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Low-energy-electron induced permanently reactive CO_2 molecules

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Ab initio quantum chemical studies show that a very weak molecular complexation of CO_2 with a dipolar molecule is able to suppress the autoionization of electron from its transient negative ion states. Since the autoionization is suppressed, the transient negative ion can efficiently relax its geometry to form the reductively activated CO_2 moiety. Unlike the reductively activated isolated CO_2 molecules, which are deactivated immediately due to their thermodynamic metastability, the reductively activated CO_2 moieties of the weak molecular complexes are infinitely long-lived and, hence, permanently reactive.

Manipulating the reactivity of chemical species has become one of the most fascinating consequences of the low-energy electron-molecule collision studies [1–8]. Low energy electron beams and tunnelling electrons have been developed as the most comparative tools for inducing the site-selective and path-selective chemical reactivity [1, 2, 5–8]. A most significant mode of low-energy electron induced chemical reactions occurs when the molecule captures a low-energy free-electron of particular energy, i.e. resonance capture of electron, to form an electron-molecule transient negative ion (TNI) state [1, 2, 8, 9]. The electronic state of the TNI can be viewed as a molecular quantum state embedded in the electron-target continuum [10, 11]. The TNI-state of a molecule is characterized by the kinetic energy of the free-electron (KE_{e^-}) at which the resonant capture occurs and the autodetachment decay width (Γ) of the excess electron from the resulting TNI-state. The most important consideration to take into account when discussing the chemical reactivity of TNI-state is its Γ value. If the TNI-state is stable against autodetachment of the excess electron, i.e. the lifetime of the TNI-state is in the order of the vibrational period, then the TNI can relax by disposing the excess electronic energy to its geometrical relaxation mode; a path which may ultimately lead to an energetically stable, yet chemically reactive, radical anion.

CO_2 is a potential source for many valuable chemicals and reactants. Even though it is abundant in nature, the natural linear form of CO_2 is chemically inert due to its thermodynamic and kinetic stabilities. There are several ways to activate CO_2 which include photochemical, electrochemical, and homogeneous and heterogeneous catalytic routes [12]. The common factor for these activation processes is either the coordination of CO_2 to a transition metal center or adsorption to a metal surface as a bent radical anion. The reactivity of the anion is due to its bent structure in which the CO bonds are weakened and the carbon center exhibits distinct radical character. Thus, as Schröder *et al.* stated, geometrically bent radical anion of CO_2 constitutes a new type of highly reactive distonic ion where charge and the unpaired electron are located in different symmetry planes and, hence, it can be regarded as an activated carbon dioxide unit [13].

A direct route for inducing chemical reactivity on CO_2 molecule in the gas-phase is to reductively activate the CO_2 via the resonant capture of a free-electron. However, this direct approach is not an efficient way to induce the chemical reactivity. A very high autoionization decay width of the electron in the Frank-Condon region precludes an efficient geometric relaxation for the TNI-state to form the radical anion. Further, the radical anion, even if it is formed, disintegrates back to its ground equilibrium geometry of the neutral CO_2 molecule due to its thermodynamic metastability [14].

In the following part of this Communication, using high level *ab initio* quantum chemical methods, we show how to efficiently induce permanent reactivity on CO_2 molecules by suppressing the autoionization of electron from its TNI-states and subsequently stabilizing its radical anion. The free-electron induced permanent reactivity (i.e. the formation of a stable and geometrically bent radical anion of CO_2) is accomplished due to a dipolar neighbour molecule, where the strong dipole moment of the neighbour plays an important role in reductively activating the CO_2 molecule. A dipolar HCN molecule, which is also considered to be the naturally-occurring reactant and a source of fixed nitrogen to the early biosphere, is used as the dipolar neighbour molecule that suppresses the autoionization of the TNI-state and stabilizes the reactive radical anion. Interestingly, a linear isomer of the molecular complex of HCN with the CO_2 is also found to be weakly stable in the gas-phase environment with a potential well depth of 590 cm^{-1} [15]. Furthermore, the dipole moment of the linear isomer of the CO_2.HCN molecular complex (3.9 D) is larger than the critical value ($\approx$1.625 D) to bind an excess electron [16] and hence, the TNI-states are expected to be stable.

In order to check the effectiveness of free-electron induced reductive activation of the CO_2 moiety in the linear isomer of CO_2.HCN molecular complex, we first computed the Γ value of its TNI-states. We have used an one-electron continuum remover complex absorbing potential method (CRCAP) [10, 11] for calculating KE_{e^-} and Γ values of the TNI formation. Since the details of the CRCAP method has been described elsewhere [10, 11], only the essential computational details pertaining to this work are discussed. The CRCAP potential used in this study was of the frequently used box-shaped quadratic potential where the potential is turned-on only in the peripheral of the molecule. By adding the CRCAP with variable strengths η and λ to the Hamiltonian of the electron-molecule compound system, the TNI-states can be found as complex-energy stabilized points in the η-trajectories of the complex eigenvalues

$$[\hat{H} + (\lambda - i\eta)\hat{V}_{CRCAP}]|\Psi_{TNI}\rangle = E_{TNI}|\Psi_{TNI}\rangle \quad (1)$$

where the real part of the stabilized energy point gives the energy position relative to the target molecule (KE_{e^-}) and the imaginary part gives the half width ($\Gamma/2$) [10]. The real part (λ) of the CRCAP helps us to separate the physical from the non-physical complex energy stabilized points [11]. Since the TNI-states mixed significantly with dipole orbitals, in order to avoid CRCAP-induced artificial perturbation of the η-trajectories, we took the turn-on point of the potential to be very far away from the interaction region where the isodensity value of the dipole orbitals fell below 10^{-4}. A value of $\lambda = 0.5$ was used for the calculations. The basis set for the quantum chemical computation was selected as follows. An atom-centered 6-311+G* basis that is commonly used for the ground state was selected as the one-electron parent basis set. The energy values reported in this work were computed using an augmented basis constructed by adding an atom-centered set of even-tempered primitive Gaussian functions to the parent basis set.

The computed Γ values of the electron-CO_2.HCN (linear) system, which are very close to zero (see Figure 1), show remarkable stabilization of the TNI-states of the CO_2.HCN molecular complex against autodetachment of the excess electron. The η-trajectories shown in Fig. 1 were computed by diagonalizing the CRCAP added mean-field Hamiltonian in the one-particle (1p) sub-space where η-values varied from 0 to 4. One may note that the energy position, i.e., KE_{e^-} of the electron shown in Fig. 1 was computed at the 1p level. However, the kinetic energy of the electron with which the TNI-state is formed, i.e. the energy position of the TNI-state, and the vertical dissociation energy (VDE) reported in this work were calculated using the active-space electron-attached equation-of-motion coupled-cluster method with singles, doubles, and active-space triples (EA-EOMCCSDt) code available in the Gamess-US quantum chemical package [17]. Since the TNI-states were uncovered in the complex-energy plane even with the use of small η in the limit of zero (see Fig. 1), we used $\eta = 0$ and $\lambda = 0.5$ for all the numerical calculations reported here. The first forty valence-virtual orbitals [11] were included in the active-space for the triple-excitation calculation of the EA-EOMCCSDt method.

The strong stabilization of the TNI-states of linear complex against autodetachment of the electron can be easily understood by using the singly occupied molecular orbital of the corresponding TNI-state, as explained below. Due to the alignment of the CO_2 moiety along the molecular axis of the HCN moiety, the valence-type π^*-orbital of the isolated HCN moiety mixes with its own a_1 symmetric dipole-type orbital. The dipole-type orbital of the complex is very diffuse and polarized away from the molecule on the positive end of its strong dipole (3.9 D). The splitting of the π^*-orbital of the HCN moiety into two orbitals of the complex also occurs due to strong mixing of the π^*-orbital of the HCN moiety with its own dipole-type orbital, as shown in Fig. 2a and Fig. 2b. The singly occupied orbitals of the electron attached states, as shown in Fig. 2, were plotted using a normalized one-particle (1p) contribution from the EOMCCSDt calculation for the corresponding vertical electron attachment process, i.e. each of the orbitals shown in Fig. 2 are occupied by an excess electron from the corresponding electron attached state. The TNI formation for the π^* orbitals shown in Fig. 2a and Fig. 2b occurs through the resonant capture of an electron with a kinetic energy 1.18 eV and 4.10 eV, respectively. However, since these two TNI-states of the complex are localized on the HCN moiety, they do not contribute to the reductive activation of the CO_2 moiety. Further, upon complexation, one of the mixed valence-dipole orbitals of the HCN moiety covalently mixes with the extended three-center π^*-orbital of the CO_2 moiety to form a set of inter-moiety bonding and anti-bonding molecular orbitals of the complex, as shown in Fig. 2c and Fig. 2d. The TNI formation occurs through the resonant capture of a free-electron with kinetic energy 2.75 eV and 3.74 eV, respectively, to these orbitals. The mixing of the valence type resonance orbitals of the complex with the dipole type orbitals near the boundaries of the interaction region, where the two orbitals have comparable electron densities, help the TNI-state to hold its detaching electron in the interaction region for a longer period of time, i.e. the TNI-states of the CO_2.HCN molecular complex are strongly stable against autodetachment. Since the TNI-states are strongly stable against the autodetachment, these states can efficiently relax the geometry in the respective anionic potential energy surfaces and form the reductively active bent CO_2.

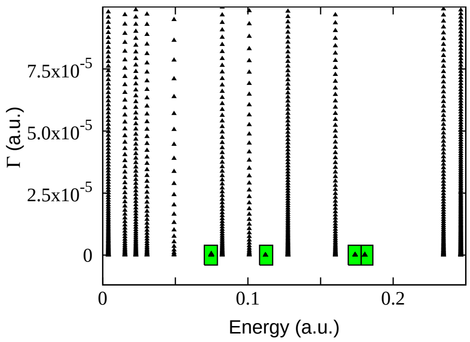

FIG. 1: **Transient negative ion states of the CO_2.HCN (linear) molecular complex.** The computed autoionization decay width (Γ) of the excess electron from the electronically unbound negative ion states of the CO_2.HCN molecular complex are plotted as η-trajectories against their energy position, where η is the strength of the potential that was used to absorb the autodetaching electron from the TNI-state. The stabilized points of the η-trajectories correspond to the TNI-states and are shown inside rectangles.

As far as the TNI-state of the molecular complex that geometrically relax to form the reductively activated CO_2 moiety in the CO_2.HCN molecular complex is concerned, it is the inter-moiety bonding orbital (Fig. 2c) of the complex that is

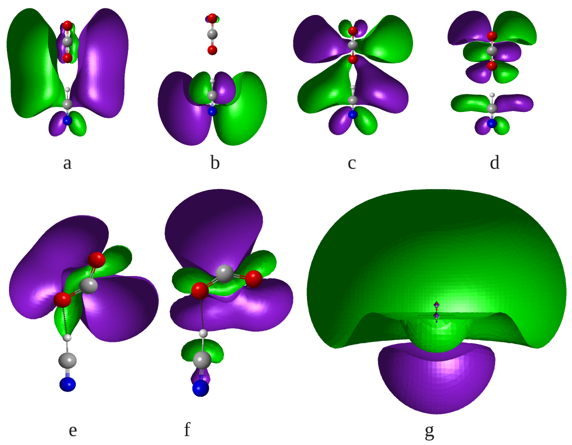

FIG. 2: **Singly occupied orbitals of the electron attached states.** The singly occupied orbitals of the corresponding electron attached states of the CO_2.HCN molecular complex are shown for; (a) and (b) the two π^*-orbitals of the molecular complex resulting from valence-dipole orbital mixing (see text), (c) the inter-moiety bonding orbital, (d) the inter-moiety anti-bonding orbital, (e) and (f) the singly-occupied orbital of the two isomers of the molecular complex with the reductively activated CO_2 moiety, where the excess electron is localized on the CO_2 moiety, and (g) the dipole-bound orbital of CO_2.HCN molecular complex.

responsible for the resonant capture of a free-electron (with kinetic energy 2.75 eV). As discussed earlier, the TNI-states of the CO_2.HCN molecular complex are stable against autodetachment. Because of the long lifetime of the TNI-states of the CO_2.HCN molecular complex, subsequent to the resonant capture of a free-electron into the inter-moiety bonding orbital of the complex, reductive activation of CO_2 moiety occurs via geometrical relaxation of the corresponding TNI-state. On the contrary, in the case of the isolated CO_2 molecule, the average autodetachment decay width of its TNI-state, which is formed after the resonant electron capture of a near 4 eV electron into its extended three-center π^*-orbital, is very high and lies between 0.13 and 0.26 eV [18]. As a result of the significantly large decay width, the geometrical relaxation channels become very week. Even if a small number of TNIs of the isolated CO_2 molecules are converted to the geometry of the reductively activated CO_2 molecule, due to thermodynamically controlled autoionization (i.e., the oxidative-like deactivation process) associated with the negative adiabatic electron affinity of the neutral CO_2 molecule, the reductively activated CO_2 molecules will immediately disintegrate back to its non-reactive neutral form [14].

In order to check the above mentioned thermodynamically controlled deactivation of the reductively activated CO_2 moiety of the molecular complex, we have computed the oxidative-like deactivation path that connects the reductively activated CO_2 to its non-activated equilibrium geometry. The equilibrium molecular geometries and the minimum-energy deactivation paths reported in this work were computed by the second order Møller-Plesset perturbation method. A zero-point energy correction calculated at this level is also applied for the energy values reported here. An augmented Hessian technique with very small step-length (trust radius = 0.001) and repeated Hessian re-computation every five steps were essential to follow the deactivation energy path. The vertical binding energy of the electron along the deactivation path was computed using the EA-EOMCCSD and EA-EOMCCSDt methods [17]. Consistent results for the target and the anionic surfaces were obtained with CCSD/EA-EOMCCSD methods and CCSD(T)/EA-EOMCCSDt methods. In Fig. 3 the deactivation path and the geometric parameters that contribute to the deactivation path (i.e. bending of CO_2 (θ_{COO}), flipping of CO_2 from the molecular axis of HCN (θ_{NHO}), and the hydrogen bond length ($R_{O..H}$)) are shown. Most important result is that the electron is bound all along the minimum energy deactivation path that connects the reductively activated complex to its non-activated equilibrium geometry (see Fig. 3). Hence, the thermodynamic metastability, which couples the reductively activated CO_2 to the neutral CO_2 through the autodetachment of the excess electron, is not pertinent to the molecular complex. The activated complex is stabilized by an energy barrier of 0.35 eV and the excess electron of the reductively activated CO_2.HCN molecular complex is stabilized by a vertical detachment energy (VDE) of 1.82 eV. In sharp contrast to the negative adiabatic electron affinity (AEA) of the isolated CO_2 molecule (-0.66 eV), the AEA of the CO_2.HCN molecular complex is positive, i.e. EA_{ad}=0.1 eV. The singly occupied molecular orbital of the two isomers of the reductively activated molecular complex is shown in Fig. 2 (e) and (f) where the isomers are isoenergetic (0.02 eV). As in the case of reductively activated isolated CO_2, the excess electron is localized on the CO_2 moiety of the complex. Most interestingly, along the deactivation path, the valence-bound anionic state of the reductively activated complex becomes a dipole-bound anionic state.

Since the dipole moment of the neutral complex in its equilibrium linear geometry (3.9 D) is larger than the critical value ($\approx$1.625 D) to bind an excess electron [16], it can also support a dipole-bound anionic state (see Fig. 2g) with a vertical detachment energy of 0.015 eV. Dipole-binding is primarily due to the electrostatic charge-dipole attractive interaction and dispersion interaction between the electron and the molecule [16]. Presently, dipole-bound anions have been produced by free-electron attachment techniques under nozzle expansion conditions, Rydberg electron capture technique and the field detachment charge transfer techniques [19]. It has been demonstrated recently that dipole-binding of an electron can also serve as a doorway to the capture of a near zero-energy electron to form a valence-bound anion [16]. In our case, the dipole-binding is due to the dipolar HCN moiety. It is interesting to note that reverse of the deactivation path shown in Fig. 3 is the conversion path for a dipole-bound anion to a valence-bound anion, i.e. reductive activation of the CO_2 moiety is possible through the dipole-binding of an electron to the HCN moiety. However, the reductive activation

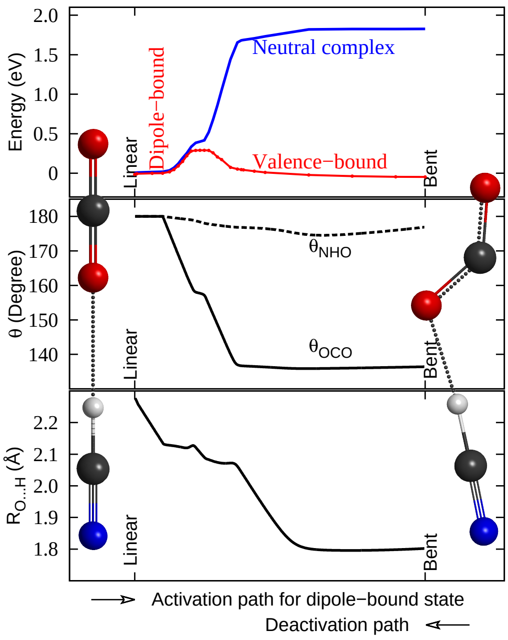

FIG. 3: **Deactivation path for the reductively activated CO$_2$.HCN molecular complex** The minimum energy anionic path, which is analogous to the deactivation path for isolated reductively activated CO$_2$, connects the reductively activated CO$_2$.HCN to the CO$_2$.HCN and is shown (red line) in the upper panel. The variation in the energy of the neutral complex along the deactivation path of the anion is also shown (blue line) in the upper panel. The three prominent geometrical changes that constitute the deactivation path, i.e. θ_{OCO}, θ_{NHO}, $R_{O..H}$, are also shown.

through dipole-binding proceeds via a small thermal energy barrier of 0.30 eV.

It is also important to note that in the absence of an active resonance stabilization mechanism, the fragmentation of the complex into two moieties will be competitive after the resonant capture of the electron. The resonant stabilization process involves the relaxation of the TNI to a stable anion by its interaction (transferring of energy) with the local environment [9]. Hence, an efficient reductive activation may be possible only when HCN and CO$_2$ molecules are present at moderately high vapour pressure. One may also note that, for the CO$_2$.HCN molecular complex, the dissociative electron attachment channels that are competitive for the isolated moieties are either closed or can be accessed only by a higher energy electron compared to the electron energy at which the reductive activation of the CO$_2$ moiety in the CO$_2$.HCN molecular complex is initiated (i.e. 2.75 eV). The interlocking of the hydrogen atom between the -CN group and the oxygen atom prevents its elimination. On the other hand, the dissociative elimination of CO/O$^-$ moiety is initiated only by a higher energy (4-5 eV) electron [20].

In summary, the suppression of the autodetachment of the electron from the CO$_2$.HCN molecular complex provide enough lifetime for the TNI-state to relax its geometry to form the reductively activated bent CO$_2$ moiety. Unlike the metastability of the reductively activated isolated CO$_2$ molecules, the reductively activated moiety of the CO$_2$.HCN molecular complex is thermodynamically stable due to the positive AEA of the molecular complex. Hence a weak molecular complexation of CO$_2$ with the HCN molecule in their ground states help the CO$_2$ molecule to get reductively activated by resonantly capturing a free-electron and to survive in its resulting distonic ion like reactive form. The clear analysis which follows from our accurate numerical findings on the reductively activated CO$_2$.HCN molecular complex makes it clear that the reductive activation predicted and discussed here is by no means limited to the molecular complex of CO$_2$ containing HCN moiety. In principle, it may be expected that the reductive activation mechanism for the CO$_2$ molecule is possible for any heterogeneous molecular cluster or van der Waals molecular complexes of CO$_2$ containing strongly dipolar moieties via the resonance capture of a low-energy-electron or via the dipole-binding of a near zero energy electron.

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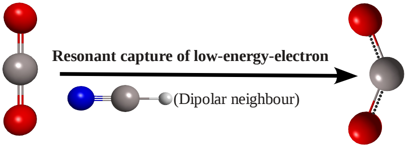

The low-energy-electron induced conversion of non-reactive CO_2 molecule to its permanently reactive distonic-type radical anion.