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Physical Chemistry Chemical Physics

Electronic Supplementary Information

Implementation of the interacting quantum atoms energy decomposition with the CASPT2 method

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Table S 1: Structural and spectroscopic parameters for the noble gas complexes. R_e and E_{bind} respectively correspond to the equilibrium geometry and binding energy, whereas E_f refers to the energy difference between the excited and ground states at the equilibrium geometry of the excited one. Values are given in eV and distances in Å.

	Ground state ($1^1\Sigma_g^+$ or $1^2\Sigma^+$)				Excited complex ($1^1\Sigma_u^+$ or $2^2\Sigma^+$)					
	R_e		E_{bind}		R_e		E_{bind}		E_f	
	Calc.	Others	Calc.	Others	Calc.	Others	Calc.	Others	Calc.	Others
He_2	3.102	2.970	0.002	0.001	1.011	1.041	2.536	2.455	15.009	18.260
Ne_2	2.971	3.150	0.007	0.002	1.881	1.760[a]	0.889	0.626[a]	17.485	16.663
Ar_2	3.908	3.758	0.012	0.011	2.501	2.825	0.629	0.621[b]	11.064	11.455
Kr_2	4.177	4.030	0.014	0.016	2.783	2.772[c]	0.614	0.598[d]	9.622	9.886
Xe_2	3.730	4.361	0.610	0.023	3.058	2.850[e]	1.355	0.709[e]	7.431	7.290
HeNe	3.137	3.035[f]	0.002	0.002[f]	1.370	–	0.912	–	16.063	–
					4.165	–	0.047	–	21.764	–
HeF	–	–[g]	–	b –[g]	1.658	1.058[h]	6.163	1.670[h]	13.518	9.820[h]
NeF	3.127	2.960[i]	0.001	0.005[i]	2.000	2.010[j]	5.312	6.380[j]	10.564	10.840[j]
ArF	3.183	3.190[i]	0.077	0.010[i]	2.331	2.400[j]	4.778	5.520[j]	6.460	6.490[j]
KrF	3.328	3.120[k]	0.012	0.017[k]	2.456	2.530[j]	4.455	5.360[j]	5.016	5.270[j]
XeF	2.751	2.360[k]	0.208	0.112[k]	2.486	2.720[j]	4.195	5.120[j]	3.860	4.030[j]

Unless otherwise indicated, the data in columns "Others" were obtained from reference [1]. [a] MCSCF/5s3p [2]. [b] MCSCF/PP-4s4p3d [3]. [c] CIPSI/5s5p3df [4]. [d] Ref. [5]. [e] Estimated using experimental data [6]. [f] CCSD(T)/cc-pV5Z [7]. [g]. Not bonded according to MRCI-SD+Q/d-aug-cc-pVQZ [8]. [h] MRCI-D/aug-cc-pVDZ [9]; the state $2^2\Sigma^+$ does not dissociate at the correct limit. [i] CCSD(T)/AVTZ [10]. [j] CI /D95V [11]. [k] MR-ACPF/STUT-AVTZ [10].

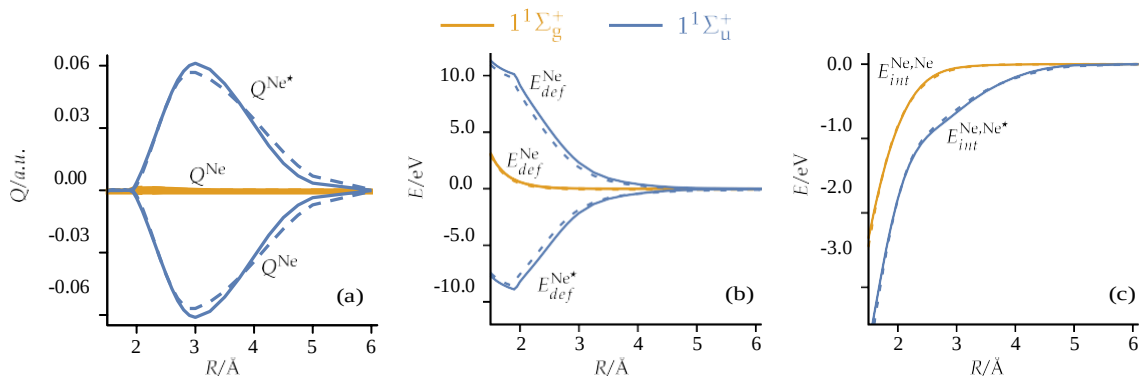

Fig. S1: (a) Atomic charges, (b) deformation and (c) interaction energies as a function of the inter-nuclear distance for the electronic $1^1\Sigma_g^+$ and $1^1\Sigma_u^+$ states of Ne_2. The data of the solid and dashed lines respectively correspond to the aug-cc-pVDZ and aug-cc-PVTZ basis sets. $Ne^\times$ denotes the excited atom at the dissociation limit.

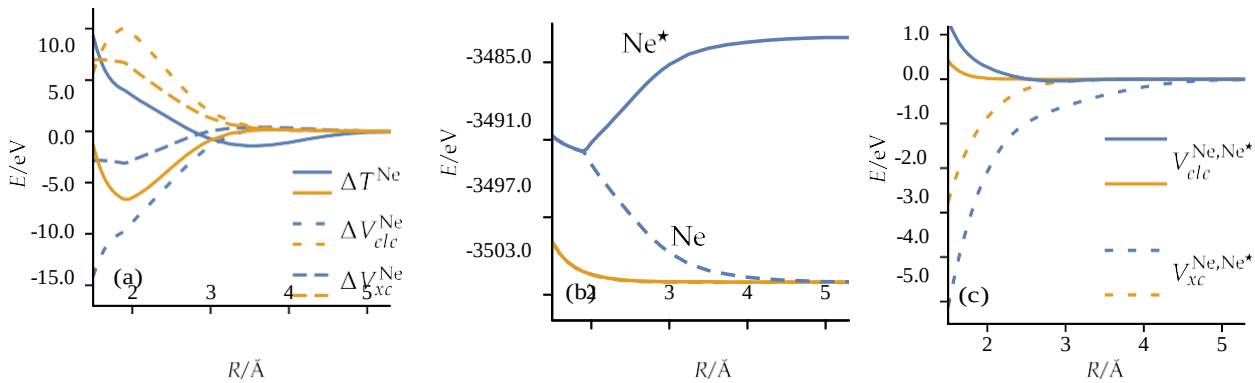

Fig. S2: a) Changes on the atomic components (e.g. $\Delta T^{He} = T^{He}_{R} - T^{He}_{R\to\infty}$) as a function of the internuclear distance for the $1^1\Sigma^+_u$ state of Ne_2; the yellow and blue colors correspond respectively to the Neon atoms that dissociate in a ground or excited state. b) Self-energies of neon atoms for the $1^1\Sigma^+_g$ and $1^1\Sigma^+_u$ states. c) Contributions of the interaction energy. $Ne^{\times}$ denotes the excited atom at the dissociation limit.

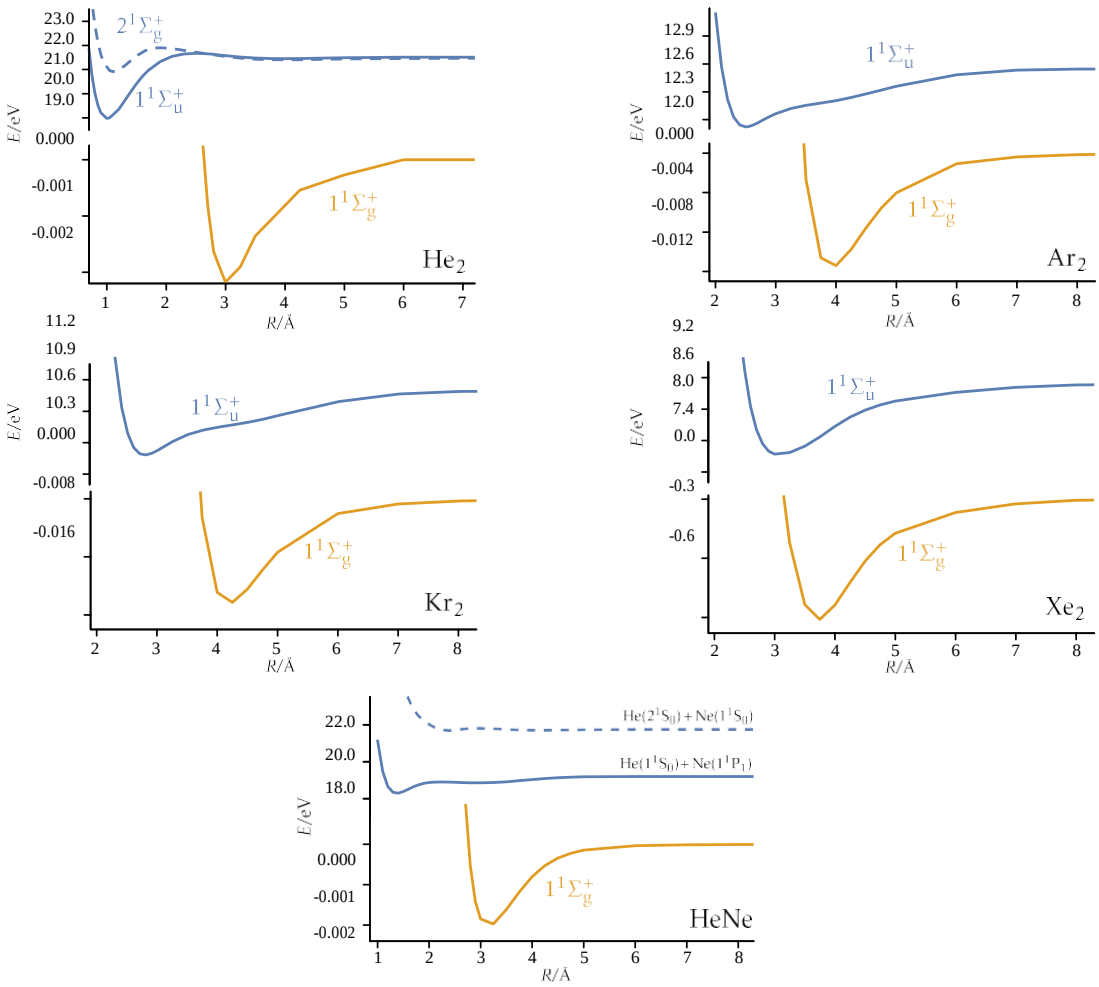

Fig. S3: Potential energy curves for low-energy singlet states of noble gas complexes.

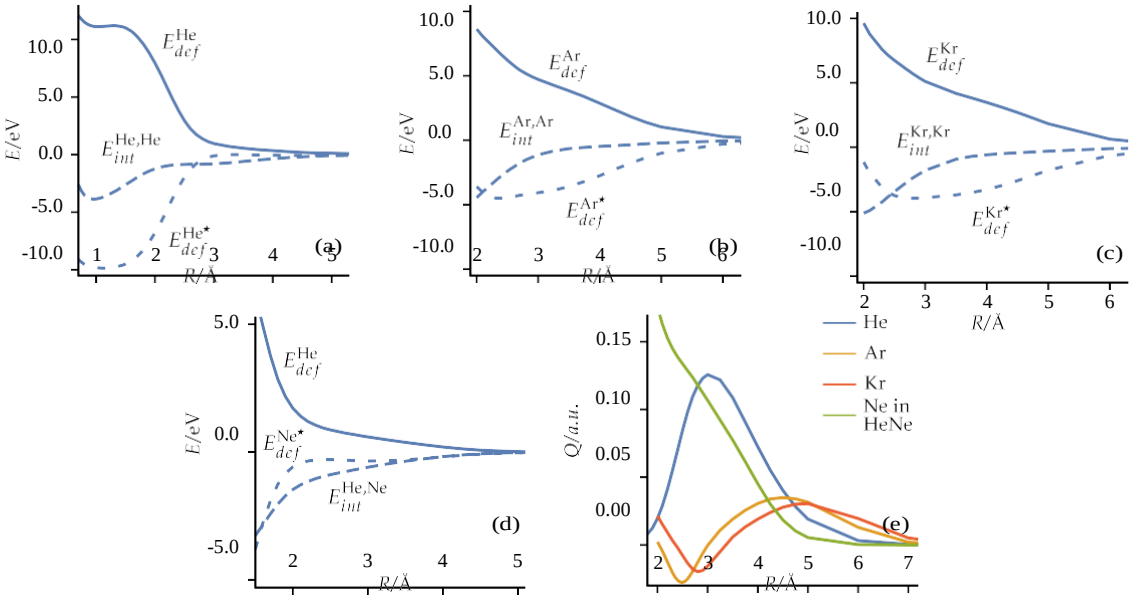

Fig. S4: Deformation and interaction energies as a function of the internuclear distance for the $1^1\Sigma^+_g$ state of He_2 (a), Ar_2 (b), Kr_2 (c) and HeNe (d). e) Atomic charge of the excited atom for the Noble gases complexes.

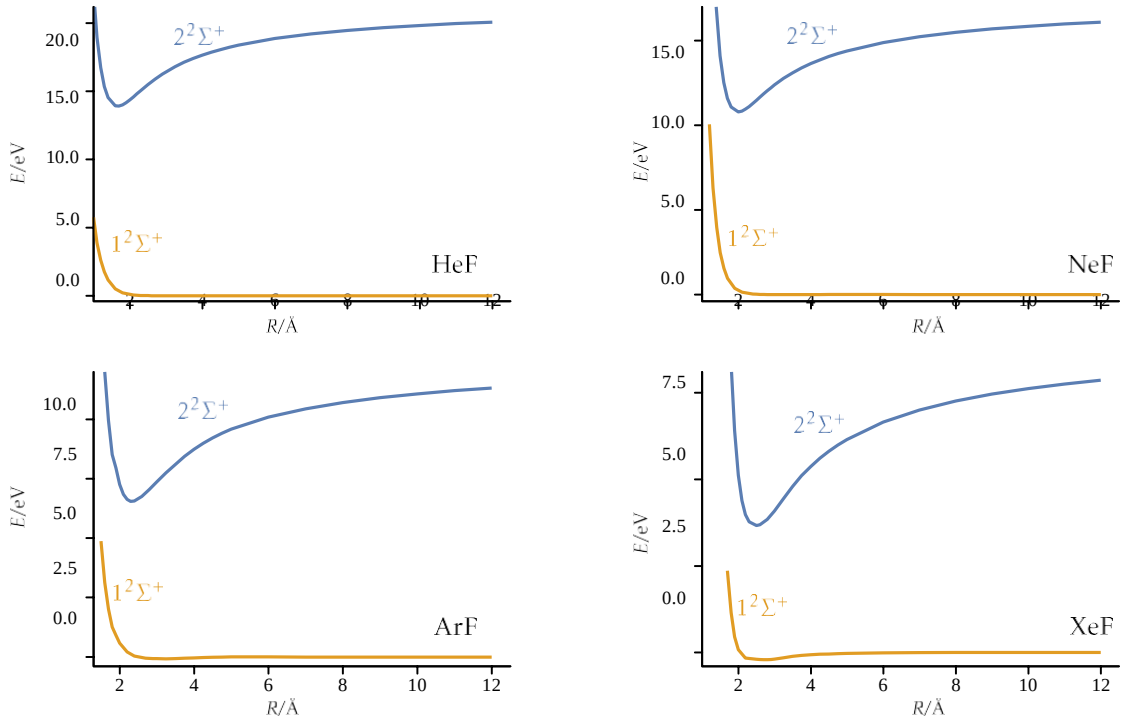

Fig. S5: Potential energy curves for low-energy singlet states of RgF complexes.

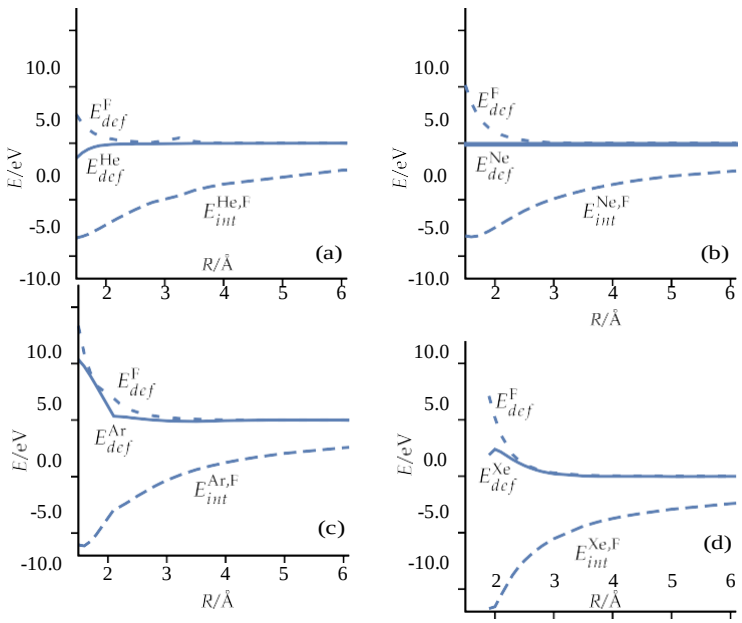

Fig. S6: Deformation and interaction energies as a function of the internuclear distance for the $2^2\Sigma^+$ state of HeF (a), NeF (b), ArF (c) and XeF (d).

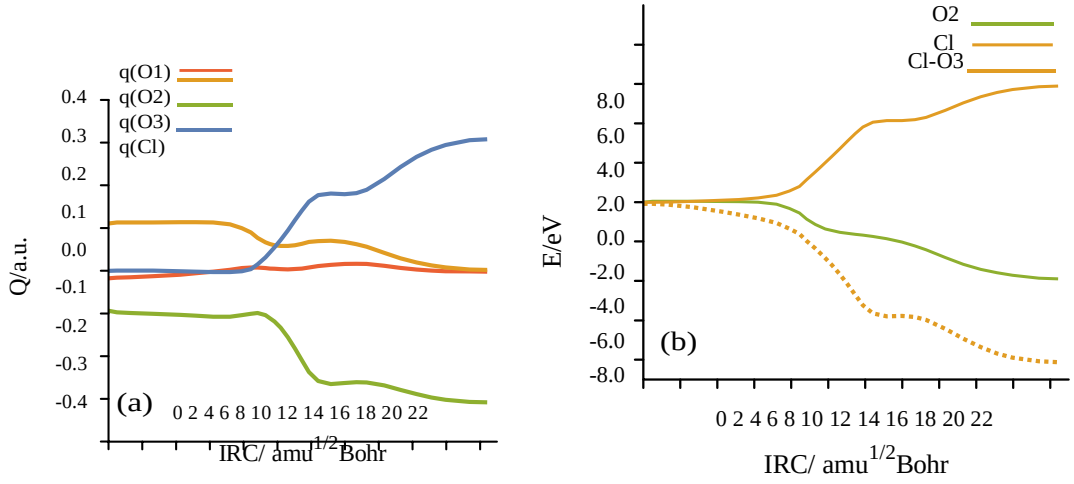

Fig. S7: (a) Atomic charges (b) V_{xc} contribution to E^{Cl}_{self} $_{self}$ $_{inter}$, E^{O3}, $E^{Cl,O3}$ along the intrinsic reaction coordinate for the $Cl + O_3 \longrightarrow ClO + O_2$ process.

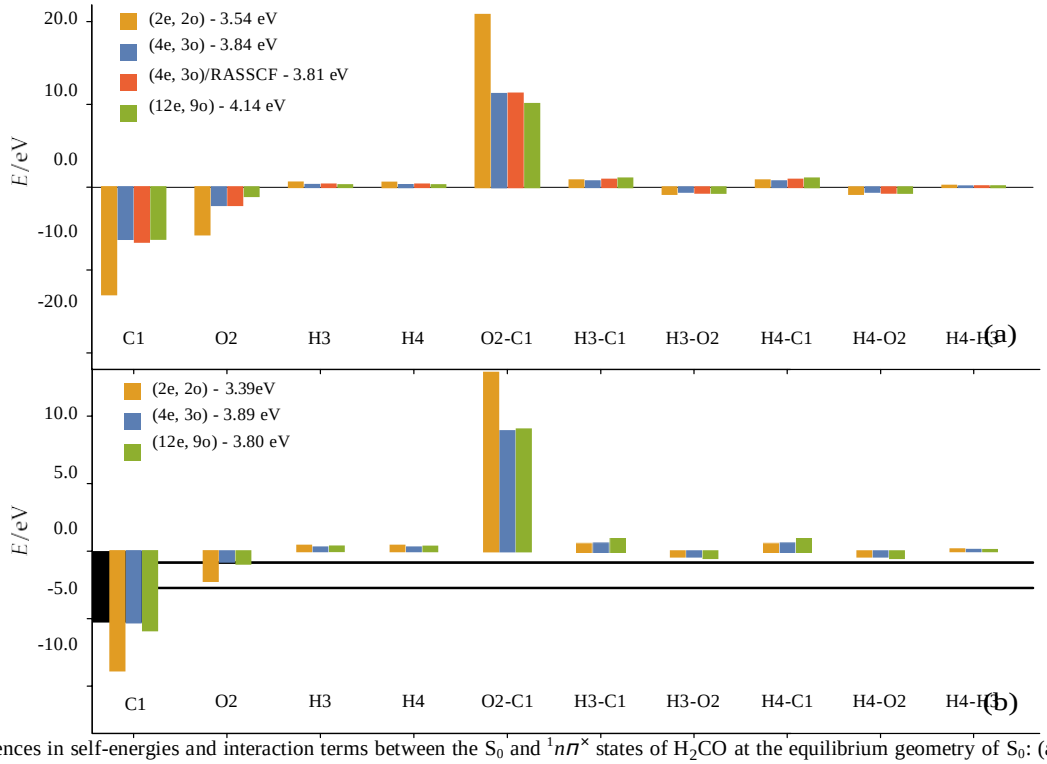

Fig. S8: Differences in self-energies and interaction terms between the S_0 and $^1n\pi^\times$ states of H_2CO at the equilibrium geometry of S_0: (a) IQA/CASSCF and (b) IQA/CASPT2 decompositions as a function of the size of active space. The RASSCF space correlates all the electrons of the systems, with two holes for RAS1, (4e, 3o) for RAS2 and zero electrons in RAS3.

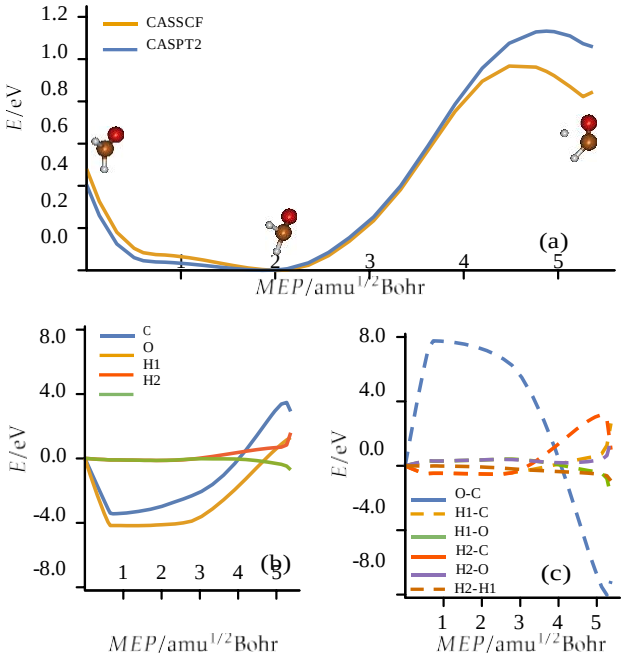

Fig. S9: (a) Minimum energy path of $^1n\pi^\times$ state for H_2CO evaluated at the CASPT2 level of theory; the yellow line corresponds to single point CASSCF (12e,9o) calculations along the MEP. In both cases, the energies are presented relative to the minimum of $^1n\pi^\times$. Changes on the b) self-energies and c) Interaction terms for the $^1n\pi^\times$ state along the MEP. The data in b and c take as reference the value at the starting point, and correspond to the CASSCF calculations. For CASPT2 see the figure 5 in the manuscript.

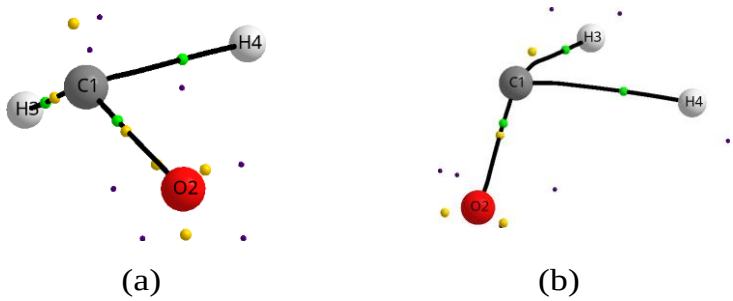

Fig. S10: Critical points (3,+3) and (3,-1) of the laplacian of the electron density for H_2CO at the structure associated with the conical intersection of the MEP (see fig. 5a). a) Ground state, b) first singlet excited state.

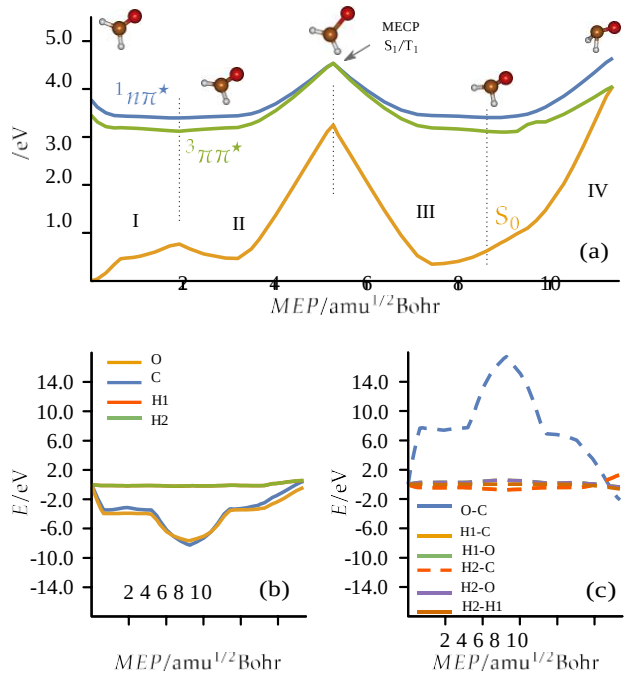

Fig. S 11: a) Energies of the low-lying states of H_2CO along the minimum energy path (MEP) of $^1n\pi^\times$-$^3\pi\pi^\times$. Changes on the b) self-energies and c) Interaction terms for the excited state along the MEP. The data in b and c take as reference the value at the starting point, and also, correspond to $^1n\pi^\times$ before the MECP and $^3\pi\pi^\times$ after the MECP.

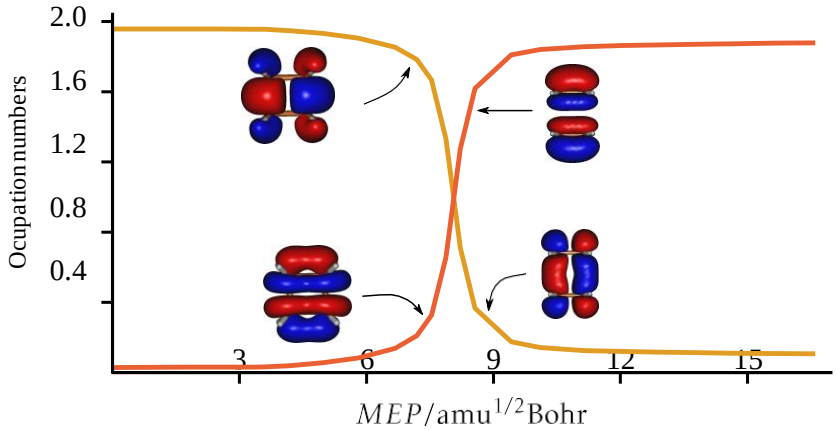

Fig. S12: Occupation numbers of relevant molecular orbitals of C4H8 along the intrinsic reaction coordinate for the ground state concerted dissociation.

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