Thermally accessible triplet state of π-nucleophiles does exist. Evidence from first principles study of ethylene interaction with copper species

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SUPPORTING INFORMATION

RSC Advances

LIST OF SUPPLEMENTARY FIGURES AND TABLES:

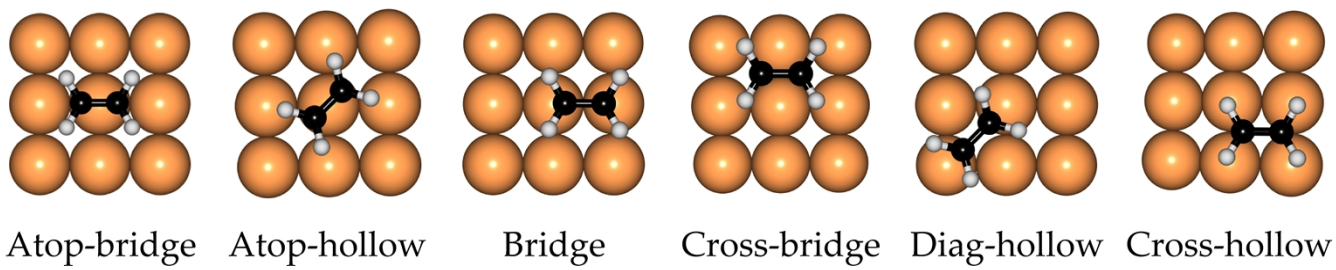

Figure S1. Six possible adsorption sites of ethylene on Cu(100) surface.

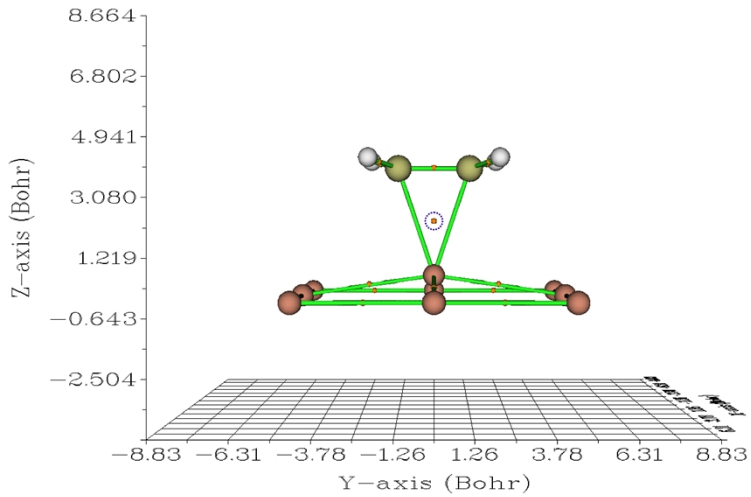

Figure S2. Bond critical points, which are found in the supercell content.

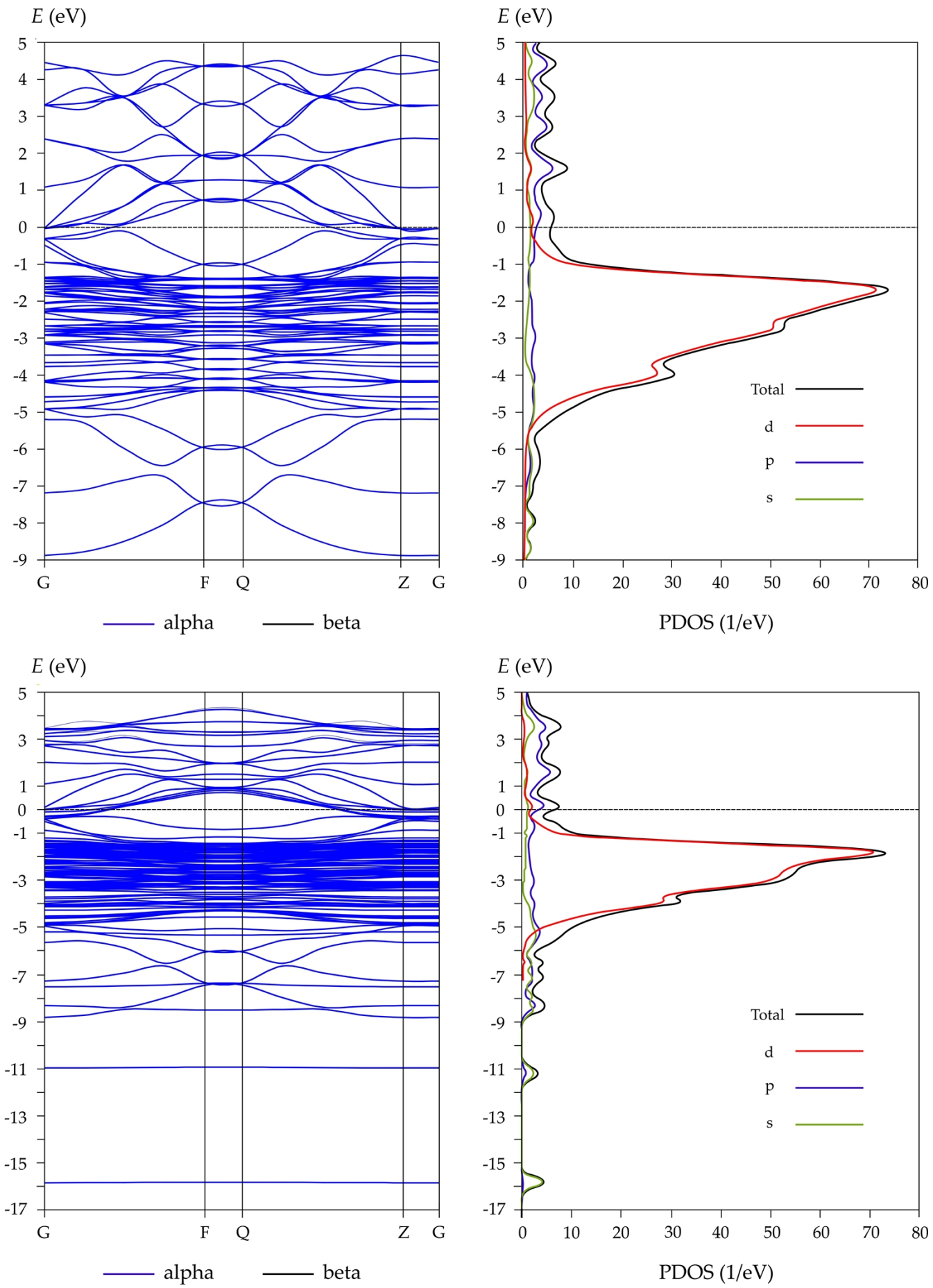

Figure S3. Electronic band structure (left) and partial density of states (right) plots of clean Cu(100) surface (top) and covered by ethylene (bottom).

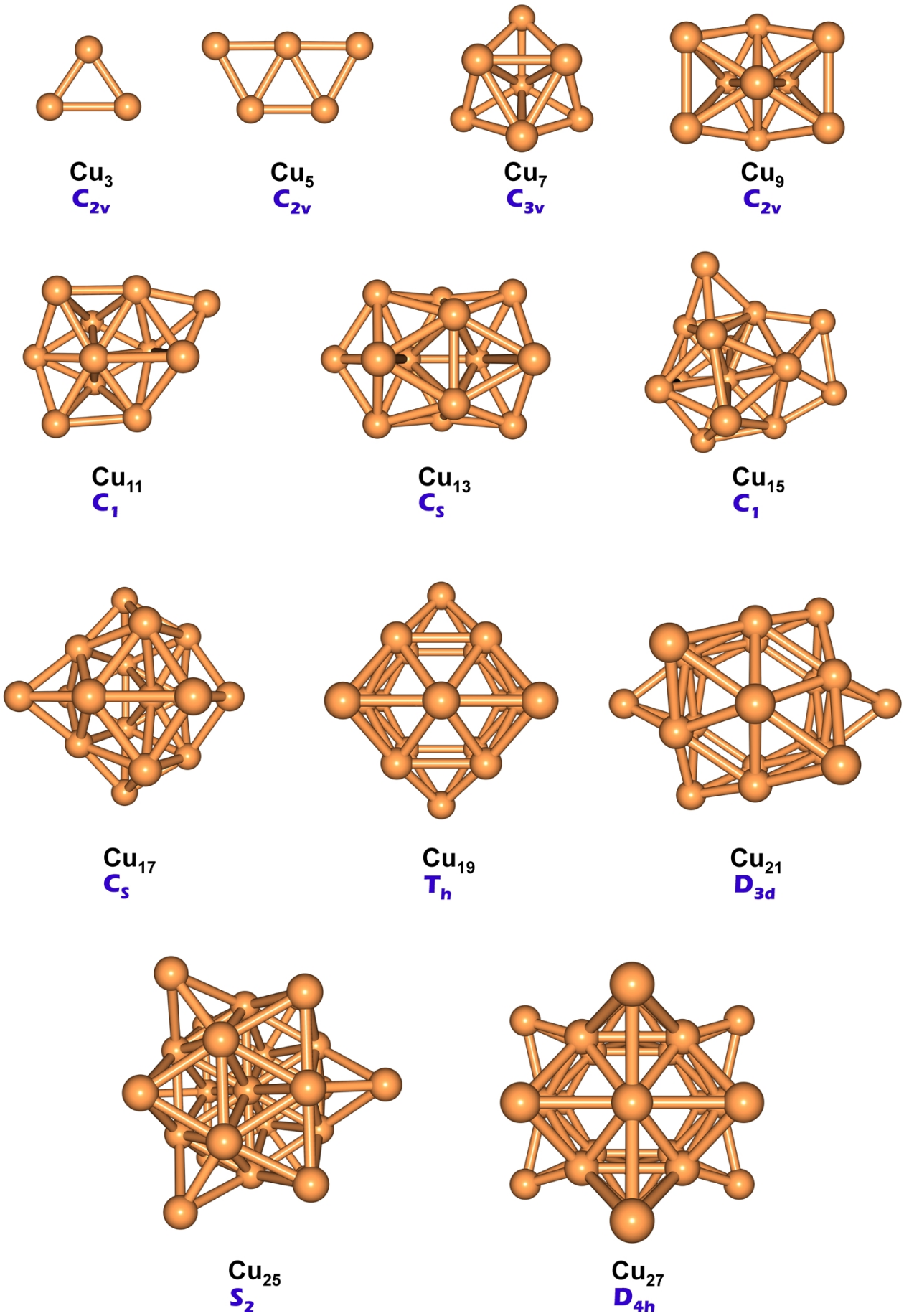

Figure S4. Structures of the odd-numbered copper clusters optimized by the DFT(UM06)/LANL2DZ method in ethanol medium. Blue labels correspond to the point group symmetry.

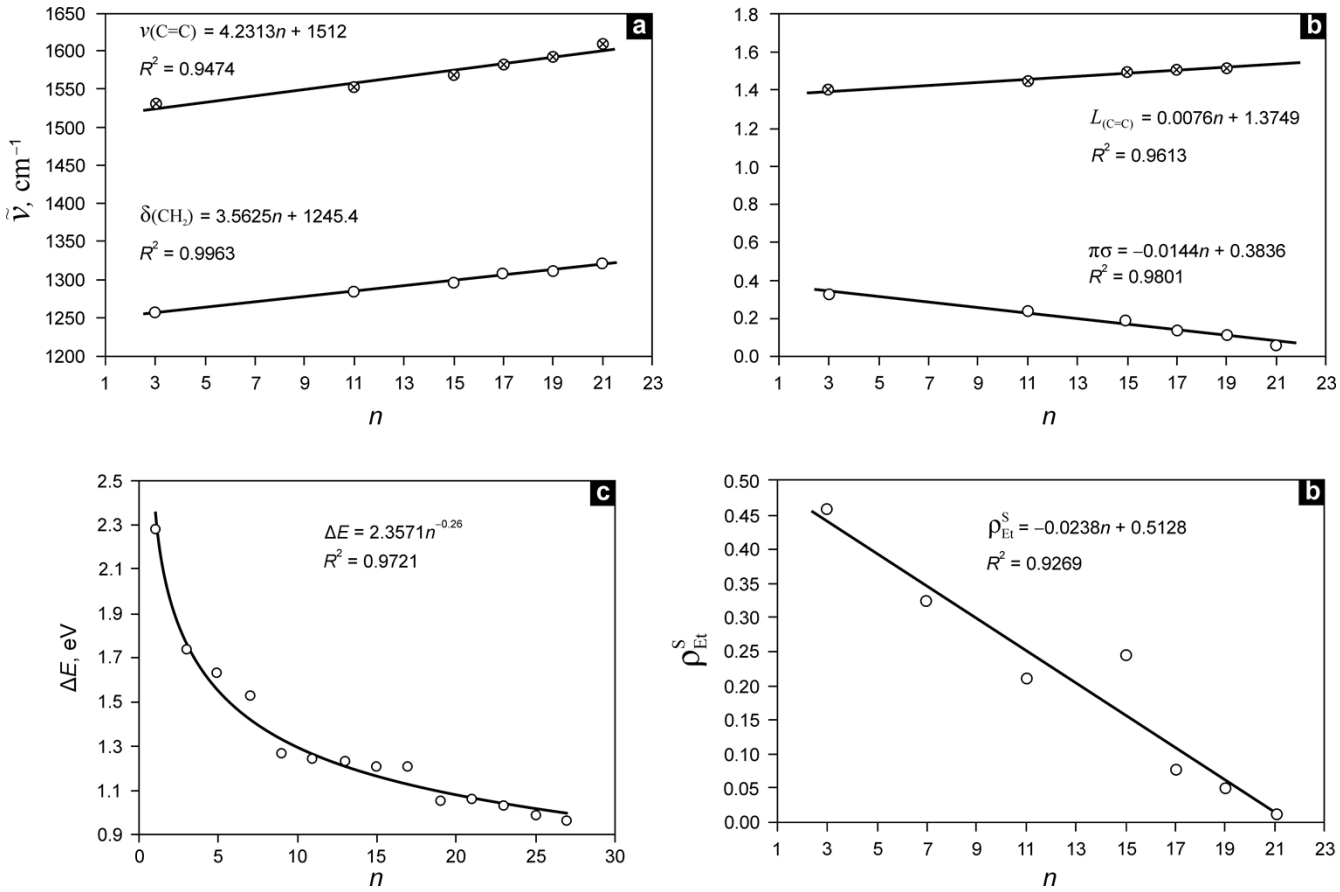

Figure S5. Correlation of different parameters with the number of copper atoms *n*: a) vibrational frequencies of the band I and II; b) the C=C Laplacian bond order and the πσ parameter; c) the SOMO-LUMO gap; d) spin density on the reacting copper atom.

Table S1. The SOMO and the LUMO energies of the calculated copper clusters; Δ*E* is the SOMO-LUMO energy gap.

n	E_{SOMO}, eV	E_{LUMO}, eV	Δ*E*, eV
1	-5.03	-2.75	2.28
3	-3.87	-2.13	1.74
5	-4.50	-2.88	1.63
7	-4.56	-3.03	1.53
9	-3.81	-2.54	1.27
11	-4.10	-2.85	1.25
13	-4.15	-2.91	1.23
15	-4.23	-3.02	1.21
17	-4.67	-3.46	1.21
19	-4.52	-3.47	1.05
21	-4.56	-3.49	1.06
23	-3.98	-2.94	1.04
25	-4.31	-3.32	0.98
27	-4.19	-3.23	0.96

Table S2. Coordination numbers and free valence values of the carbon atoms in the C_2H_4/Cu_n complexes.

n	Coordination number[a]		Free valence[b]	
	C1	C2	C1	C2
3	3.9490	3.9490	0.0022	0.0020
7	3.9320	3.9330	0.0055	0.0054
11	3.9822	3.9612	0.0015	0.0029
15	3.9281	3.9189	0.0008	0.0007
17	3.9170	3.9047	0.0002	0.0003
19	3.9244	3.9244	0.0010	0.0010
21	3.9042	3.9051	0.0021	0.0016

[a] Calculated as the following:[S1]

$$CN_A = \sum_{B \neq A} \frac{1}{1+\exp\left(-16\cdot\left((4/3)(R_A+R_B)/r-1\right)\right)}$$

Herein R is covalent radius taken from Ref. S2.

[b] Calculated as the following:[S3]

$$F_A = V_A - \sum_{\substack{B \\ B\neq A}} B_{AB} = \sum_{\mu,\nu} \left(\mathbf{P}^S\mathbf{S}^A\right)_{\mu\nu} \left(\mathbf{P}^S\mathbf{S}^A\right)_{\nu\mu}$$

where $\mathbf{P}^S$ is the spin density; V_A is the total valence of atom A and is calculated according to the following equation:

$$V_A = 2Q_A - \sum_{\mu,\nu} \left(\mathbf{DS}^A\right)_{\mu\nu} \left(\mathbf{DS}^A\right)_{\nu\mu}$$

Herein Q_A is Hirshfeld's atomic population; $\mathbf{D}$ is total density.[S3]

[S1]Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate ab initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H–Pu. *J. Chem. Phys*. **2010**, *132*, 154104.

[S2]Pyykkö, P.; Atsumi, M. Molecular Single-Bond Covalent Radii for Elements 1–118. *Chem.—Eur. J*. **2008**, *15*, 186–197.

[S3]Mayer, I.; Salvador, P. Overlap Populations, Bond Orders and Valences for "Fuzzy" Atoms. *Chem. Phys. Lett*. **2004**, *383*, 368–375.

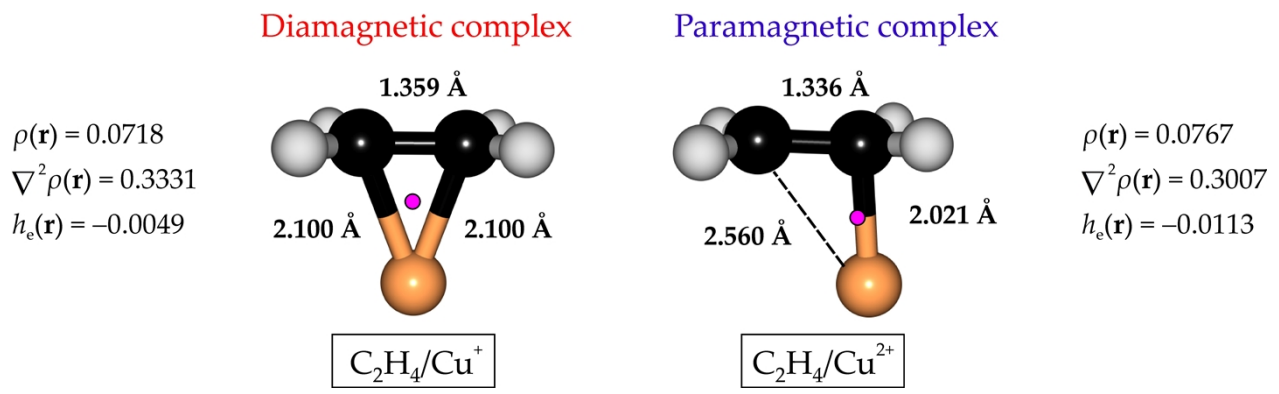

Figure S6. Selected structural and QTAIM topological parameters of the C_2H_4/Cu^+ and C_2H_4/Cu^{2+} complexes. Magenta circles indicate the bond critical points between the ethylene moieties and the copper ion.

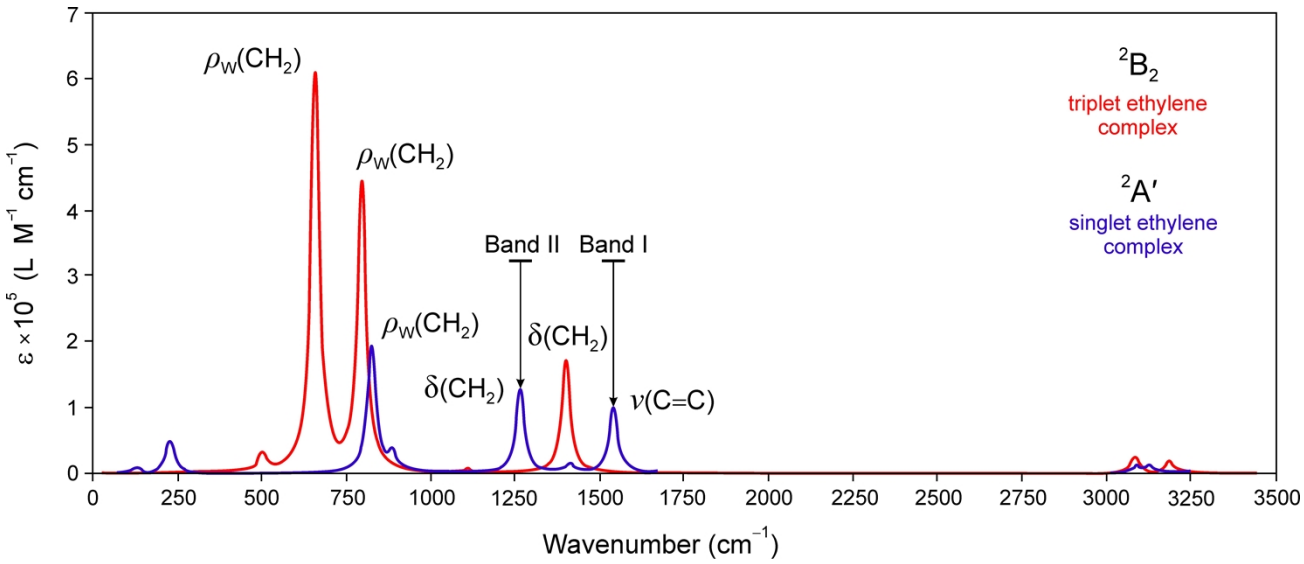

Figure S7. Calculated IR spectra of the C_2H_4/Cu complex in the $\tilde{X}^2A'$ (blue) and $^2B_2$ (red) states. The band I and II are indicated by vertical arrows.

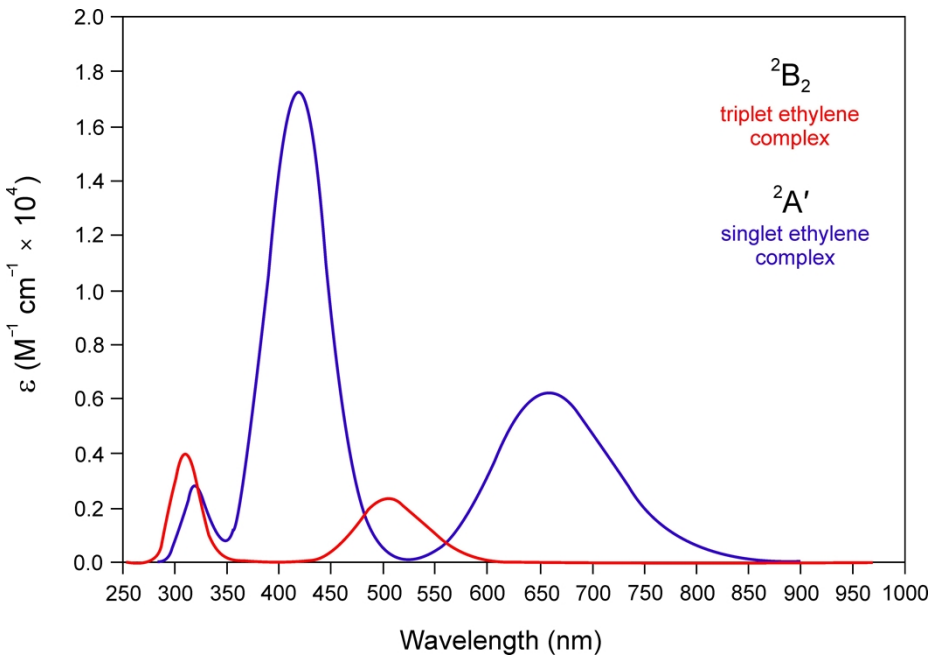

Figure S8. Calculated UV-vis spectra of the C_2H_4/Cu complex in the $\tilde{X}^2A'$ (blue) and $^2B_2$ (red) states.

Table S3. Performance of different functionals in prediction of the two experimentally observed bands in the UV-vis spectrum of the C_2H_4/Cu complex ($\tilde{X}^2A'$ state).

M062X	BMK	B3LYP	PBE0	HSE06	ωB97XD	B97D	mPW1PW91	BH&HLYP	CAM-B3LYP
441	392	398	412	405	415	394	408	424	398
344	313	338	333	331	323	–	331	337	319

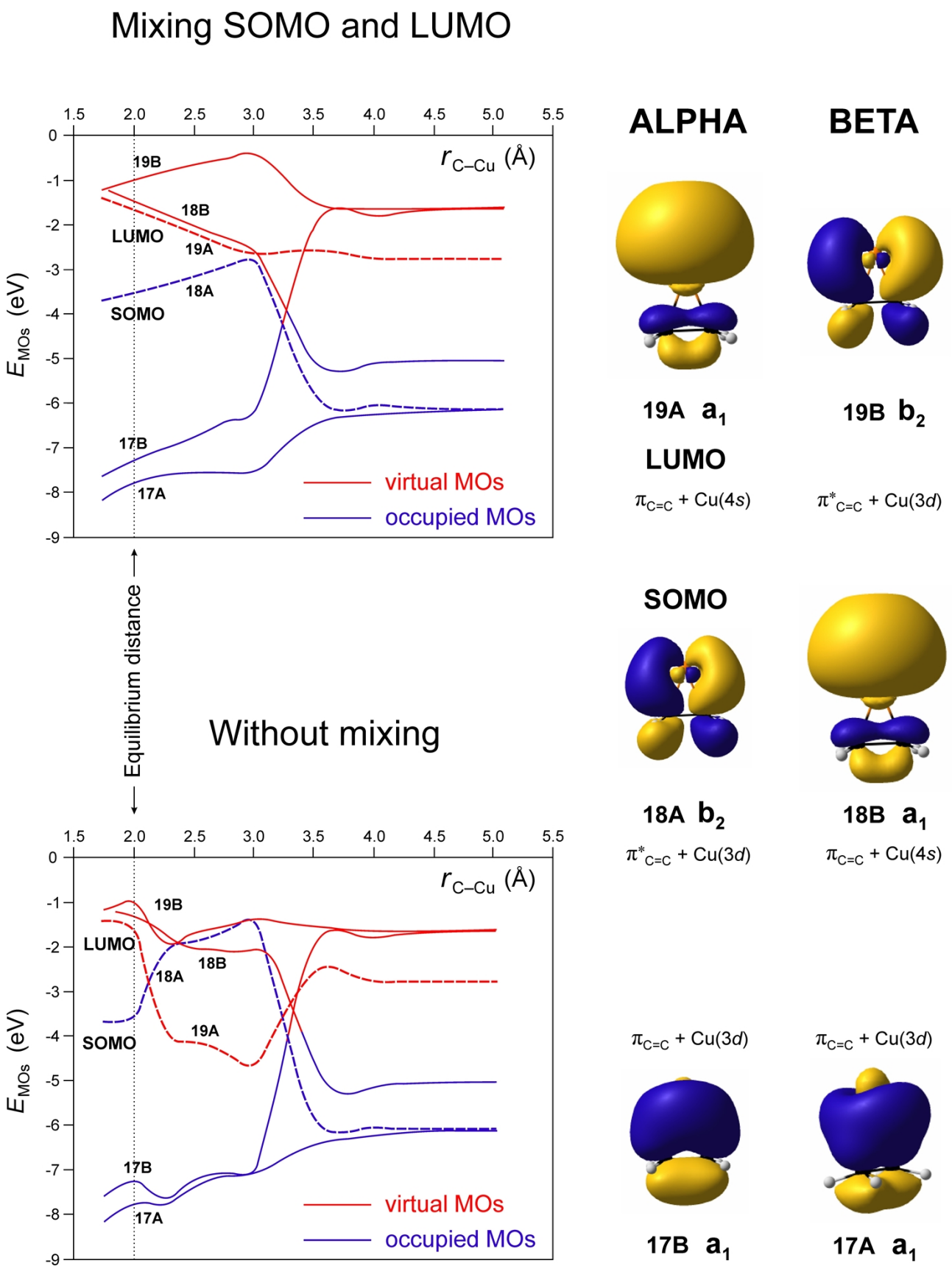

Figure S9. Energies of frontier molecular orbitals of the C_2H_4/Cu complex ($^2B_2$ state) as function of the C–Cu interatomic distance.

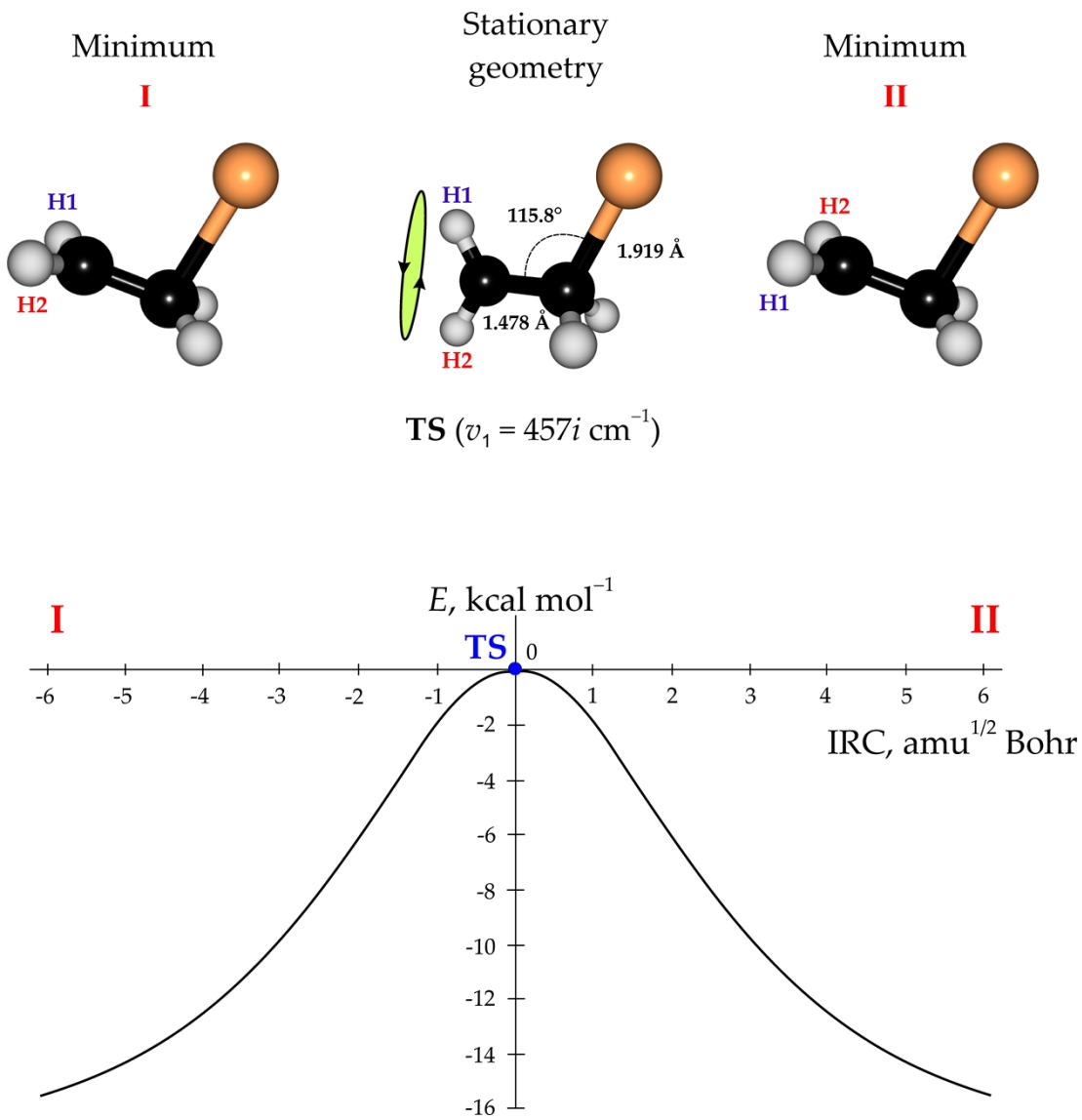

Figure S10. The QST3-optimized transition state structure and the related minima (top); the corresponding IRC path (bottom).