Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary material for : *Electronic structure investigation of the evanescent* AtO^+ *ion.*†

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Table S1 Composition of the ground and excited-state wavefunctions from IHFSCCSD calculations for **IO** and **AtO**, at the respective equilibrium geometries.

	IO			AtO		
Ω	E (eV)	configuration(s)	weigth(s)	E (eV)	configuration(s)	weigth(s)
3/2	0.00	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.91	0.00	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.88
		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.09		$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.12
1/2	0.28	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.90	0.72	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.75
		$\pi^{(1)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.07		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.19
		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.02		$\pi^{(1)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.06
3/2	3.22	$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.91	2.78	$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.90
		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.09		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.10
1/2	3.47	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.51	3.07	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.75
		$\pi^{(1)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.41		$\pi^{(1)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.22
		$\pi^{(2)}_{1/2}\,\pi^{21)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.07		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.03
1/2	4.22	$\pi^{(1)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.53	5.12	$\pi^{(1)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.92
		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.46		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.07
		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.01		$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.01

Table S2 Composition of the ground and excited-state wavefunctions from IHFSCCSD calculations for IO^+ and AtO^+, at the respective equilibrium geometries.

	IO^+			AtO^+		
Ω	E (eV)	configuration(s)	weigth(s)	E (eV)	configuration(s)	weigth(s)
0^+	0.00	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(0)}_{3/2}$	0.75	0.00	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(0)}_{3/2}$	0.83
		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(0)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.19		$\pi^{(2)}_{1/2}\,\bar{\pi}^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.05
		$\pi^{(2)}_{1/2}\,\pi^{(0)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.02		$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\bar{\pi}^{*(1)}_{3/2}$	0.05
		$\pi^{(2)}_{1/2}\,\bar{\pi}^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.02		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(0)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.03
		$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\bar{\pi}^{*(1)}_{3/2}$	0.02		$\pi^{(2)}_{1/2}\,\pi^{(0)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.02
1	0.13	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.95	0.63	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.83
		$\pi^{(1)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(0)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.02		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.12
		$\pi^{(1)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.02		$\pi^{(1)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.04
		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.01		$\pi^{(1)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.01
2	0.72	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.91	1.02	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.77
		$\pi^{(1)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.05		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.12
		$\pi^{(1)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.03		$\pi^{(1)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.06
		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.01		$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.02
		$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(1)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.01		$\pi^{(1)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.02
0^-	2.39	$\pi^{(2)}_{1/2}\,\bar{\pi}^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.49	1.94	$\pi^{(2)}_{1/2}\,\bar{\pi}^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	0.50
		$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\bar{\pi}^{*(1)}_{3/2}$	0.49		$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\bar{\pi}^{*(1)}_{3/2}$	0.50
3	2.45	$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	1.00	1.98	$\pi^{(2)}_{1/2}\,\pi^{(1)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(1)}_{3/2}$	1.00
0^+	1.38	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(0)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.73	2.75	$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(0)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.81
		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(0)}_{3/2}$	0.15		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\bar{\sigma}^{(1)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.04
		$\pi^{(0)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.05		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\bar{\pi}^{*(1)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.04
		$\pi^{(2)}_{1/2}\,\pi^{(0)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.03		$\pi^{(0)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.04
		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(0)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.01		$\pi^{(2)}_{1/2}\,\pi^{(0)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.02
		$\bar{\pi}^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(1)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.01		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(2)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(0)}_{3/2}$	0.01
		$\pi^{(1)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(1)}_{1/2}\,\bar{\pi}^{*(1)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.01		$\pi^{(2)}_{1/2}\,\pi^{(2)}_{3/2}\,\sigma^{(0)}_{1/2}\,\pi^{*(2)}_{1/2}\,\pi^{*(2)}_{3/2}$	0.01

Table S3 Spin-free excitation energies (in eV), calculated at $R = 1.806$ Å for IO^+ and $R = 1.903$ Å for AtO^+, respectively, for SFDC-IHFSCCSD, MRCI+DC and NEVPT2.

	SF states	SFDC-IHFSCCSD	MRCI+DC	QD-NEVPT2
IO^+	$^3\Sigma^-$	0.00	0.00	0.00
	$^1\Delta$	0.61	0.61	0.61
	$^1\Sigma^+$	1.08	1.06	1.13
	$^1\Sigma^-$	2.53	2.66	2.66
	$^3\Delta$	2.71	2.84	2.81
	$^3\Sigma^+$	2.80	2.94	2.90
	$^3\Pi$	–	4.05	4.06
	$^3\Pi$	4.44	4.35	4.48
	$^3\Sigma^-$	5.10	4.49	4.48
	$^1\Pi$	–	4.72	4.77
	$^1\Pi$	5.22	5.16	5.22
AtO^+	$^3\Sigma^-$	0.00	0.00	0.00
	$^1\Delta$	0.55	0.56	0.56
	$^1\Sigma^+$	0.99	0.98	1.03
	$^1\Sigma^-$	2.15	2.28	2.28
	$^3\Delta$	2.32	2.45	2.43
	$^3\Sigma^+$	2.41	2.55	2.51
	$^3\Pi$	–	3.69	3.70
	$^3\Sigma^-$	4.58	4.02	4.02
	$^3\Pi$	4.12	4.03	4.14
	$^1\Pi$	–	4.33	4.39
	$^1\Pi$	4.76	4.76	4.81

Table S4 Spectroscopic constants and electronic excitation energies (in eV) for SOCI/MRCI+DC.

	Ω	R_e (Å)	ω_e (cm^{-1})	T_e	T_v
IO^+	X 0^+	1.823	787	0.00	0.00
	a 1	1.825	776	0.10	0.10
	a 2	1.839	737	0.66	0.69
	a 0^+	1.857	662	1.24	1.26
	b 0^-	2.043	503	1.87	2.44
	a 3	2.036	518	1.96	2.51
AtO^+	X 0^+	1.923	810	0.00	0.00
	a 1	1.939	727	0.53	0.53
	a 2	1.959	671	0.95	0.97
	a 0^+	2.115	497	1.75	2.12
	a 3	2.126	500	1.93	2.37
	b 0^-	1.987	583	2.24	2.29

Table S5 TDDFT electronic excitation energies (in eV) for different DFAs for the isolated IO^+ (at R(IO^+) = 1.806 Å) and AtO^+ (at R(AtO^+) = 1.903 Å).

	Ω	SAOP	M06-L	M06	M06-2X
IO^+	X 0^+	0.00	0.00	0.00	0.00
	a 1	-0.60	-0.61	-0.72	-0.86
	a 2	0.52	0.51	-0.78	-1.03
	a 0^+	[3.74][1]	[3.93][1]	[3.60][1]	[3.65][1]
	b 0^-	2.61	2.81	1.09	-2.21
	a 3	2.63	2.82	1.03	-2.32
AtO^+	X 0^+	0.00	0.00	0.00	0.00
	a 1	-0.55	-0.48	-0.76	-1.04
	a 2	1.07	1.05	0.46	-0.69
	a 0^+	[3.74][1]	[3.87][1]	[3.48][1]	[3.39][1]
	a 3	2.33	2.46	0.64	-2.36
	b 0^-	2.32	2.45	0.64	-2.32

1. States with singly excited character, whereas WFT methods indicate doubly excited character.

Table S6 Coordinates (in Å) for the AtO^+-water complex, obtained with the SO-ZORA Hamiltonian, TZ2P basis and M06-2X exchange-correlation functional.

Atom	x	y	z
O	0.000000	0.000000	1.896392
At	0.000000	0.000000	-0.003392
H	0.000000	0.767071	-3.246187
O	0.000000	0.000000	-2.658634
H	0.000000	-0.767071	-3.246187