

SUPPORTING INFORMATION

Low energy electron catalyst: Electronic origin of catalytic strategies

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COMPUTATIONAL METHODS

Theoretical background

In order to study the feasibility of the low energy electron (LEE) catalyzed isomerization reaction, the kinetic energy of the LEE at which it is resonantly captured to the target isomer (i.e., the attachment energy), the minimum energy isomerization path for the resulting *eS-adduct* and the autoionization decay width along the reaction path are to be computed. If the *eS-adduct* is stable against autoionization, i.e., the lifetime of the *eS-adduct* is in the order of vibrational period, then the *eS-adduct* can relax its geometry by disposing the excess electronic energy to one of its nuclear relaxation modes; a path that may then evolve to the *eP-adduct*. The quantum chemical computation of resonant formation and the relaxation of the *eS-adduct* is a highly challenging task due to the autoionization of the resonantly captured electron, i.e., the wavefunction correspond to the *eS-adduct* belongs to the non- L^2 domain of the Hamiltonian. Recently, however, methods based on the analytical continuation of the Hamiltonian to its non- L^2 domain were developed which enable one to directly use the existing L^2 computational methods, i.e., bound state *ab initio* methods, for computing the resonant formation and autoionization of the *eS-adducts* [1]. The associated eigen functions of the analytically continued Hamiltonian are square integrable, i.e., they can be represented in L^2 space. This enable us to use the *ab initio* bound state methods for the *eS-adduct*. The corresponding electronic energy of the *eS-adduct* is complex-valued.

$$E = E_{res} - i\Gamma/2 \quad (1)$$

The real and imaginary parts of the complex eigenvalues of the analytically continued Hamiltonian correspond to the energy position and the autoionization decay width (twice the imaginary part), of the *eS-adduct*, respectively. The physical eigen solutions of the analytically continued Hamiltonian are identified as stabilized eigen functions in the complex energy plane, where the stabilization is determined against the variation of the analytical continuation parameter [1].

Negative imaginary potentials (NIP) have been traditionally used for the analytical continuation for the *eS-adduct* of the molecular substrates [1–4]. The molecular Hamiltonian of the *eS-adduct* is perturbed by an appropriate local, positive-semidefinite one-electron negative imaginary potential, $-i\eta\hat{W}$, with the property of being zero in the interaction region [3, 4].

$$\hat{H}(\eta) = \hat{H} - i\eta\hat{W} \quad (2)$$

This potential enforces an absorbing boundary condition and, consequently, the autoionizing (decaying) wavefunction is transformed into a bound state eigen solution of the resulting analytically continued Hamiltonian. The physical solutions are identified as the stable solutions against the variation of the strength of the non-negative parameter η . Recently, we have proposed a continuum remover complex absorbing potential where a real-valued potential is added to the conventionally used negative imaginary potential in the peripheral of the molecule [5–7]. While the negative imaginary part of the continuum remover complex potential introduces the analytical continuation, the real part of the potential perturbatively remove the artificial stabilization of the discretised continuum due to the use of finite basis sets. We have used this continuum remover potential as our choice of the analytical continuation method for computing the electronic energy and the reaction path of the *eS-adduct*.

A Cartesian box-shaped continuum remover complex absorbing one-electron potential of the form

$$\hat{W}_{modified} = (1 - i\eta) \sum_{\chi=x,y,z} \chi^2 (1 - 0.5[\tanh(\chi + 7.5 + \chi_0) - \tanh(\chi - 7.5 - \chi_0)]) \quad (3)$$

is used for the calculation, where χ_0 is the average distance between the two terminating atoms of the molecule along the χ -axis and η is the strength of the negative imaginary part of the complex potential. When used with out the negative imaginary part, i.e., for $\eta = 0$, the remaining real-valued continuum remover potential method acts as a modified *L²-stabilization method*, where the electronic state of the *eS-adduct* are localized in the interaction region of the physical Hamiltonian [6]. We have used the real-valued continuum remover potential method [6] in conjunction with *ab initio* electron correlation methods to get the reaction paths and the attachment energies. The real-valued continuum remover potential also shares the property of the NIP, that it leaves the interaction region untouched and only ‘turns on’ asymptotically with the NIP. When used with a large basis set, the real-valued continuum remover potential method gives the optimally projected wavefunction of the *eS-adduct* inside the interaction region of the Hamiltonian. Hence, the real-valued continuum potential method is a very powerful, yet easily employable method for computing the chemical reactions of the *eS-adduct*. Since the details of this method is described elsewhere [6, 7], only the essential computational details pertaining to this work are briefly discussed here.

Computational details

The computation of the energy of *eS-adduct* is done as follows. Since the real-valued continuum remover potential is a one- electron potential, we have added the potential directly to the Fock operator. This also implies that no modifications to the post Hartree-Fock methods needed to be made. The user-modified one-electron integral subroutines are used for implementing the continuum remover potential to Hartree-Fock calculation. All the molecular calculations presented in this Communication are carried out using an in-house modified GAMESS-US quantum chemistry package [8]. An atom-centred STO 6-311G+* basis set is used as a parent basis set for all the calculation. This parent basis set is further augmented with a set of even-tempered primitive Gaussian functions. Such large basis set is essential to get the geometrically important points and accurate reaction paths corresponding to the *eS-adduct* [6].

| Atom | Type | Exponent | Atom | Type | Exponent | Atom | Type | Exponent |
|------|------|-----------|------|-----------|-----------|-----------|------|-----------|
| C | s | 0.0043800 | O | s | 0.0084500 | S | s | 0.0087255 |
| | | 0.0004380 | | | 0.0008450 | | | 0.0018798 |
| | | 0.0000438 | | | 0.0000845 | | | 0.0004050 |
| | | 0.0000044 | | | 0.0000085 | | | 0.0000636 |
| | p | 0.0004380 | p | 0.0008450 | p | 0.0090561 | | |
| | | 0.0000044 | | 0.0000085 | | 0.0020250 | | |

The minimum energy path of the non-catalytic reaction and the *eS-adduct* are computed using second order restricted and restricted-open-shell Møller-Plesset methods, respectively. A planar symmetry of the molecule is saved for all the reactions paths given in this Communication. In the case of cyclic dimer reported in the Communication, the molecular symmetry is also preserved for a symmetric migration of the two hydrogen atoms. Electronic energy along the isomerization path corresponding to the neutral molecule and the *eS-adduct* are further improved using the coupled cluster singles and doubles (CCSD) method and electron-attachment equation-of-motion coupled cluster singles and doubles (EA-EOMCCSD) method [9], respectively. The electronic energies plotted in figures 1-4 are computed using these two methods. The EA-EOMCCSD method in conjunction with the real-valued continuum remover potential is capable of computing the kinetic energy of the LEE corresponding to the resonant capture processes and the electronic energy of the *eS-adduct* using a direct difference approach where consistent treatment of electron correlation

is applied for both the ground state of the neutral molecules and their *eS-adducts* [6]. Finally, the autoionization decay width is computed using continuum remover complex absorbing method at the static and exchange level. The lifetime of the *eS-adduct* is in the order of 10^{-14} s and remains more or less constant along the non-catalytic path.

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- [1] N. Moiseyev, Non-Hermitian Quantum Mechanics, Cambridge University Press, Cambridge, **2011**.
- [2] N. Moiseyev, J. Phys. B **1998**, 31, 1431.
- [3] U. V. Riss, H. D. Meyer, J. Phys. B **1993**, 26, 4503.
- [4] R. Santra, Phys. Rev. A **2006**, 74, 034701.
- [5] Y. Sajeev, V. Vysotskiy, L. S. Cederbaum, N. Moiseyev, J. Chem. Phys. **2009**, 131, 211102.
- [6] Y. Sajeev, Chem. Phys. Lett. **2013**, 587, 105–112.
- [7] Y. Sajeev, A. Ghosh, N. Vaval, S. Pal, Int. Rev. Phys. Chem. **2014**, 33, 397–425.
- [8] M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, J. Comp. Chem. **1993**, 14, 1347–1363.
- [9] J. R. Gour, P. Piecuch, J. Chem. Phys. **2006**, 125, 234107.