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

SUPPORTING INFORMATION

Inducing chemical reactivity on specific site of a molecule using the Coulomb interaction exerted by a low energy electron

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Contents

Atom	Type of primitive	Parent basis set	
		6-311+G*	cc-pVTZ
H	s	0.0036000	0.0102700
		0.0003600	0.0010270
		0.000360	0.0001027
	p	0.0530330	0.0274357
		0.0037500	0.0019400
C	s	0.0043800	0.0128500
		0.0004380	0.0012850
		0.0000438	0.0001285
	p	0.0030971	0.0085489
		0.0002190	0.0006045
N	s	0.0063900	0.0178700
		0.0006390	0.0017870
		0.0000639	0.0001787
	p	0.0045184	0.0121976
		0.0003195	0.0008625
O	s	0.0084500	0.0238400
		0.0008450	0.0023840
		0.0000845	0.0002384
	p	0.0059751	0.0151321
		0.0004225	0.0010700

TABLE I: Even-tempered primitive Gaussian basis functions used for augmenting the 6-31+G* and the cc-pVTZ basis sets. The cc-pVTZ basis set is used for studying the basis set dependency in the computation of the kinetic energy, which is included in Table II.

Parent basis set	Method	
	MP2	EA-EOMCCSD
6-311+G*	0.75	0.96
cc-pVTZ	0.92	0.87

TABLE II: A comparison of kinetic energy of LEE calculated at analytically continued MP2 and EA-EOMCCSD levels of theory for the molecular complex containing diazene and CO_2 moieties. The kinetic energy is given in eV. Since the LEE is captured into a very localized two-center orbital, i.e., the π^* orbital of the azo group, the kinetic energy does not quantitatively vary much with respect to the basis sets and the levels of theory we have chosen. An in-house modified GAMESS-US quantum chemistry package is used for these energy calculations [1, 2].

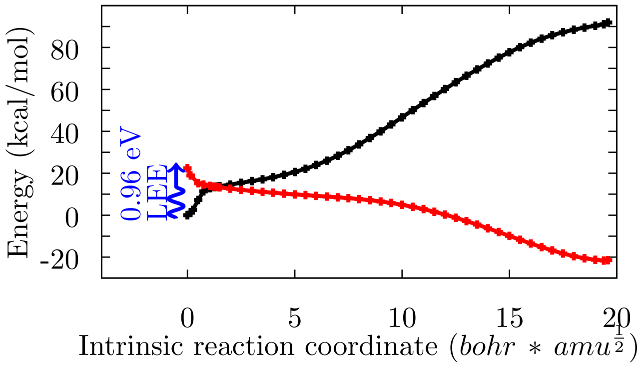

FIG. 1: **The electronic energy computed using coupled cluster theories for the intrinsic reaction path (IRP) shown in Fig. 3 of the main article**. While the potential energy curve for the electron attached state (shown in red color) is computed using the analytically continued EA-EOMCCSD method, the electronic energy of the neutral complex is computed using CCSD method (shown in black color).

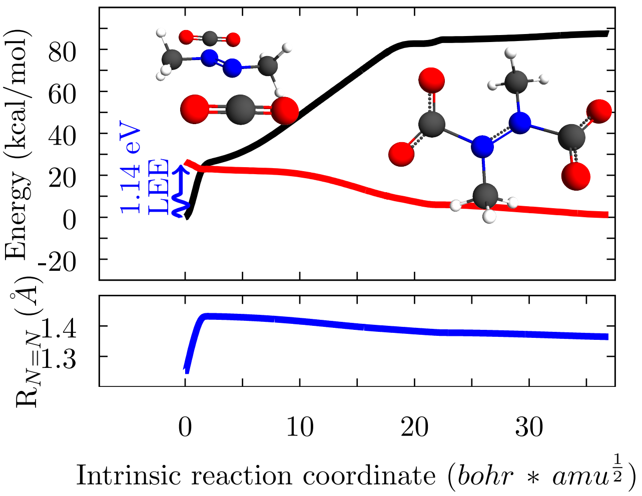

FIG. 2: **The intrinsic reaction path (IRP) for the LEE induced conversion of (CO_2) (CH_3-N=N-CH_3) (CO_2) complex to its mono anion covalent adduct**. The resonant attachment of LEE is represented with a wavy arrow. The potential energy curves of the neutral molecular complex (black color) and its LEE attached state (red color) along the IRP of the LEE attached state are shown in the upper panel. The change of N=N bond length along the IRP is shown in the bottom panel.

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[1] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, et al., J. Comp. Chem. **14**, 1347 (1993).

[2] J. R. Gour and P. Piecuch, J. Chem. Phys. **125**, 234107 (2006).