Supplementary Information

1. Tables SI1-SI3

Table SI1 Relative intensities of iodine atoms obtained in this work compared with the work of references 7 and 72.

$I^+ \leftarrow I(^2P_{3/2})$ bands Ionic State	Berkowitz and Goodman (72) [a]	Ref. 7 [b]	This work, at hν = 21.22 eV
$^3P_2$	1.00 (1.00)	1.00 (1.00)	1.00 ± 0.03
$^3P_1$	0.34 (0.31)	0.39 ± 0.05 (0.31)	0.47 ± 0.03
$^3P_0$	0.17 (0.15)	0.18 ± 0.03 (0.15)	0.25 ± 0.02
$^1D_2$	0.79 (0.57)	0.80 ± 0.04 (0.57)	0.58 ± 0.03
$^1S_0$	0.06 (0.058)	0.04 ± 0.01 (0.05)	0.047 ± 0.005

[a] In reference 72, I atoms were generated by heating solid silver iodide and relative intensities were obtained from a HeIα PE spectrum. The values shown in brackets are relative intensities computed with an intermediate coupling model.

[b] In reference 7, I atoms were generated from the F + HI reaction and relative intensities obtained from a HeIα PE spectrum. The values shown in brackets are relative intensities computed with an intermediate coupling model.

Table SI2 Comparison between the measured positions of the vibrational components of the first two IF PE bands as obtained in PE and TPE spectra.

v^+	$IF^+(X^2\Pi_{3/2})$ PES	$IF^+(X^2\Pi_{3/2})$ TPES	$IF^+(^2\Pi_{1/2})$ PES	$IF^+(^2\Pi_{1/2})$ TPES
0	10.539 ± 0.001	10.539 ± 0.001	11.244 ± 0.001	11.245 ± 0.001
1	10.625 ± 0.001	10.625 ± 0.002	11.329 ± 0.001	11.333 ± 0.001
2	10.709 ± 0.001	10.709 ± 0.002	11.413 ± 0.001	11.413 ± 0.001
3	10.792 ± 0.003	10.793 ± 0.002	11.497 ± 0.002	11.496 ± 0.002

Table SI3

Energy of resonances converging to the $I^+(^1S_0)$ threshold at 14.109 eV, recorded in CIS spectra for the fourth, $I^+(^1D_2) \leftarrow I(^2P_{3/2})$, band of iodine atoms at $\theta = 54°44'$. Also shown, are the effective and principal quantum numbers, n^* and n, the fitting parameters, q, Γ, ρ^2 and the Γn^{*3} for each Rydberg state.

(i) ns [0] ½ series

E_n/eV	n*	n	q	Γ/meV	Γn^{*3}
13.261 ± 0.001	4.00 ± 0.01	8	-1.19 ± 0.18	10.2 ± 0.8	0.66 ± 0.10
13.575 ± 0.001	5.05 ± 0.01	9	-0.92 ± 0.24	6.8 ± 1.4	0.88 ± 0.18
13.744 ± 0.001	6.10 ± 0.03	10	-0.77 ± 0.23	5.4 ± 1.3	1.24 ± 0.29

13.839 ± 0.001	7.10 ± 0.04	11	-2.99 ± 1.62	7.6 ± 2.4	2.71 ± 0.87
13.905 ± 0.001	8.17 ± 0.07	12	-0.68 ± 0.22	5.3 ± 1.4	2.89 ± 0.79

(i) nd $[2]_{5/2,3/2}$ series

E_n/eV	n*	n	q	Γ/meV	$Γn^{*3}$
13.060 ± 0.001	3.60 ± 0.01	6	-1.93 ± 0.38	24.9 ± 2.8	1.16 ± 0.14
13.472 ± 0.001	4.62 ± 0.01	7	-1.42 ± 0.24	8.9 ± 1.6	0.88 ± 0.16
13.685 ± 0.001	5.66 ± 0.02	8	-1.43 ± 0.24	8.9 ± 1.6	1.61 ± 0.28
13.806 ± 0.001	6.70 ± 0.04	9	-1.56 ± 0.34	6.8 ± 1.4	2.05 ± 0.46
13.880 ± 0.001	7.71 ± 0.06	10	-1.70 ± 0.71	8.4 ± 2.3	3.85 ± 1.08
13.930 ± 0.001	8.72 ± 0.08	11	-4.09 ± 1.97	10.5 ± 2.9	6.97 ± 1.96

2. Figures SI1-SI9

Figure SI1

A schematic potential energy diagram for non-resonant ionization.

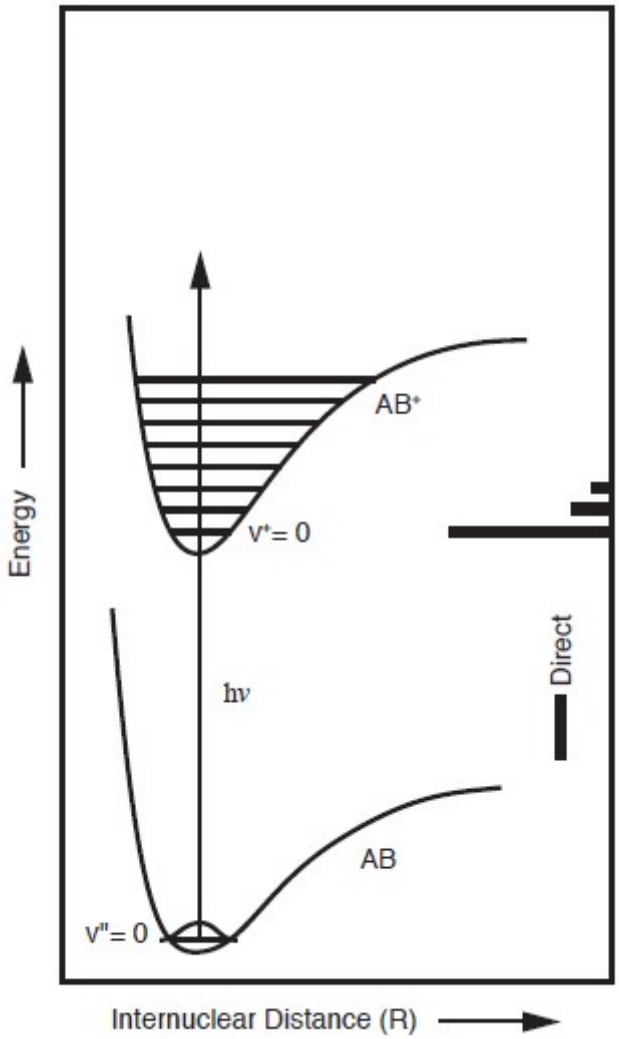


Figure SI2

Phase-sensitive detection HeI photoelectron spectrum recorded for discharged oxygen. The discharge is pulsed and a phase sensitive detection method is used. Features above the horizontal baseline are in-phase with the discharge and features below are out-of-phase with the discharge. Hence the features above the baseline correspond to discharge products. (Reproduced from ref.(29) with permission of AIP Publishing).

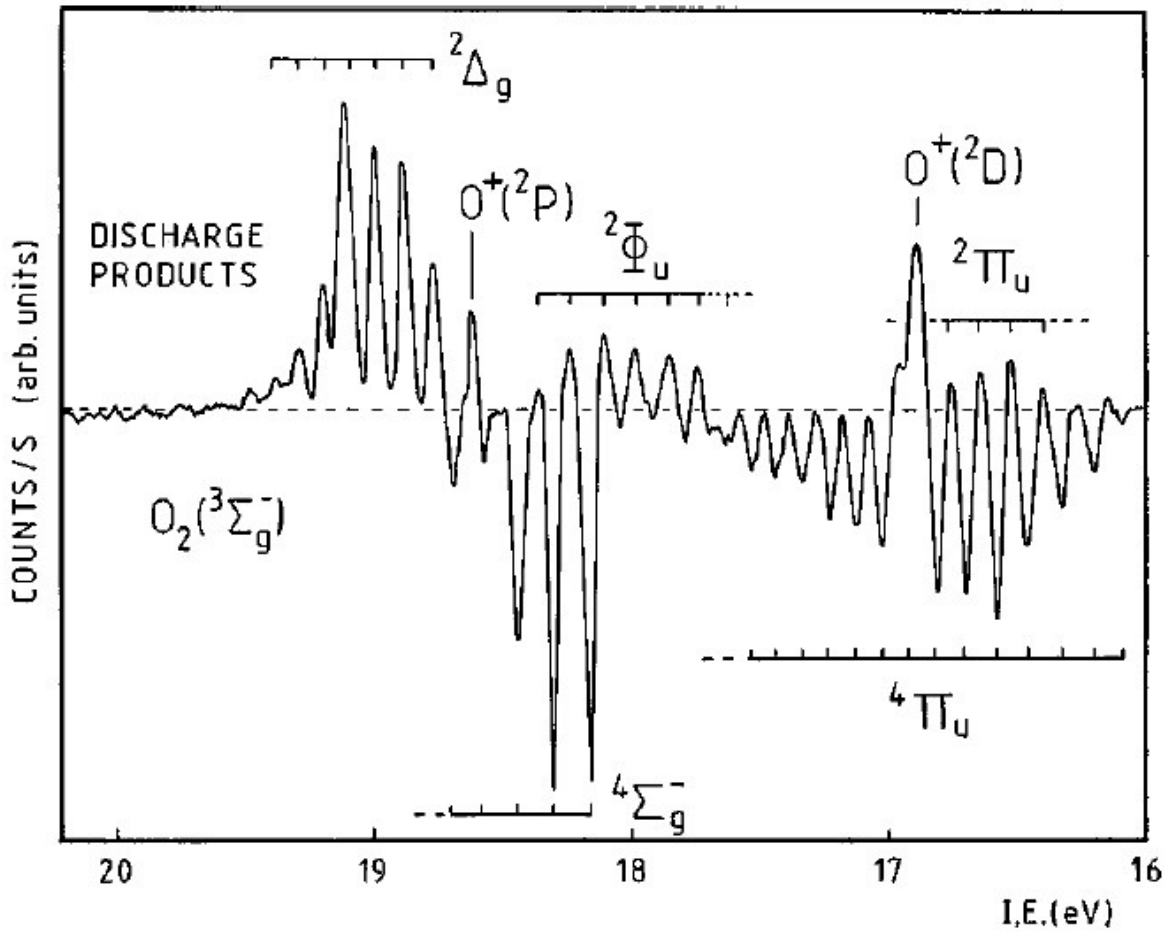


Figure SI3

Photoelectron spectra recorded at hν =14.11 eV (i.e. at the position of band A in Fig. 5) for discharged and undischarged oxygen, in the ionization energy region 11.0–14.1 eV. The black circles in the lower part of this figure represent relative vibrational intensities obtained by summing the direct and autoionization computed envelopes. (see the text; reproduced from ref.(29) with permission of AIP Publishing).

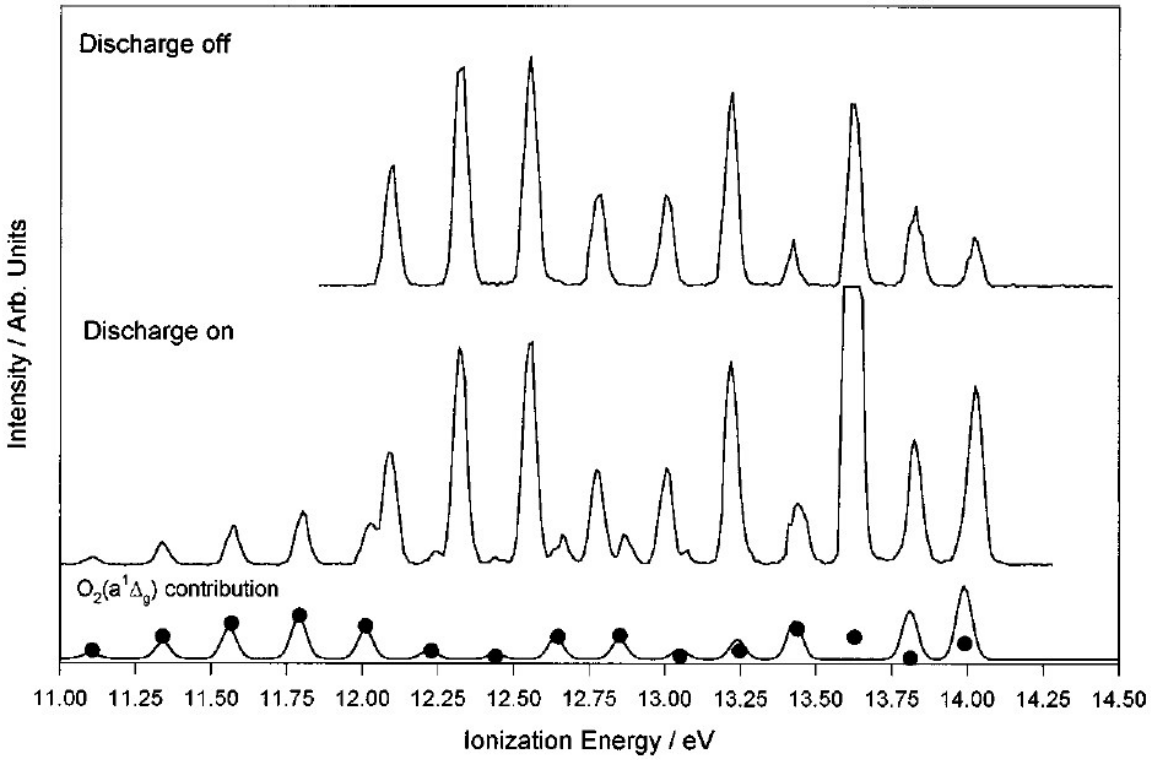


Figure SI4

Asymmetry parameter plots for the O_2^+ ($X^2\Pi_g$, $v^+ = 0, 1, 2, 3$) ← O_2 ($a^1\Delta_g$, $v'' = 0$) O_2 ionization processes recorded in the photon energy range 13.8-15.2 eV.
The symbols indicate the β parameters obtained from PE spectra for:-

○ $v^+=0$; ■ $v^+=1$; □ $v^+=2$; • $v^+=3$. The vertical bar represents a typical error.

(Reproduced from ref.(31) with permission of AIP Publishing).

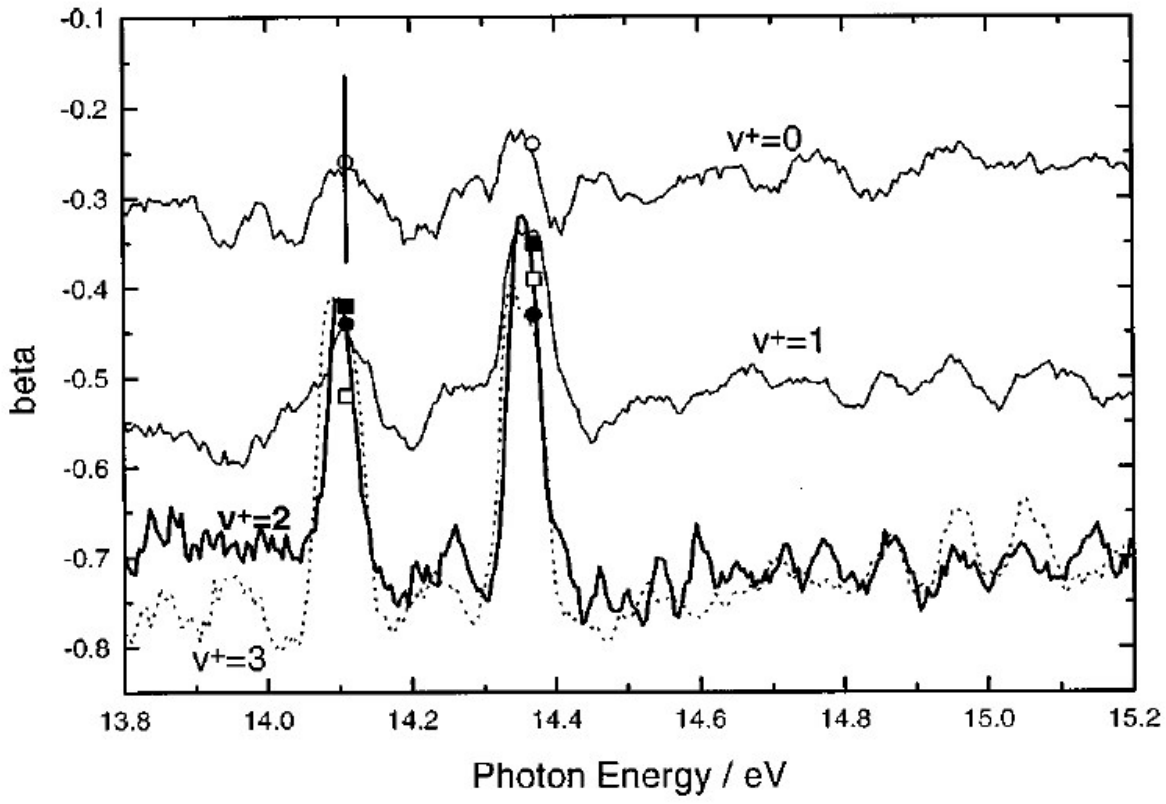


Figure SI5

UV photoelectron spectrum recorded at a photon energy of 21.0 eV for a microwave discharge of a flowing mixture of hexafluoropropene, C_3F_6, in argon. Spectra obtained under these conditions show that all the C_3F_6 is destroyed and converted into CF_2 and C_2F_4 (Reproduced from ref.(39) with permission from Wiley-VCH Verlag GmbH & Co. KGaA).

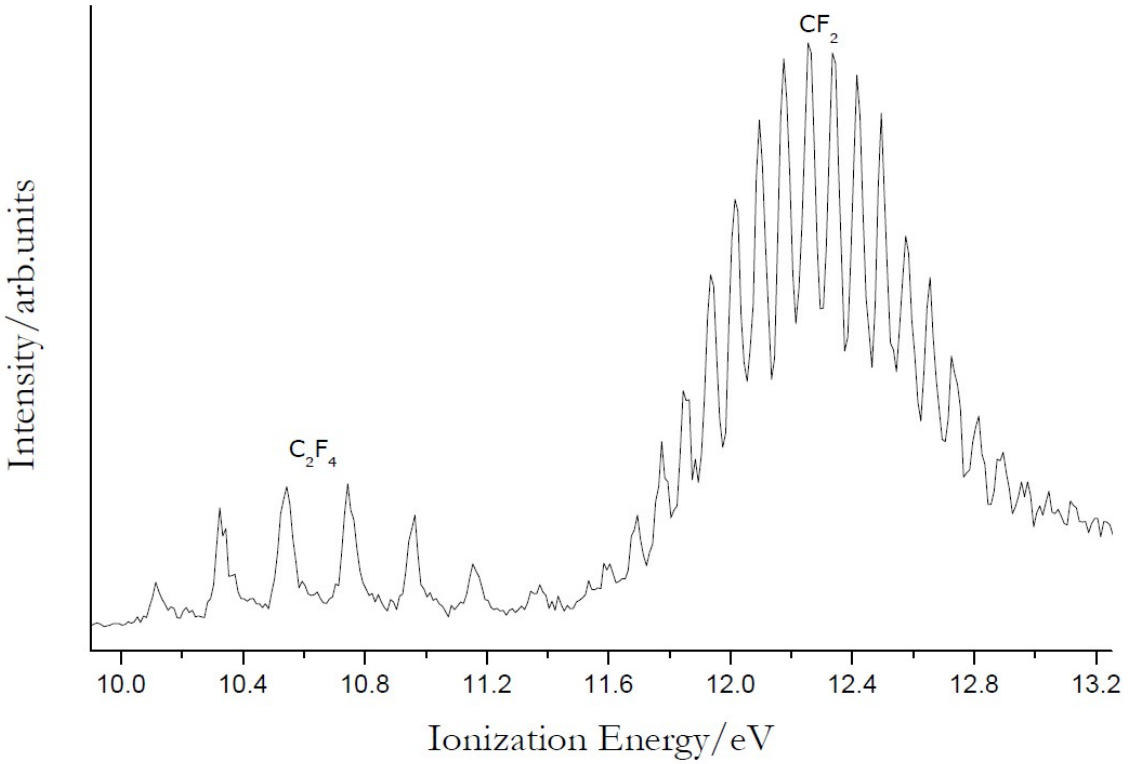


Figure SI6

TPE spectrum recorded for a flowing CF_2 and Ar mixture in the 11.3-13.2 eV photon energy region (upper). Simulated CF_2^+ (X^2A_1) ← CF_2(X^1A_1) photoelectron spectrum for 0 K Boltzmann vibrational temperature (lower). (Reproduced from ref.(39) with permission from Wiley-VCH Verlag GmbH & Co. KGaA).

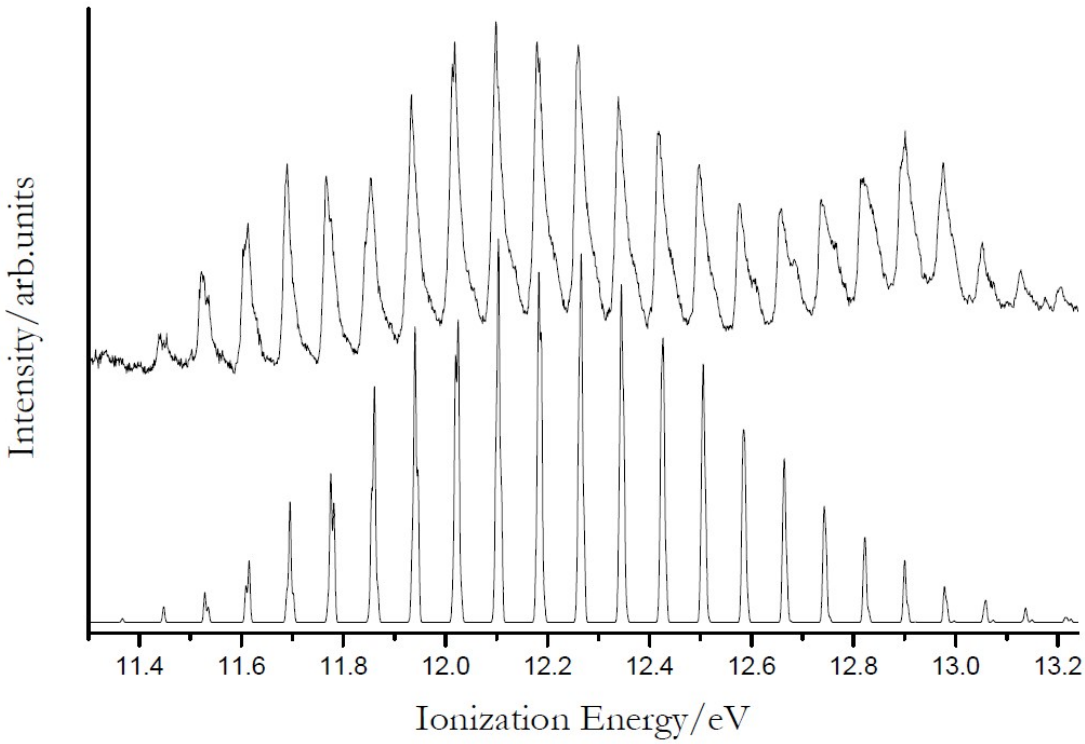


Figure SI7

TPE spectrum recorded for a flowing CF_2 and Ar mixture in the 11.3-13.2 eV photon energy region (upper). Simulated CF_2^+ (X^2A_1) $\leftarrow$ $CF_2(X^1A_1)$ photoelectron spectrum for 600 K Boltzmann vibrational temperature (lower). (Reproduced from ref.(39) with permission from Wiley-VCH Verlag GmbH & Co. KGaA).

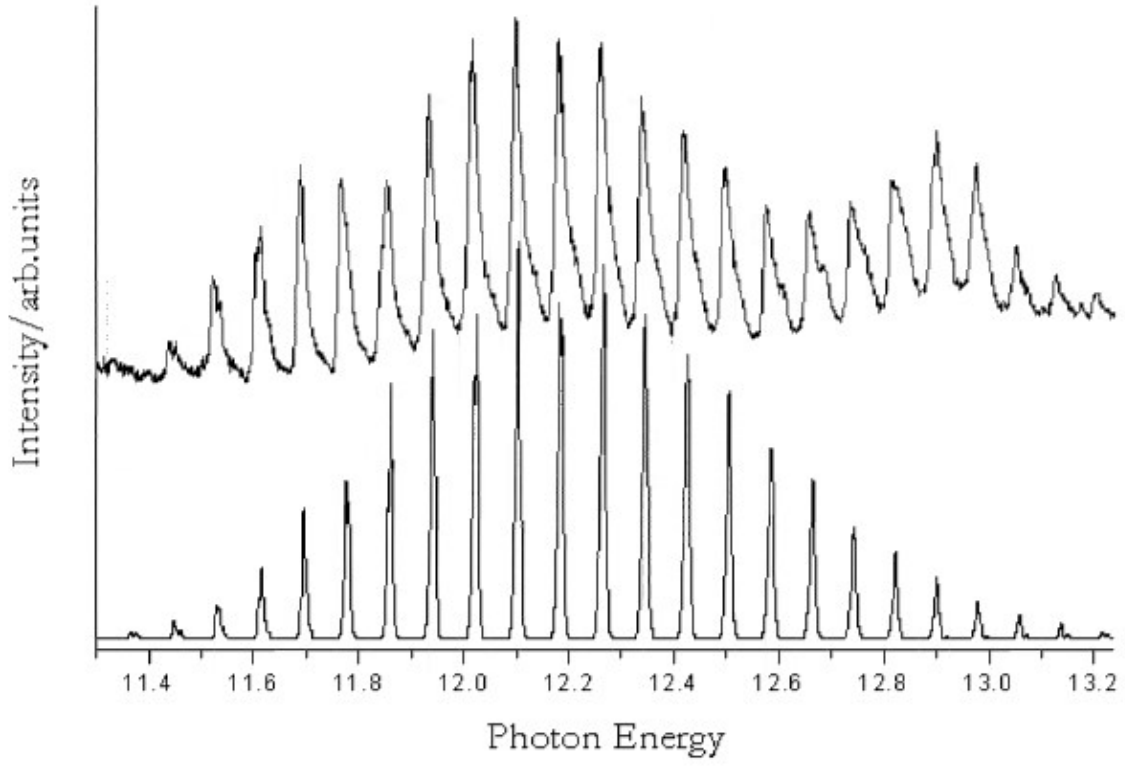


Figure SI8

Relative intensities obtained for the IF components in the $IF^{+}(X^{2}\Pi_{3/2}) \leftarrow IF(X^{1}\Sigma)$ PE band.

(Reproduced from ref.(23) with permission of ACS Publishing).

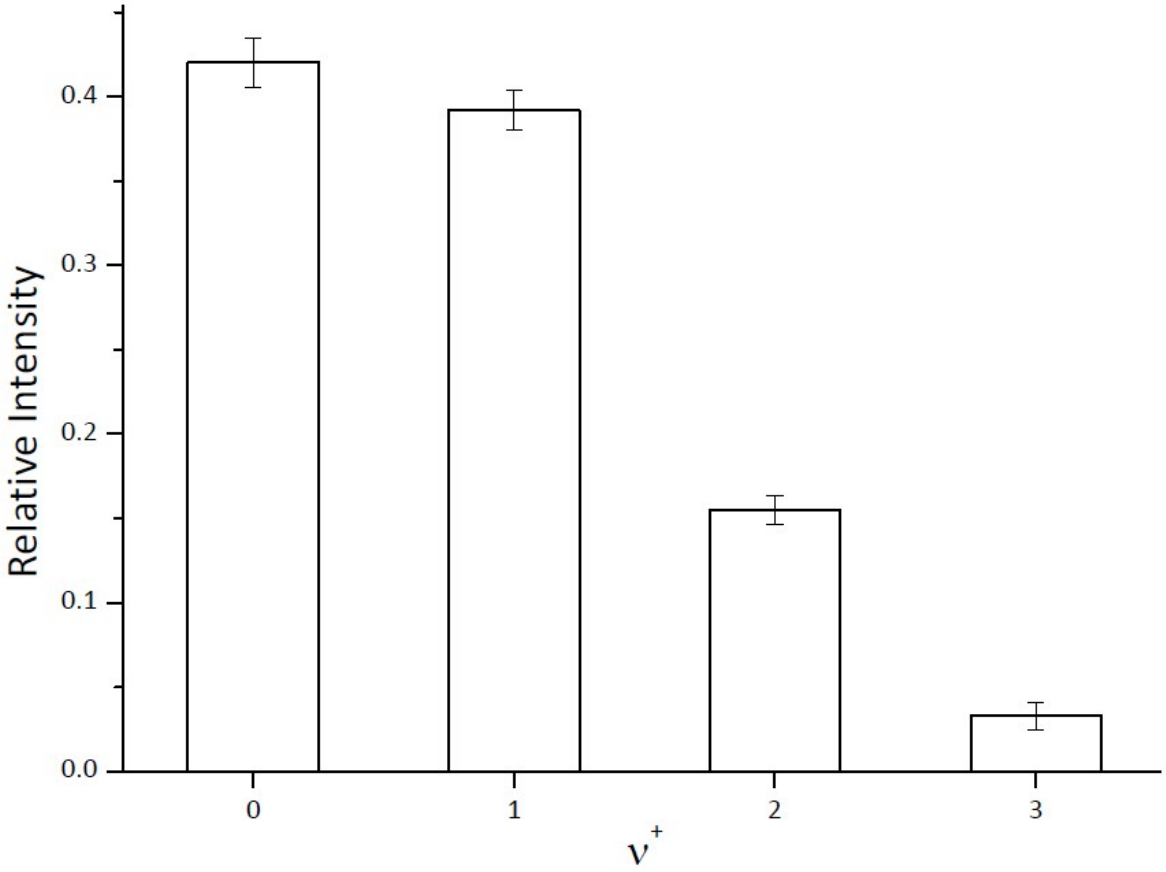


Figure SI9

Relative intensities obtained for the IF components in the $IF^{+}(^{2}\Pi_{1/2}) \leftarrow IF(X^{1}\Sigma)$ PE band.

(Reproduced from ref.(23) with permission of ACS Publishing).

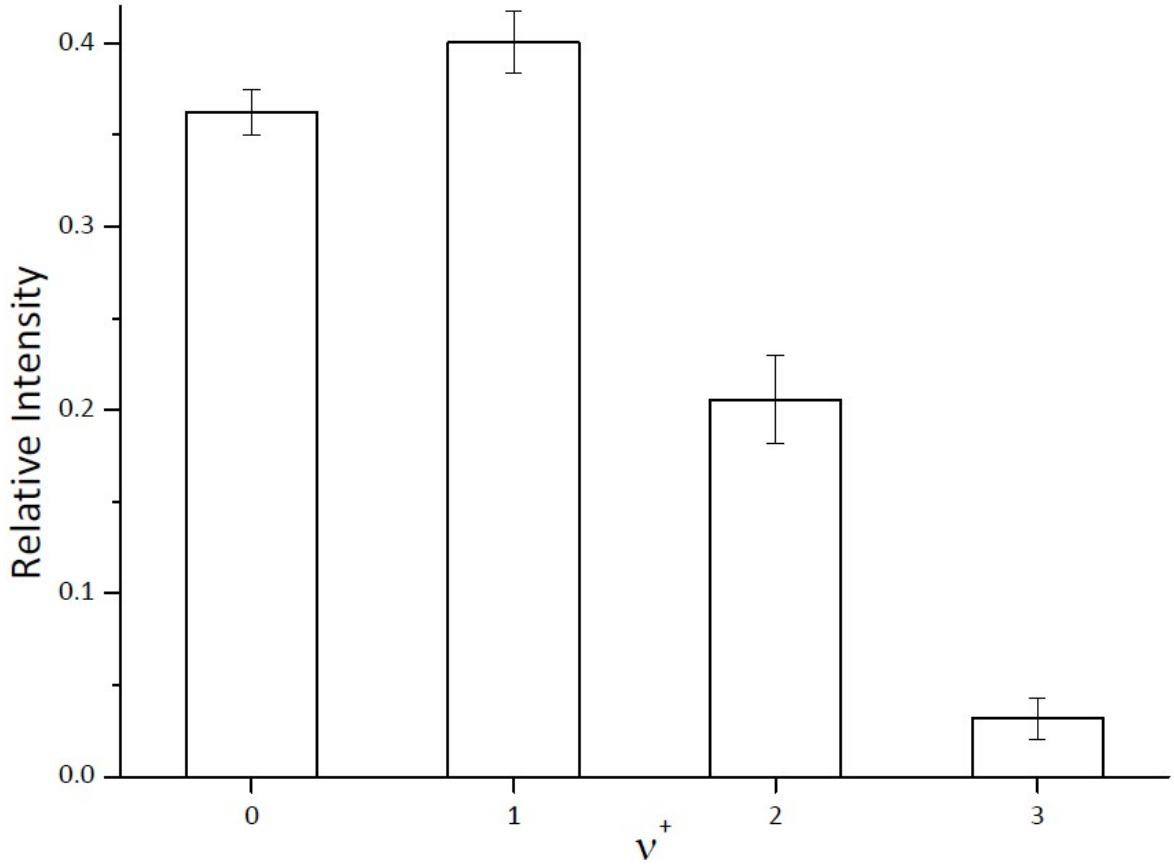
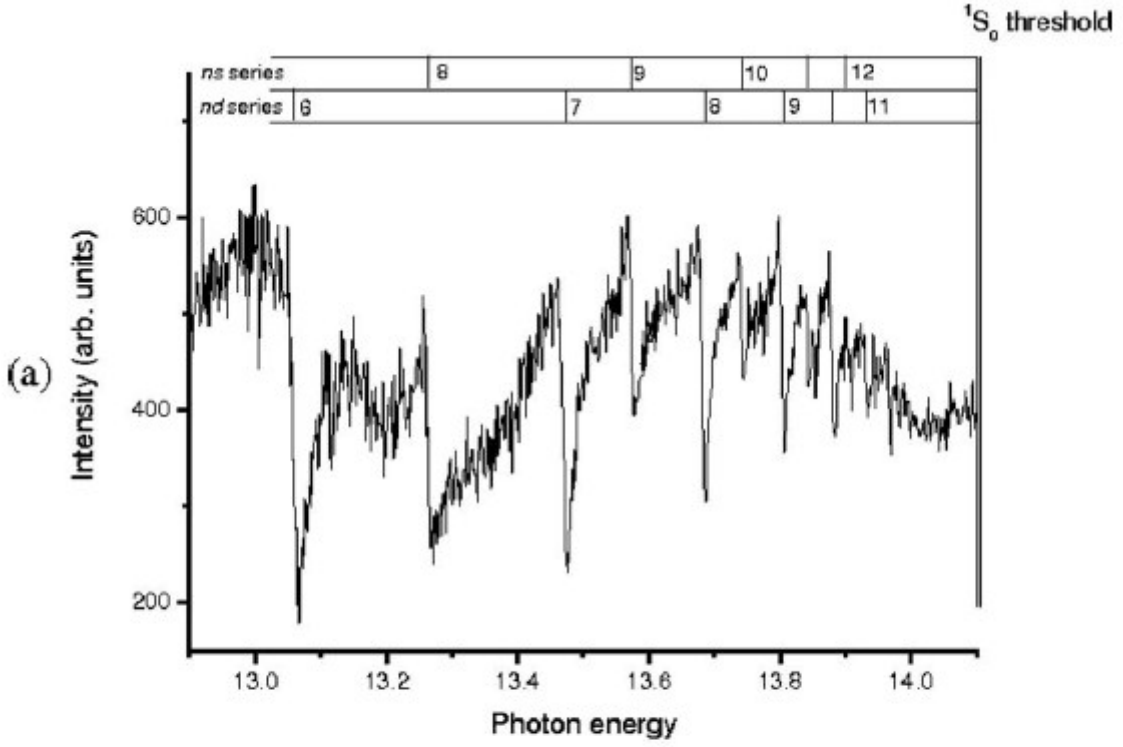
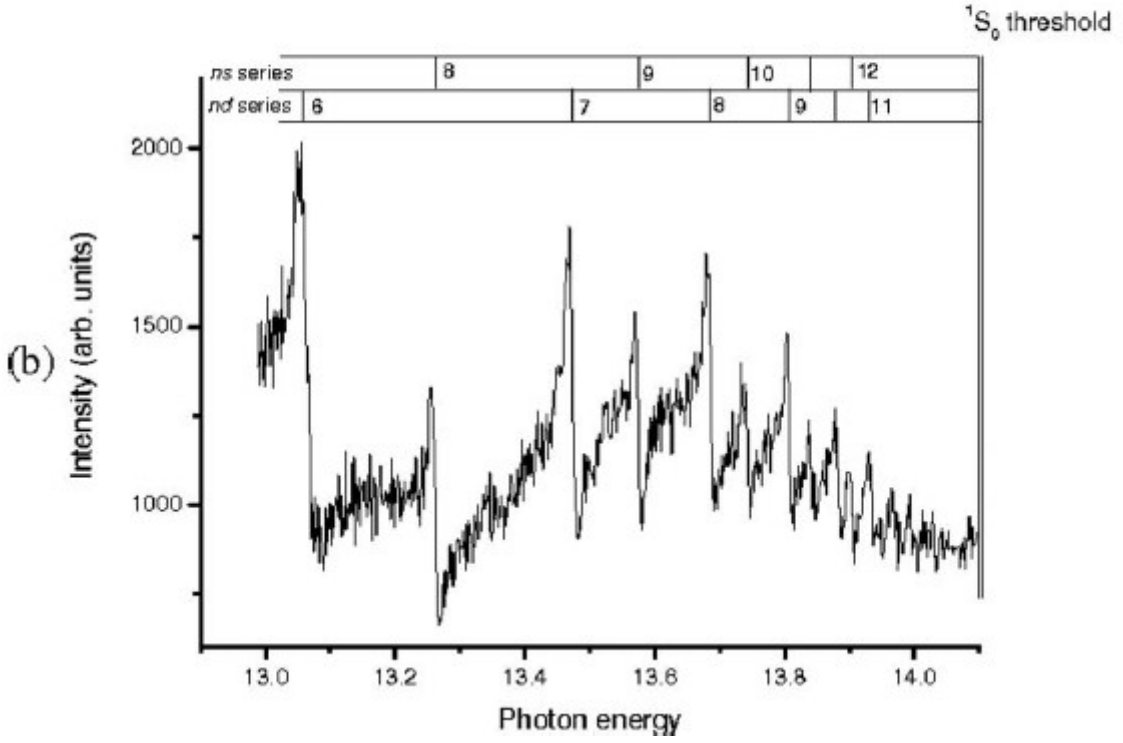


Figure SI10

CIS spectra of the fourth PE band of iodine atoms ($I^+(^1D_2) \leftarrow I(^2P_{3/2})$) recorded at an angles of (a) $\theta = 0°$ and (b) $\theta = 54°44'$ in the photon energy region 12.9 to 14.1 eV, showing autoionizing resonances converging to the $I^+(^1S_0)$ threshold at 14.109 eV. (Reproduced from ref.(40) with permission of AIP Publishing).


(a)
$^1S_0$ threshold
ns series
nd series
8
9
10
12
6
7
8
9
11
Intensity (arb. units)
600
400
200
13.0
13.2
13.4
13.6
13.8
14.0
Photon energy


(b)
$^1S_0$ threshold
ns series
nd series
8
9
10
12
6
7
8
9
11
Intensity (arb. units)
2000
1500
1000
13.0
13.2
13.4
13.6
13.8
14.0
Photon energy