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

Electronic Supplementary Information (ESI)

Energetics and Ionization Dynamics of Two Diarylketone Molecules: Benzophenone and Fluorenone

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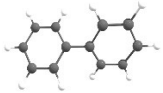
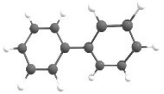
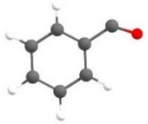
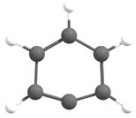
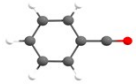
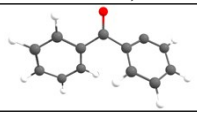
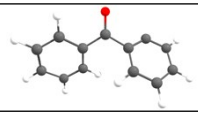
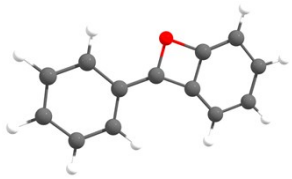
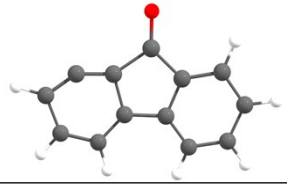
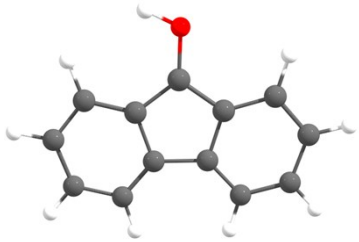
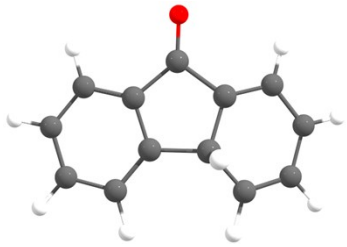
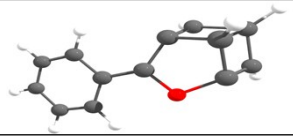
Table S1: Total energies and ionization energies of Benzophenone and of Fluorenone as computed using DFT and explicitly correlated coupled cluster approaches.

	Benzophenone	Benzophenone$^+$	Fluorenone	Fluorenone$^+$
PBE0/aug-cc-pVDZ / Hartree	-576.02394855	-575.71167206	-574.83845670	-574.54018049
ZPVE/PBE0/aug-cc-pVDZ / eV	5.221	5.209	4.635	4.612
DFT/PBE0$_{(opt)}$/AVDZ Adiabatic ionisation energy / eV	8.461		8.095	
Exp. (This work)	8.923		**8.356**	
(R)CCSD(T)-F12/aug-cc-pVDZ (Hartree)	-575.69002899	-575.36234063	-574.49724310	-574.19091868
(R)CCSD(T)-F12 Adiabatic ionization energy / eV	8.905		8.313	
CCSD(T)-F12 of cation from geometry of neutral	-		-574.18509681	
CCSD(T)-F12 du neutral from geometry of neutral	-		-574.49724310	
(R)CCSD(T)-F12 Vertical ionization energy CCSD(T)-F12	-		8.493	

Table S2: Total energies, zero point vibrational energies (ZPVE) and appearance energies (AE) of the main fragmentation channels of Benzophenone^{+} cation as computed using DFT and explicitly correlated coupled cluster approaches.

	CO	**Biphenyl+**	**CO^{+}**	**Biphenyl** neutral	**Aldehyde***	**Phenyl***	**Aldehyde+**	**Phenyl***
								
PBE0/aug-cc-pVDZ / Hartree	-113.20070934	-462.51100660	-112.68608228	- 462.80118647	-344.56293517	-231.00077186	-344.32571932	-231.30717290
ZPVE/PBE0/aug-cc-pVDZ / eV	0.137	4.93	0.654	4.946	2.659	2.312	2.708	2.381
DFT/PBE0(opt) /AVDZ AE with ZPVE correction from DFT / eV	8.35		14.99		12.28		10.51	
(R)CCSD(T)-F12/aug-cc-pVDZ (Hartree)	-113.17831819	-462.20340472	-112.6647530	-462.50385125	-344.37327953	-230.84946345	-344.13953221	-231.15388442
(R)CCSD(T)-F12(sp)/PBE0(opt) /AVDZ AE with ZPVE correction from CCSD(T)-F12 / eV	8.24		14.56		12.46		10.67	
	Benzo-h)+		**H**		**Benzo –h**		**H^{+}**	
								
PBE0/aug-cc-pVDZ / Hartree	-575.02316308		-0.49922372		-575.33742922		0	
ZPVE/PBE0/aug-cc-pVDZ / eV	4.83		0.0		4.863		0.0	
DFT/PBE0(opt) /AVDZ AE with ZPVE correction from DFT /eV	13.29				18.33			
(R)CCSD(T)-F12/aug-cc-pVDZ (Hartree)	-574.66628583		-0.49956907		-574.99812707		0	

(R)CCSD(T)-F12(sp)/PBE0(opt) /AVDZ AE with ZPE correction from CCSD(T)-F12 / eV	13.88		18.47	
	c-Benzo-h)+	**H**	**Fluo –h)+**	**H**
				
PBE0/aug-cc-pVDZ / Hartree	-575.10195251	-0.49922372	-573.85576369	-0.49922372
ZPVE/PBE0/aug-cc-pVDZ / eV	4.92	0.0	4.23	0.0
DFT/PBE0(opt) /AVDZ AE with ZPVE correction from DFT /eV	11.21		12.76	
(R)CCSD(T)-F12/aug-cc-pVDZ (Hartree)	-574.75552405	-0.49956907	-573.50996504	-0.49956907
(R)CCSD(T)-F12(sp)/PBE0(opt) /AVDZ AE with ZPVE correction from CCSD(T)-F12 / eV	11.53		12.87	
	fluoOH)+ **from benzo neutre**	H	Fluoc+)+ **from benzo neutre**	H
				
PBE0/aug-cc-pVDZ / Hartree	-575.18490141	-0.49922372	-575.12207645	-0.49922372
ZPVE/PBE0/aug-cc-pVDZ / eV	4.98	0.0	4.89	0.0

DFT/PBE0(opt) /AVDZ AE with ZPVE correction from DFT /eV	9.01		10.63	
(R)CCSD(T)-F12/aug-cc-pVDZ (Hartree)	-574.83804887	-0.49956907	-574.77676113	-0.49956907
(R)CCSD(T)-F12(sp)/PBE0(opt) /AVDZ AE with ZPVE correction from CCSD(T)-F12 / eV	9.35		10.93	
	Cyl5bzo-h]+	H		
				
PBE0/aug-cc-pVDZ / Hartree	-574.95905815	-0.49922372		
ZPVE/PBE0/aug-cc-pVDZ / eV	4.885	0.0		
DFT/PBE0(opt) /AVDZ AE with ZPVE correction from DFT /eV	15.05			

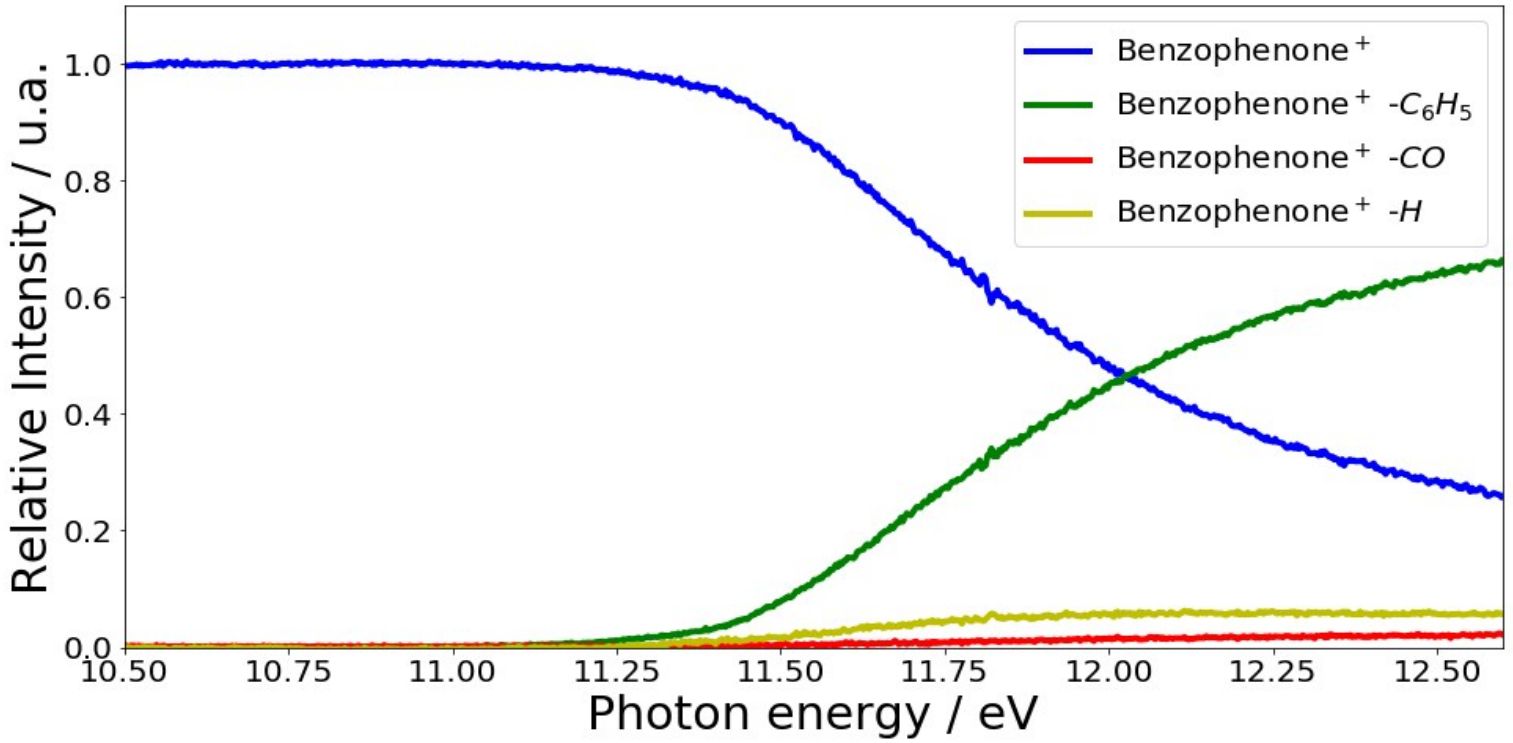


Figure A: Relative Ion Yield for the formation of the fragment ions of Benzophenone (full scale, zoom is the Figure 6-bottom of the paper).