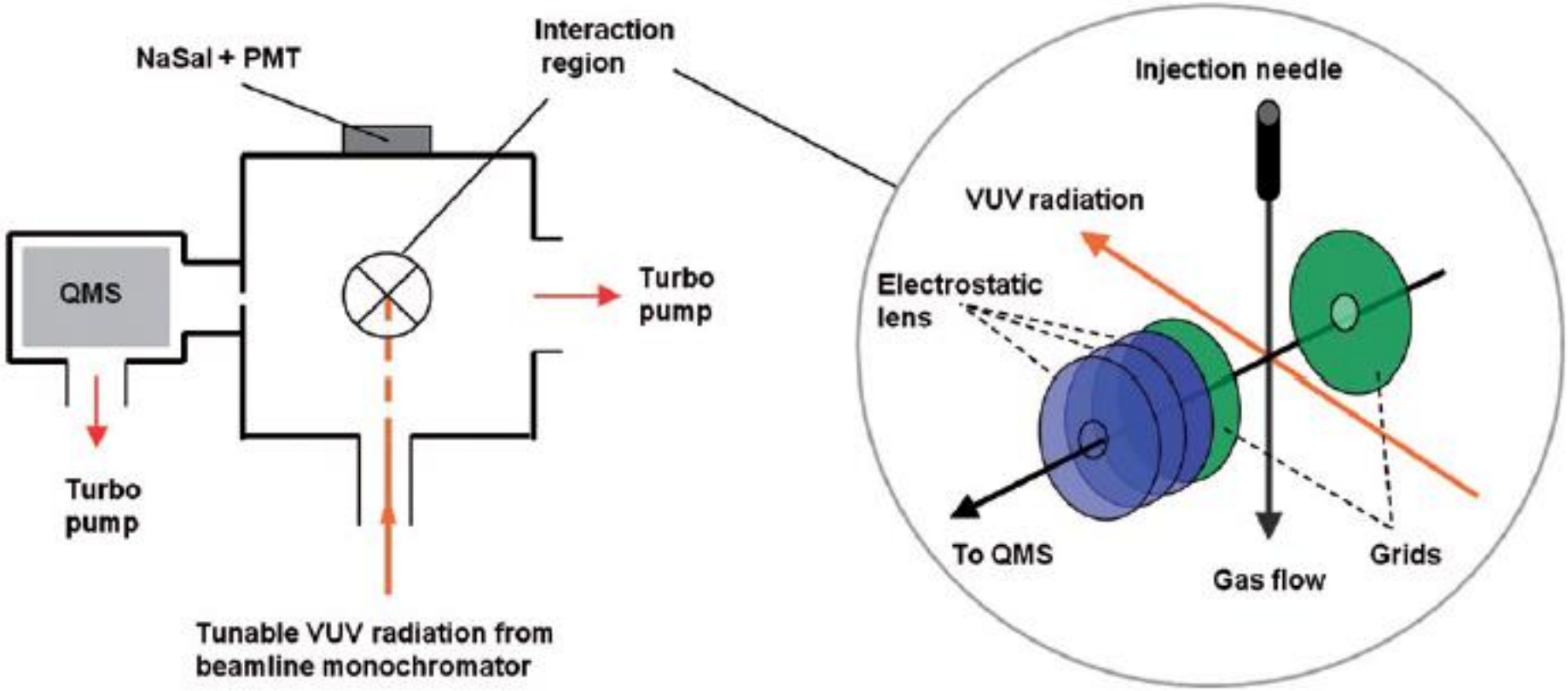


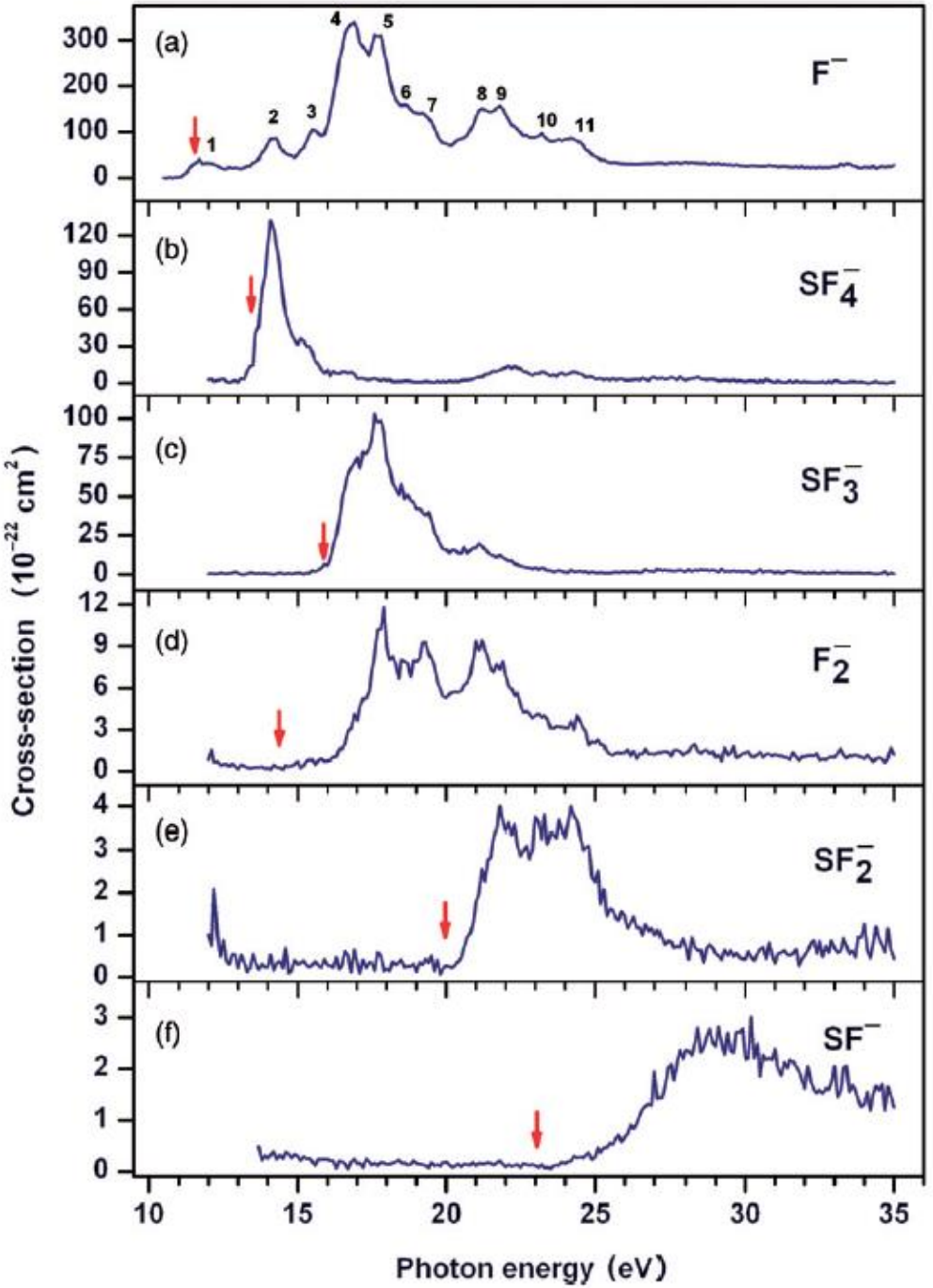
Predissociation into ion pairs



Simpson and Tuckett, *Intern. Rev. Phys. Chem.*, (2011) 30, 197–273

Apparatus to detect negative photoions (*or* anions) as a function of photon energy : collaboration with Latimer (Queens University, Belfast)



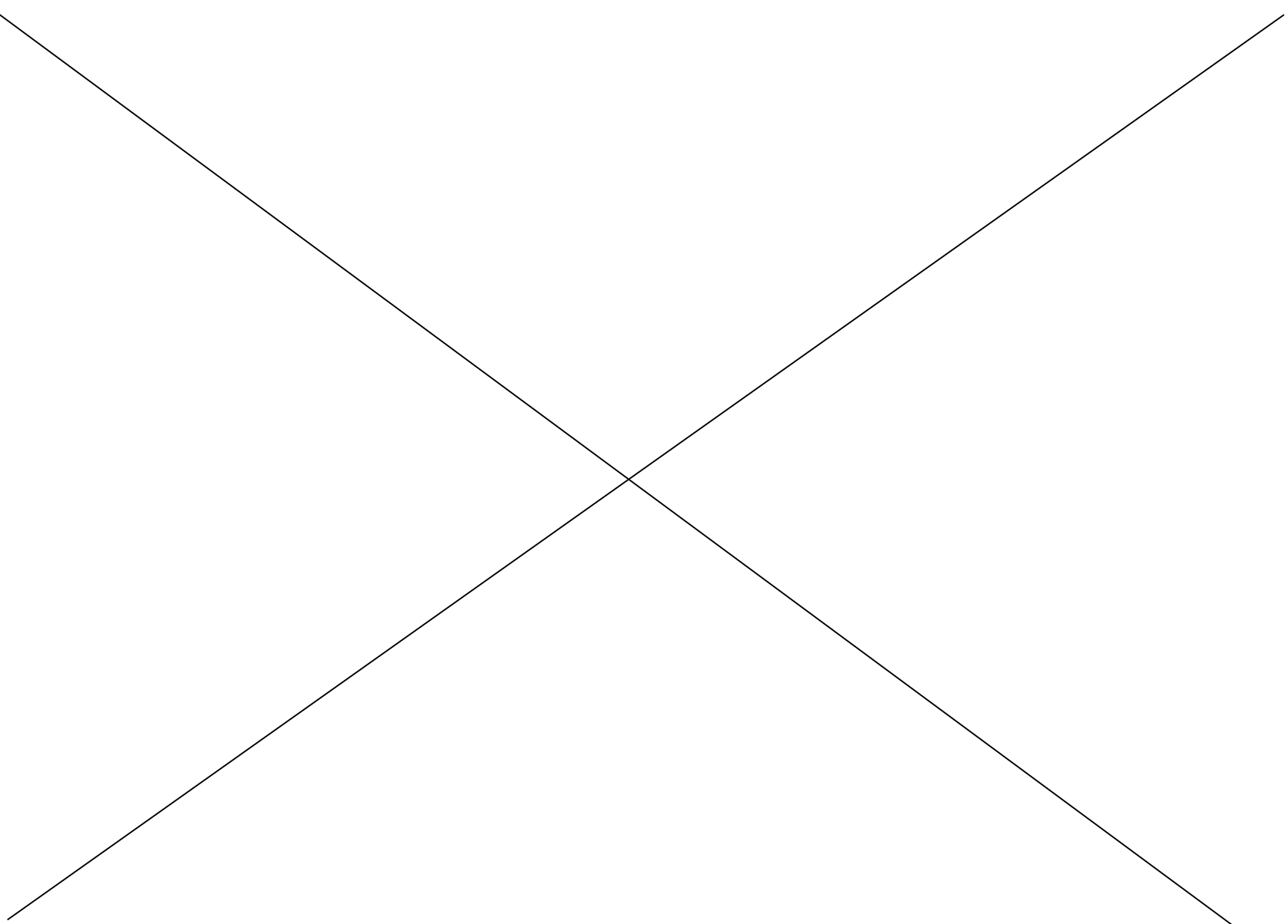


Anion production from SF_5CF_3

Large number of anions are observed. F^- is the strongest, followed by SF_4^- and SF_3^-. F_2^-, SF_2^- and SF^- anions are the weakest.

By calibration initially with CF_4 and SF_6, *absolute* values of cross sections and quantum yields could be determined.

J. Chem. Phys., (2008) 128, 124315

Table 2. Appearance energies, cross-sections and quantum yields for anions observed from photoexcitation of SF_6, CF_4, and SF_5CF_3.

Molecule [AIE[a] (eV)]	Anion	AE[b] (eV)	Cross-section[c] (cm^2)	Energy[d] (eV)	Quantum yield[e]
SF_6 [15.1]	F^-	12.7	7.1×10^{-21}	14.2	2.4×10^{-4}
	F_2^-	16.3	1.4×10^{-22}	18.3	1.9×10^{-6}
	SF_5^-	15.1	_[f]	17.5	_[g]
	SF_6^-	15.1	_[f]	17.1	_[g]
CF_4 [15.4]	F^-	13.0	1.4×10^{-21}	14.0	2.8×10^{-5}
	F_2^-	20.1	4.0×10^{-23}	21.6	5.6×10^{-7}
SF_5CF_3 [12.9]	F^-	11.05	3.4×10^{-20}	16.9	3.4×10^{-4}
	F_2^-	16.1	1.2×10^{-21}	17.9	1.1×10^{-5}
	SF^-	24.0	2.8×10^{-22}	28.8	2.4×10^{-6}
	SF_2^-	20.2	3.9×10^{-22}	24.2	2.5×10^{-6}
	SF_3^-	15.4	1.0×10^{-20}	17.6	1.0×10^{-4}
	SF_4^-	13.0	1.3×10^{-20}	14.1	1.7×10^{-4}
	SF_5^-	12.9	_[f]	17.0	_[g]