SUPPLEMENTAL MATERIAL FOR PUBLICATION

A concerted synchronous [2+2] cycloreversion repair catalyzed by two electrons

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1   Computational details

1.1   Continuum remover potential

Recent advances in *ab initio* electronic structure theories have established successful computational methods for studying the chemical reactions induced by the resonantly captured LEE.[1] Of particular note is the recent introduction of a L^2 stabilization method known as the real-valued continuum remover method.[2] The working principle underlying this method can be understood as follows. The NIRS wavefunction is a scattering solution of negative-ion Hamiltonian which can be viewed as a bound state coupled and interacting with the autoionization continuum. Adding a real-valued continuum remover potential, which does not support the autoionization continuum, to the non-interacting asymptote of the negative ion Hamiltonian removes the outgoing part of the continuum wavefunction contributing to the NIRS wavefunctions, which are thereby converted into a bound state wavefunction localized in the interaction region.[1,2] In other words, the NIRS wavefunction is obtained as a bound eigenstate of the continuum remover potential ($\hat{W}$) added modified negative ion Hamiltonian.

$$(\hat{H}_{elec} + \hat{W^{CR}}) |\Psi^{CR}\rangle = E^{CR} |\Psi^{CR}\rangle \tag{1}$$

Hence, this method enables us to study the chemical reactions induced by the resonantly captured LEE in terms of a well defined potential energy surface corresponding to the negative ion resonance state (NIRS). This method has also been successfully used for removing the non-physical resonances of the complex absorbing potential based analytically continued molecular Hamiltonian.[3]

When a large basis set which span the entire interaction region is used, the Ψ^{CR} is an optimally projected wavefunction of the NIRS inside the interaction region, i.e.,

$$\langle \Psi^{CR} | \Psi^{NIRS} \rangle_{\text{inside interaction region}} = 1 \tag{2}$$

Since the energy position of the NIRS is decided by the many-electron effects inside the inter-action region of the Hamiltonian, the electronic energy corresponding to the optimally projected NIRS is a very good approximation to the energy of the NIRS.

$$E^{CR} \approx E^{NIRS} \tag{3}$$

For our numerical calculations, we have used a box-shaped quadratic-potential of the form

$$\hat{W}^{CR}_{elec} = \lambda \sum_{i=1}^{All\ electrons} (\hat{W}_{x_i} + \hat{W}_{y_i} + \hat{W}_{z_i})$$

$$\hat{W}_\chi = \chi^2(1 - 0.5[tanh(\chi + \chi_t) - tanh(\chi - \chi_t)]) \tag{4}$$

as the one-electron continuum remover potential, where χ_t is a point in the non-interacting asymp-tote at which the potential is turned-on. Since the potential $\hat{W}$ is taken to be zero inside the many-electron interaction region of the physical Hamiltonian, the E^{CR} is not directly perturbed by the potential $\hat{W}$, i.e.,

$$\langle \Psi^{CR}|\hat{W}|\Psi^{CR}\rangle = 0 \tag{5}$$

One may note that, in numerical calculations, the turn-on point for the potential, χ_t, is taken far enough from the geometrical center of the molecule such that the condition given in Eq. 5 is achieved. However, in practical calculations using finite basis set, the condition given in Eq. 5 is difficult to be satisfied, even for large values of χ_t, if any Rydberg type orbitals or dipole stabilized orbitals contribute to the NIRS. Hence, for such cases, there can be an error in the energy position due to the continuum remover potential. Since in our case, the NIRS are mixed significantly with dipole orbitals, in order to avoid CRCAP-induced artificial perturbation, we took the turn-on point of the potential to be far away from the interaction region (10 au away from the peripheral atom) where the iso-density value of the dipole orbitals fell below 10^{-4}. This choice of the potential helps us to minimize the artificial perturbation due to the continuum remover potential. The perturbation is further minimized in the computed energy by subtracting the perturbation energy due to the

continuum remover potential.

$$E^{CR}_{corrected} = E^{CR} - \langle \Psi^{CR}|\hat{W}|\Psi^{CR}\rangle \qquad (6)$$

1.2 Ab initio methods

The continuum remover potential method has been used successfully within the framework of *ab initio* electronic structure methods for computing the LEE induced reaction paths.[4–7] The non-catalyzed and the LEE catalyzed reaction paths are computed at the second order perturbation level using the closed shell and restricted open-shell Møller-Plesset perturbation methods, respectively.[8] In order to restrict the repair to the least-motion path, a C_s molecular-symmetry is enforced in the reaction path. The electron-attached and electron-ionized equation-of-motion coupled cluster singles and doubles (EA-EOMCCSD and IP-EOMCCSD) methods[9] are used respectively for computing the kinetic energy of the LEE corresponding to the first and the second resonant attachments. An in-house modified Gamess-US quantum chemical code is used for all the molecular calculations.

1.3 Basis sets

The basis set for the quantum chemical computation is selected as follows. Atom centered valence triple zeta contracted [5s3p] basis set derived from (10s6p) primitive basis sets of Huzinaga[10] is selected as the one-electron parent basis set. This parent basis set for the C atoms and the O atoms of the uracil dimer are further augmented with a diffuse set of even-tempered primitive Gaussian functions. This augmented basis set is used as the atomic basis set for the molecular calculation. The exponents of the even-tempered Gaussian functions are calculated using

$$\xi_i^{s/p/d} = \left(\zeta^{s/p/d}\right)^{(1/N^{s/p/d})} \xi_{i-1}^{s/p/d} \qquad (7)$$

where N is the total number of the even-tempered basis functions and ζ is the orbital exponent of the most diffused function in the parent basis set.

Table 1: Even-tempered primitive Gaussian basis set

Oxygen		Carbon	
Type	Exponent	Type	Exponent
s	0.0808911		0.0339356
	0.0255800		0.0085242
	0.0080891	s	0.0021412
	0.0025580		0.0005378
	0.0008089		0.0001351
	0.0002558		0.0091060
	0.0000809	p	0.0009106
	0.0000256		0.0000911
p	0.0261666		
	0.0041471		
	0.0006573		
	0.0001042		
	0.0000165		

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