Dissociative electron attachment in C₂H via electronic resonances

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Investigation of microwave-activated CH₄/H₂ plasma used in chemical vapor deposition of diamond revealed the presence of electronically excited C₂^{-*} (B²Σ_u⁺). Using high-level electronic structure methods, we investigate electronic structure of C₂H⁻ and suggest possible routes for formation of C₂⁻ in the ground (X²Σ_g⁺) and excited (B²Σ_u⁺) states via electronic resonances. To describe electronically metastable states, we employ the equation-of-motion coupled-cluster method augmented by the complex absorbing potential. The resonance wavefunctions are analyzed using natural transition orbitals. We identified several resonances in C₂H⁻, including the state that may lead to C₂^{-*} (B²Σ_u⁺).

I. INTRODUCTION

In high-energy environments, electrons have sufficient energy to overcome their attraction to the nuclei, giving rise to a fourth state of matter: plasma. Plasma consists of charged particles (electrons, ions) and metastable atomic and molecular species. Plasma constitutes 99.999% of the visible universe, as it is the main component of stars. In our everyday lives, plasma is generated by electric discharge such as in lightning or in plasma TVs. Cosmic radiation produces plasmas in the atmosphere, giving rise to the northern lights. Plasma can also be generated in the course of decomposition of energetic materials.

Plasma can play an important role in chemistry. Free electrons can attach themselves to molecules forming stable or transient anions. Depending on the type of orbital to which the electron attaches different types of structural transformations ensue. This electron-induced chemistry^{1,2} is akin to photochemistry³, wherein the bonding pattern of a molecule is altered by promoting electrons from occupied to virtual orbitals. An example of an electron-induced reaction is dissociative electron attachment (DEA), in which molecules fall apart upon the attachment of an electron⁴⁻⁷. DEA occurs in interstellar media, planetary atmospheres, radiolysis, and in plasma reactors. One fascinating example^{8,9} of DEA is double-strand breaking in DNA by slow electrons: electrons with energies as low as 1-2 eV can break two covalent bonds (of total energy ~10 eV) in DNA. In these examples, DEA

(or, more generally, plasma-induced processes) are of a destructive nature: plasma breaks molecules apart. Significant efforts have been directed towards controlling and mitigating such electron-induced processes in fusion reactors and in cases of matter exposed to high-energy radiation. In contrast, some technologies exploit the destructive ability of plasma to clean NO_x and SO_x from the exhaust of power plants and engines as well to remove organic pollutants from contaminated water^{10–14}.

Recently, significant efforts have been directed towards exploiting plasma-induced chemistry in a more constructive way, for example, to use electrons for making new molecules that are difficult to make by other means. One historic example of that nature is nitrogen fixation by electric arc—before the Haber-Bosch process was developed to its full potential, the Birkeland-Eyde process was used on an industrial scale. If we can use plasma for converting nitrogen into chemically bound forms¹⁴, then, perhaps, we can use electrons to facilitate such stubborn processes as methane activation^{15–17} of carbon dioxide reduction¹⁸.

The idea of electron catalysis has been around for quite some time^{2,12,19,20}, yet there are no examples of new, controlled chemistry deliberately achieved via electron attachment. The challenge in developing new chemistry is that we do not understand processes initiated by electron attachment to even rather small molecules. Superficially, electron-induced processes are similar to photochemistry, which is a mature field: there are many established photochemical synthetic reactions, e.g., electrocyclic and Norrish reactions, routinely used in the lab and even on an industrial scale. Quantum chemistry, both conceptual (molecular orbital theory) and quantitative, has been instrumental for developing a mechanistic understanding of photochemistry³. However, this arsenal of tools cannot be routinely applied to study DEA because of the nature of the initial state, which is metastable with respect to electron ejection. This metastable nature is the main stumbling block for the theoretical modeling of electron-induced processes.

States that are metastable with respect to electron detachment are called resonances^{7,21–24}; they have finite lifetime and decay by ejecting an electron. Hence, resonances are located above the electron detachment (or ionization) threshold and belong to the continuum part of the spectra. Resonances play an important role in plasma physics, atmospheric chemistry, fusion reactors, interstellar medium, and in other high-energy environments. These states can be produced by electronic excitation, ionization, or electron attachment. Recent theoretical developments have extended standard quantum chemistry

approaches, such as equation-of-motion coupled-cluster (EOM-CC) theory^{25–27}, to treating resonances²⁴, by using non-Hermitian quantum mechanics framework^{21,23,24,28}. These tools (as well as related CAP-SAC-CI methods²⁹) have been used to study a variety of processes, ranging from spectroscopy of stable and transient anions^{30–32}, possible routes of astrochemical formation of cyano-polyynes³³, DEA in chloroethylenes³⁴, and electron-transfer reactions³⁵.

In this contribution, we employ EOM-CC methods^{25–27} augmented with the complex absorbing potential (CAP)^{24,36,37} to interrogate electronic structure and DEA in C_2H^- . This study is motivated by the observation of electronically excited C_2^- (detected via fluorescence) in carbon-rich plasmas³⁸, such as microwave activated plasma in chemical vapor deposition (CVD) of diamond. C_2H^- is also relevant for astrochemistry, along with other molecular anions detected in interstellar medium and planetary atmospheres, such as CN^- , C_{2n}H^- , $\text{C}_{2n+1}\text{N}^-$, benzonitrile, etc^{39–45}.

Although C_2^- is commonly occurring in many high-energy environments^{38,46–48}, the mechanism of its formation is not fully understood. From the observed spatial distribution and its variation with changes in process conditions, the experimentalists deduced³⁸ that both ground- and excited-state C_2^- ($X^2\Sigma_g^+$ and $B^2\Sigma_u^+$, respectively) are formed directly via DEA to C_2H :

C_2^- is also formed by the DEA to acetylene⁴⁹, but it was concluded³⁸ that this channel is predominantly responsible for the production of the ground-state species. The authors³⁸ have also ruled out the formation of C_2^{-*} by other processes, such as electron attachment to C_2 or electron-impact excitation of C_2^- . The conclusion of this detailed analysis is well supported by the data³⁸, however, no explanation was given of how exactly electronically excited C_2^{-*} is formed. The goal of our study is to clarify this issue. We report the calculations of bound and metastable states of C_2H^- . By using wave-function analysis tools, we identified orbital character of the computed resonances. The main finding is that at the neutral ground-state geometry of C_2H , the anion has several resonances of $\pi \rightarrow \pi^*$ type, but none of them has antibonding character along the CH bond and none correlates with the excited C_2^{-*} ($B^2\Sigma_u^+$). The states that can lead to the CH bond dissociation appear only when the C-H bond is elongated, including the resonance that correlates with the $B^2\Sigma_u^+$ state of C_2^- . The

implications of this observation and similarities with other DEA processes⁹ are discussed below.

In what follows we first describe methods and computational protocols, followed by the discussion of electronic structure of C_2^- and C_2H^- . We then discuss potential energy scans and correlation diagram along the CH bond and discuss possible mechanism of C_2^{*-} formation.

II. THEORETICAL METHODS AND COMPUTATIONAL DETAILS

EOM-CC framework enables treating diverse types of electronic structure^{25–27,50–56}, including electronically excited and open-shell species⁵⁷. EOM-CC produces size-intensive transition energies for electronic excitations, ionization, or attachment. It treats non-dynamic and dynamic correlation in a single computational step and its accuracy can be systematically improved up to the exact solution. The major advantage of EOM-CC is its ability to treat different types of states in a balanced fashion by employing the same model Hamiltonian (similarity transformed $\bar{H}$). In particular, EOM-CC describes closed- and open-shell species on an equal footing, which enables meaningful comparisons of the energies of the anionic and the neutral states, as well as metastable and near-threshold bound states.

FIG. 1: Manifolds of target states accessed by EOM-IP and EOM-EE. In both variants, the same closed-shell reference is used. EOM-IP-CCSD describes open-shell doublet states by employing ionizing operators of the $1h$ and $2h1p$ types. EOM-EE-CCSD describes electronically excited states by employing electron-conserving excitation operators of the $1h1p$ and $2h2p$ types.

Here we apply EOM-CCSD to investigate the electronic spectrum of C_2H^- below and above the electron-detachment continuum onset. Fig. 1 illustrates the target-state manifolds accessed by EOM-EE and EOM-IP. In both calculations the same closed-shell reference state

is used; consequently all relevant states are represented with the same set of orbitals and computed using the same effective Hamiltonian,

$$\bar{H} \equiv e^{-\hat{T}} H e^{\hat{T}}, \quad (2)$$

where operator $\hat{T}$ comprises coupled-cluster amplitudes of the reference state. Here, the reference wave function corresponds to the closed-shell ground-state CCSD solution for the C_2H^- (N -electron system). The diagonalization of $\bar{H}$ in the respective sectors of Fock space yields amplitudes of the EOM operators. We determined the electron-detachment thresholds and properties of the parent neutral radical by the EOM-IP variant of the method in which the target $N - 1$ -electron states are described by the EOM operators that remove one electron (i.e., of the $1h$ and $2h1p$ types). To study bound excited states, we employed the EOM-EE variant in which the target N -electron states are described by the EOM operators that excite one or two electrons (i.e., $1h1p$ and $2h2p$). In calculations of C_2^{2-} , we used EOM-IP-CCSD with the dianionic reference state (C_2^{2-}). To describe N -electron metastable states embedded in the electron-detachment continuum, we augment the standard EOM Hamiltonian by CAP^{36,37}, which gives rise to the CAP-EOM-EE-CCSD ansatz^{24,58–62}. Note that the onset of the continuum in EOM-EE exactly corresponds to the electron detachment energy obtained from EOM-IP, which allows one to unambiguously distinguish between the bound and continuum states.

The CAP^{24,36,37,58,59} approach entails augmenting the standard Hamiltonian $\hat{H}_0$ with an imaginary potential

$$\hat{H}(\eta) = \hat{H}_0 - i\eta\hat{W}(r), \quad (3)$$

where η represents the strength of the CAP. The imaginary potential absorbs the diverging tail of a metastable state making it $\mathcal{L}^2$ -integrable. The eigen-energies of the CAP-augmented Hamiltonian are complex. The real part is the position of the metastable state and the complex part is the resonance width (which is inversely proportional to the lifetime of the resonance). In our calculations, the CAP is quadratic with cuboid shape

$$\hat{W}(r) = \hat{W}_x(r_x) + \hat{W}_y(r_y) + \hat{W}_z(r_z), \quad (4)$$

with

$$\hat{W}_\alpha(r_\alpha) = \begin{cases} 0 & \text{if } |r_\alpha| \leq r_\alpha^0 \\ (|r_\alpha| - r_\alpha^0)^2 & \text{otherwise,} \end{cases} \quad (5)$$

where the coordinates (r_x^0, r_y^0, r_z^0) define the onset of the CAP in each dimension. Following the same protocol as in previous studies^{58,59}, we fixed the CAP onset at the spatial extent of the wave function for the reference state, $R = \sqrt{\langle \Psi_{CCSD} | R | \Psi_{CCSD} \rangle}$, where Ψ_{CCSD} is the CCSD solution (CAP-free) for the ground state of the anion. In our calculations here, we include CAP already at the Hartree-Fock level, in contrast to the projective CAP approach used in combination with SAC-CI ansatz by Ehara and Sommerfeld²⁹.

The optimal value of CAP's strength parameter η is determined for each metastable state by calculating η -trajectories and searching for the minimum of the function^{37,63}:

$$|\eta \frac{dE(\eta)}{d\eta}| = \min. \quad (6)$$

This procedure minimizes the error introduced by the finite-strength of CAP used in incomplete one-electron basis sets. More accurate resonance parameters can be obtained if, instead of considering the raw η -trajectories $E(\eta)$, one analyzes the η -trajectories of deperturbed energies $U(\eta)$ from which the explicit dependence of CAP is removed in the first order⁵⁹. The deperturbed complex energies $U(\eta)$ are calculated by subtracting from raw energies $E(\eta)$ the correction $i\eta T[\gamma W]$, where γ is the one-particle density matrix of the resonance state.

To analyze the transition properties between the EOM-CCSD states, we employ reduced quantities such as one-particle transition density matrices, natural transition and Dyson orbitals. These objects are related to concrete physical observables and provide a way to derive a molecular orbital picture of the many-body wave functions^{64,65}. The one-particle transition density matrix⁶⁶⁻⁷¹ (1PTDM) connecting two many-body wave functions Ψ_I and Ψ_J is

$$\gamma_{pq}^{IJ} = \langle \Psi_I | p^\dagger q | \Psi_J \rangle. \quad (7)$$

1PTDM can be used to compute one-electron transition properties such as oscillator strengths, transition dipole moments, non-adiabatic and mean-field spin-orbit couplings. The norm of γ^{IJ} provides a measure of one-electron character of the transition⁷². The

1PTDM provides a compact representation of the difference between the two states in terms of hole-particle excitations. Singular-value decomposition of γ^{IJ} yields a set of left and right eigenvectors

$$\gamma^{IJ} = U\Sigma V^T, \quad (8)$$

which define hole (ψ_K^h) and particle (ψ_K^e) orbitals corresponding to singular value σ_K (elements of the diagonal matrix Σ)

$$\psi_K^h = \sum_q U_{qK} \phi_q, \quad (9)$$

$$\psi_K^e = \sum_q V_{qK} \phi_q. \quad (10)$$

Such pairs of hole and particle orbitals are called NTOs (natural transition orbitals). The renormalized squares of singular values (σ_K^2) can be interpreted as weights of each NTO pair in the exciton wave function.

In non-Hermitian formalism, the electronic resonances have complex energy and complex densities whose real and imaginary components are⁶²

$$Re\gamma_{pq}^{IJ} = \langle \Psi_I^{Re} | p^\dagger q | \Psi_J^{Re} \rangle - \langle \Psi_I^{Im} | p^\dagger q | \Psi_J^{Im} \rangle, \quad (11)$$

$$Im\gamma_{pq}^{IJ} = \langle \Psi_I^{Im} | p^\dagger q | \Psi_J^{Re} \rangle + \langle \Psi_I^{Re} | p^\dagger q | \Psi_J^{Im} \rangle. \quad (12)$$

The analysis of real part 1PTDM provides information about the orbitals involved in the transition, similar to bound-state analysis. The imaginary part analysis provides insight into the coupling of the resonance with the continuum and its decay channels⁶².

A. Computational details

All calculations were performed using the Q-Chem electronic structure program^{73,74}. The geometry optimizations of C_2H and its anion were performed with EOM-IP-CCSD and CCSD, respectively, using the aug-cc-pVTZ basis set. Electronic states of the neutral C_2H at the neutral and anionic geometries were computed using EOM-IP-CCSD, as electron detachment from C_2H^- . The aug-cc-pVTZ basis set was augmented by the $3s3p1d$ diffuse functions on carbons and on hydrogen. The exponents of the additional diffuse functions

were generated in an even-tempered manner, starting with the most diffuse function in the original basis set. The exponents of the first additional basis functions: $\alpha(\text{C},s) = 0.02201$, $\alpha(\text{C},p) = 0.017845$, $\alpha(\text{C},d) = 0.050000$, $\alpha(\text{H},s) = 0.01263$, $\alpha(\text{H},p) = 0.051000$, $\alpha(\text{H},d) = 0.123500$; the exponents of the subsequent sets were obtained according to $\alpha_{i+1} = 05 \cdot \alpha_i$.

We computed electronic resonances for C_2H^- with CAP-EOM-EE-CCSD/aug-cc-pVTZ+3s3p1d at the equilibrium geometry of the neutral, as well as stretched and bend geometries. Ground and excited states of C_2^- were computed using EOM-IP-CCSD/aug-cc-pVTZ with the dianionic⁷⁵ reference (C_2^{2-}), as described in detail in Ref. 75. Core orbitals were frozen in all calculations. All calculations used pure angular momentum polarization functions.

III. RESULTS AND DISCUSSION

A. Electronic structure of C_2^-

We begin by reviewing electronic states of C_2^- . To describe this open-shell molecule, we employ EOM-IP-CCSD with the dianion (C_2^{2-}) closed-shell reference. The dianionic reference is well-behaved (at least, up to the aug-cc-pVTZ basis)⁷⁵ and have been used to describe the electronic structure of C_2 , C_2^- , and C_2^{2-} .

FIG. 2: Molecular orbital diagram and electronic configuration of the ground electronic state of C_2^- . ‘Core’ denotes the three lowest molecular orbitals.

Fig. 2 shows molecular orbitals and electronic configuration of the ground electronic state of C_2^- ($X^2\Sigma_g^+$). Note that the singly occupied molecular orbital is of a σ -type and has a partial bonding character with respect to the two carbons. Table I shows the vertical

excitation energy to $A^2\Pi_u$ and $B^2\Sigma_u^+$ obtained using EOM-IP-CCSD/aug-cc-pVTZ at the equilibrium geometry of C_2^- ($X^2\Sigma_g^+$). The computed energy gap between $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$ is 2.45 eV, which is in perfect agreement to the fluorescence signal observed in the CVD experiment.³⁸ We also characterize the NTOs for excitation from the ground state of C_2^- ($X^2\Sigma_u^+$) to the $A^2\Pi_u$ and $B^2\Sigma_u^+$ excited states. NTOs are shown in Fig. 3; their shapes are consistent with molecular orbitals and electronic configuration in Fig. 2.

TABLE I: Excitation energies and oscillator strength for C_2^- at $R_{CC} = 1.219$ Å using EOM-IP-CCSD/aug-cc-pVTZ with the dianionic reference (C_2^{2-}).

State	E_{ex} , eV	f
$A^2\Pi_u$	0.57	0.01
$B^2\Sigma_u^+$	2.45	0.09

FIG. 3: Natural transition orbitals for the $X^2\Sigma_g^+ \rightarrow A^2\Pi_u$ and $X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ transitions in C_2^- at the equilibrium geometry of C_2^- using EOM-IP-CCSD/aug-cc-pVTZ with the dianionic reference.

Recall that the motivation of this study comes from the experimental observation of fluorescence at 541 nm (2.28 eV) in a microwave-activated plasma; this transition corresponds to the emission from $B^2\Sigma_u^+$ to $X^2\Sigma_u^+$. Molecular orbital picture of this transition (shown in Fig. 3) sets the parameters for the electronic structure of the precursor state. To form the excited state ($B^2\Sigma_u^+$) of C_2^{*-} from an electronic resonance of C_2H^- , the precursor resonance state should have NTOs that are similar to the NTOs of $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ transition shown Fig. 3: both should be of a σ -type, the hole NTO should have a node in the C-C bond and the particle NTO should have no node in the C-C bond. In a precursor state for the ground-state C_2^- ($X^2\Sigma_u^+$) the NTOs should be of the same type, but the hole and particle NTOs should be reversed. In addition, the precursor states for forming C_2^- should have a node in the C-H bond, to yield a repulsive potential. These considerations guide our analysis

FIG. 4: Molecular orbital diagram and electronic configuration of the ground electronic state of C_2H^- . ‘Core’ denotes the three lowest molecular orbitals. σ_2^* is of antibonding character with respect to CC and of bonding character with respect to CH.

of the C_2H^- resonances below.

B. Electronic structure of C_2H^-

Molecular orbitals diagram and electronic configuration of the ground-state C_2H^- are shown in Fig. 4. C_2H^- is a closed-shell anion, isoelectronic with CN^- . The shapes of the orbitals are similar to those in C_2^- (Fig. 2) and in CN^- . Fig. 5 shows computed detachment energies of the anion at different geometries. The ground state of C_2H corresponds to the detachment from a σ -type orbital, giving rise to $^2\Sigma^+$ state, whereas the detachment from a π -type orbital gives rise to a higher $^2\Pi$ -state; this pattern is similar to that of CN (see, for example, Ref. 33), although the gap between the Σ and Π states is smaller in C_2H (0.7 eV versus 2 eV in CN). The computed VDE (3.02 eV) is close to the experimentally determined adiabatic detachment energy^{76–78} (2.9–3.0 eV).

TABLE II: Resonance positions E_R (eV) and widths Γ (eV) at the equilibrium geometry of neutral C_2H using CAP-EOM-EE-CCSD/aug-cc-pVTZ+3s3p1d.

State	$E_R^{(0)}$	$\Gamma^{(0)}$	$E_R^{(1)}$	$\Gamma^{(1)}$
$\text{A}^3\Sigma^+$	5.54	0.44	5.59	0.33
$\text{B}^3\Pi$	5.74	0.67	5.80	0.51
$\text{C}^3\Delta$	6.17	0.61	6.25	0.47
$\text{D}^3\Sigma^-$	6.61	0.86	6.66	0.77
$\text{E}^1\Sigma^-$	6.64	0.91	6.69	0.87
$\text{F}^1\Delta$	6.73	1.12	6.77	1.06

FIG. 5: Vertical detachment energies and the respective Dyson orbitals of C_2H^- at different geometries.

TABLE III: NTOs (real part)^a at the equilibrium geometry of the neutral ($R_{\text{CC}} = 1.204$ Å and $R_{\text{CH}} = 1.062$ Å).

State	Type	σ^2	Hole	Particle
$\text{A}^3\Sigma^+$	$\pi \rightarrow \pi^*$	0.454		
		0.454		
$\text{B}^3\Pi$	$\sigma \rightarrow \pi^*$	0.894		
$\text{C}^3\Delta$ ($\text{F}^1\Delta$)	$\pi \rightarrow \pi^*$	0.451 (0.498)		
		0.451 (0.498)		
$\text{D}^3\Sigma^-$ ($\text{E}^1\Sigma^-$)	$\pi \rightarrow \pi^*$	0.468(0.473)		
		0.468 (0.473)		

^a Singlet and triplet resonances have very similar NTOs, hence, only triplet NTOs are shown. The singular values are slightly different (singlet σ_K^2 are shown in parenthesis).

The continuum begins at the detachment threshold and electronic states above the threshold are the resonances. Resonances were computed with CAP-EOM-EE-CCSD at the equi-

librium geometry of the neutral. Here we report resonance positions with respect to the ground state of the anion. Energies of the resonances with respect to the detachment threshold can be obtained by subtracting the VDE (3.02 eV). Table II lists all identified resonances below 10 eV; the corresponding η -trajectories are shown in the SI. The respective NTOs are shown in Table III. C_2H^- is isoelectronic to CN^- and their low-lying states have similar character³³— even the order of resonance states follows the same pattern. We identified 4 triplet resonances at 5.59-6.66 eV (2.57-3.64 eV above the threshold) and 2 singlet resonances at 6.7-6.8 eV (3.67-3.75 eV above the threshold). As in the CN^- case, the singlet resonances are broader than the triplet ones. Qualitatively, our results agree with the R -matrix calculations of Harrison and Tennyson⁷⁹, although our symmetry assignments are different. The differences in resonance positions and widths between the 2 sets of calculations follow the same trends as in CN^- and cyanopolyyne anions and can be attributed to the different treatment of electron correlation³³.

Among these multiple resonances, there is none with a hole NTO that has a node in the C-C bond and particle NTO that has a node in the C-H bond. Hence, none of the computed resonances show dissociative (C-H) character and none correlate with either ground-state ($\text{X}^2\Sigma_g^+$) or excited ($\text{B}^2\Sigma_u^+$) C_2^- . Because the character of the electronic state needs to change, one should anticipate a barrier along the dissociation coordinate.

In search of possible precursor states, we repeated the calculations at geometries with the stretched C-H bond. With C-H bond stretched by 0.6 Å (at $R_{\text{CH}} = 1.66$ Å), states of a desired orbital character (i.e., corresponding to excitations to σ and σ^* -type orbitals) appeared. The results of the calculation are summarized in Tables IV and V. The three lowest states show clear antibonding character with respect to CH. We observe two electronically bound states, $\text{a}^3\Sigma^+$ and $\text{b}^3\Pi$, derived by excitation from σ and π occupied orbitals to a σ^* -type orbital. These two states correlate electronically with the ground ($\text{X}^2\Sigma_g^+$) or excited ($\text{A}^2\Pi_u$) states of C_2^- . The $\text{A}^3\Sigma^+$ resonance starts to show a contribution of an additional NTO pair in which the hole orbital has a node in the C-C bond and the particle orbital has a node in the CH bond and no node in the CC bond. This means that this state can yield a repulsive CH potential and electronically correlates with C_2^{-*} ($\text{B}^2\Sigma_u^+$).

To test the effect of bending vibration on the resonance, we carried out calculations at a geometry with a CCH bend at a stretched neutral geometry. The right panel in Fig. 5 shows the vertical detachment energies and the corresponding Dyson orbitals at the bend

TABLE IV: Resonance positions E_R (eV) and widths Γ (eV) at a stretched geometry ($R_{CC} = 1.204 \text{ \AA}$ and $R_{CH} = 1.662 \text{ \AA}$); CAP-EOM-EE-CCSD/aug-cc-pVTZ+3s3p1d.

State	$E_R^{(0)}$	$\Gamma^{(0)}$	$E_R^{(1)}$	$\Gamma^{(1)}$
$a^3\Sigma^+(\text{bound})$	3.06	-	-	-
$b^3\Pi(\text{bound})$	3.14	-	-	-
$A^3\Sigma^+$	5.22	0.29	5.25	0.31
$B^3\Pi$	5.92	0.73	5.81	0.57
$C^3\Delta$	6.22	0.68	6.13	0.55
$D^3\Sigma^-$	6.60	1.00	6.47	0.93
$E^1\Sigma^-$	6.61	1.09	6.48	1.00
$F^1\Delta$	6.65	1.24	6.49	1.16

TABLE V: NTOs (real part) at stretched geometry ($R_{CC} = 1.204 \text{ \AA}$ and $R_{CH} = 1.662 \text{ \AA}$.)

State	Type	σ^2	Hole	Particle
$a^3\Sigma^+(\text{bound})$	$\sigma \rightarrow \sigma^*$	0.807		
$b^3\Pi(\text{bound})$	$\pi \rightarrow \sigma^*$	0.787		
$A^3\Sigma^+$	$\sigma^* \rightarrow \sigma^*$	0.380		
	$\pi \rightarrow \pi^*$	0.261		
	$\pi \rightarrow \pi^*$	0.261		

TABLE VI: Resonance positions E_R (eV) and widths Γ (eV) at a stretched and bend geometry ($R_{CC} = 1.204 \text{ \AA}$, $R_{CH} = 1.662 \text{ \AA}$, and $\angle CCH = 170^\circ$); CAP-EOM-EE-CCSD/aug-cc-pVTZ+3s3p1d.

State	$E_R^{(0)}$	$\Gamma^{(0)}$	$E_R^{(1)}$	$\Gamma^{(1)}$
$a^3A'(\text{bound})$	3.00	-	-	-
$b^3A'(\text{bound})$	3.14	-	-	-
$c^3A''(\text{bound})$	3.12	-	-	-
A^3A'	5.25	0.29	5.23	0.27
B^3A'	5.85	0.70	5.79	0.60
C^3A''	5.92	0.73	5.81	0.57
D^3A''	6.25	0.74	6.17	0.59
E^3A''	6.60	1.09	6.49	1.03

and stretched neutral geometry. Table VI shows the resonance positions and widths, and the respective NTOs are shown in Table VII. Due to symmetry lowering, the degeneracy of the Π states is lifted. Table VII also compares each resonance with resonances obtained

TABLE VII: NTOs (real part) at stretched and bend geometry ($R_{CC} = 1.204 \text{ \AA}$, $R_{CH} = 1.662 \text{ \AA}$, and $\angle CCH = 170^\circ$).

State	SVD(σ^2)	Hole	Particle	Similar
$^3A'$ (bound)	0.790			$^3\Sigma^+$
$^3A'$ (bound)	0.785			$^3\Pi$
$^3A''$ (bound)	0.789			$^3\Pi$
$^3A'$	0.421			$^3\Sigma^+$
	0.209			
	0.240			
$^3A'$	0.714			$^3\Pi$
	0.162			
$^3A''$	0.876			$^3\Pi$
$^3A''$	0.464			$^3\Delta$
	0.444			
$^3A''$	0.461			$^3\Sigma^-$
	0.493			

^a Correlation between states at bend and stretched geometry with states obtained at linear geometry.

from just stretched geometry. Overall, bending does not seem to have significant effect on the character of the states and their energies.

To summarize, the resonance state $A^3\Sigma^+$ has all nodal features that can lead to a formation of excited C_2^* ($B^2\Sigma_u^+$). We also observe that one of the bound excited states of C_2H^- ($a^1\Sigma^+$) correlates with the ground state of C_2^- ($X^2\Sigma_g^+$), while another correlates with the $A^2\Pi_u$ state.

Fig. 6 shows an overview of the low-lying electronic states at the three different geometries. On the left panel, the electronic states of the C_2H^- anion at the neutral geometry are shown. The middle panel shows the electronic states of C_2H^- anion with a stretched C-H bond. The ground state of the stretched C_2H^- is higher than the ground state of C_2H^- ,

which shifts all states to higher energy. At this geometry, the character of the states changes and the 3 lowest states show an antibonding CH character. The two lowest states are electronically bound (vertically) and correlate with the two lowest states of C_2^- . The third state, $A^3\Sigma^+$, is a resonance with electronic configuration that correlates with the $B^2\Sigma_u^+$ state of C_2^{*-} . The right panel of Fig. 6 shows the ground and excited states of C_2^- relative to the ground state of C_2H^- anion (to compare energy of C_2^- with C_2H^- , the energy of hydrogen atom, -0.5 Hartree, was added to the energy of C_2^-). The comparison of states allows us to establish a correlation diagram suggesting the formation of the ground-state of C_2^- via the $a^3\Sigma^+$ bound excited state of C_2H^- and formation of the excited state of C_2^{*-} ($^2\Sigma_u^+$) via the $A^3\Sigma^+$ resonance state of C_2H^- .

To estimate relative energies more accurately, we computed energy differences between total energies of the lowest state of the anions at the 3 geometries: ground-state neutral C_2H (as in panel 2 in Fig. 6), the geometry with a stretched CH bond (as in panel 3 in Fig. 6), and at the dissociation limit (as in panel 4 in Fig. 60; the respective energies are given in Table ?? in the SI. This calculation shows that the ground electronic state of the anion with the stretched bond is 2.519 eV above the ground electronic state of the anion at the equilibrium geometry of the neutral ground state. The dissociation limit (C_2^- ($X^2\Sigma_g^+$) + H) is 5.289 eV above and the excited-state dissociation limit (C_2^- ($B^2\Sigma_u^+$) + H) is 7.74 eV above the ground-state energy of C_2H^- at the equilibrium geometry of the neutral. Hence, all resonances below 10 eV (see Table II) have enough energy to produce ground-state C_2^- , but not C_2^- ($B^2\Sigma_u^+$). For this channel to open up, additional ~ 2 eV are needed. We note that the experiment was carried out in high-energy plasma, which was microwave activated. Thus, electron attachment to rotationally and vibrationally hot molecules could lead to the formation of C_2^- ($B^2\Sigma_u^+$). If the bond is already stretched up to 1.662 Å (which is equivalent to imparting 2.8 eV to the neutral C_2H or 2.5 eV to the C_2H^-) then resonances above 5.2 eV (vertically) can lead to the formation of excited C_2^- . Although the temperature of the plasma in the CVD experiment³⁸ is an order of magnitude lower than the required amount (2,900 K versus 29,000 K ≈ 2.5 eV), there should be sufficient number of highly energetic molecules capable of forming C_2^{*-} . Indeed, by using the Maxwell-Boltzmann distribution, we estimate that 0.02% of molecules have energy above 29,000 K.

We note that the shape of the potential energy surfaces of C_2H and C_2H^- (as well as larger species from this family) has implications for astrochemical routes of formation of

carbon-chain anions⁸⁰.

FIG. 6: Right: Electronic states of C_2H^- at the ground state equilibrium geometry of the neutral. Middle: Electronic states of C_2H^- at the geometry with an elongated C-H bond. Left: Electronic states of C_2^- at the equilibrium geometry of C_2^- ($X^2\Sigma_g^+$).

This observed pattern is suggestive of multiple processes initiated by the electron capture by C_2H . Attachment of electrons with energies below 10 eV to cold molecules can lead to multiple resonances of π^* type, which can inter-convert in the course of non-adiabatic dynamics. For example, a π -type resonance can undergo a transition to a σ -type resonance. Energetically, all identified resonances can lead to the CH bond fission and the formation of the ground-state C_2 . However, the excited-state channel require additional 2.5 eV of energy; hence, it can be accessed only by electron attachment to highly energetic molecules. Importantly, none of the resonances identified at the equilibrium geometry of C_2H correlate electronically to either C_2^- or C_2^{*-} ; only when CH bond is sufficiently stretched, the resonance states of the desired orbital character appear. This suggests that the formation of C_2^-/C_2^{*-} can occur either diabatically, via electron capture by the molecules with stretched CH bonds into $a^3\Sigma^+$ or $A^3\Sigma^+$, or non-adiabatically, by forming another type of a resonance that, given sufficient energy, can adiabatically evolve into the desired state.

This is reminiscent to the proposed mechanism of double-strand breaking in DNA⁴⁻⁷: it is believed that the capture of the electron proceeds via a π^* -type resonance that undergoes

a non-adiabatic transition to a σ^* -type resonance leading to eventual bond-breaking. This motif is also similar to photochemical bond breaking in aromatic molecules, such as pyrrole: the essential feature of photoinduced dynamics⁸¹ in many heteronuclear aromatic compounds is that the initial excitation to the bright $^1\pi\pi^*$ state eventually leads to the X-H bond breaking via non-adiabatic transition to a $\sigma\sigma^*$ state.

IV. CONCLUSION

We presented a detailed electronic structure analysis of the bound and metastable states in C_2H^- . By analyzing the characters of the states by means of NTOs, we identified possible precursor states that can lead to the formation of the ground-state and electronically excited C_2^- observed in carbon-rich plasmas. To fully elucidate the mechanism of DEA requires dynamics simulations including non-adiabatic transitions and we hope that our results lay a ground-work for future, more detailed investigations of DEA. By investigating DEA C_2H^- , we identified intriguing similarities with DEA in and photochemical processes in more complex systems (aromatic heterocycles). This study contributes towards better understanding of electron-induced processes occurring in nature and explored in existing and emerging technologies.

Data Availability

Data available in article or supplementary material.

Conflicts of interest

A.I.K. is the president and a part-owner of Q-Chem, Inc.

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- ¹ C. R. Arumainayagam, H.-L. Lee, R.B. Nelson, D. R. Haines, and R. P. Gunawardane, Low-energy electron-induced reactions in condensed matter, *Surf. Sci. Rep.* **65**, 1 (2010).
- ² H. Chevreau, F. Gardebien, C. Dezarnaud-Dandine, and A. Sevin, On the potential catalytic role of electron capture in gas-phase condensation reactions: A theoretical exploratory study of the CH₂O₂ and CH₃ON systems, *ChemPhysChem* **2**, 583 (2001).
- ³ J. Michl and V. Bonačić-Koutecký, *Electronic Aspects of Organic Photochemistry*. Wiley, New York, 1990.
- ⁴ J. Simons, Molecular anions, *J. Phys. Chem. A* **112**, 6401 (2008).
- ⁵ J. Simons, Theoretical study of negative molecular ions, *Annu. Rev. Phys. Chem.* **62**, 107 (2011).
- ⁶ J. Simons, Detachment processes for molecular anions, in *Photoionization and Photodetachment*, edited by C. Y. Ng, volume 10, Part II of *Advanced Series in Physical Chemistry*. World Scientific Publishing Co., Singapore, 2000.
- ⁷ J. M. Herbert, The quantum chemistry of loosely-bound electrons, *Rev. Comp. Chem.* **28**, 391 (2015).
- ⁸ B. Boudaïffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, Resonant formation of DNA strand breaks by low-energy (3 to 20 eV) electrons, *Science* **287**, 1658 (2000).
- ⁹ J. Simons, How do low-energy (0.1-2 eV) electrons cause DNA-strand breaks?, *Acc. Chem. Res.* **39**, 772 (2006).
- ¹⁰ B.M. Penetrante, M.C. Hsiao, J.N Bardsley, B.T. Merritt, G.E. Vogtlin, A. Kuthi, C.P. Burkhardt, and J.R. Bayless, Identification of mechanisms for decomposition of air pollutants by non-thermal plasma processing, *Plasma Sources Sci. Technol.* **6**, 251 (1997).
- ¹¹ T. Matsumoto, D. Y. Wang, T. Namihira, and H. Akiyama, Energy efficiency improvement of nitric oxide treatment using nanosecond pulsed discharge, *IEEE Transactions on Plasma Science* **38**, 2639 (2010).
- ¹² P. Rumbach and D.B. Go, *Topics in Catalysis*, volume 56, chapter Perspectives on Plasmas in Contact with Liquids for Chemical Processing and Materials Synthesis. Springer, 2013.
- ¹³ S. M. Thagard, G. R. Stratton, F. Dai, C. L. Bellona, T. M. Holsen, D. G. Bohl, E. Paek, and E. R. V. Dickenson, Plasma-based water treatment: Development of a general mechanistic

- model to estimate the treatability of different types of contaminants, *J. Phys. D: Appl. Phys.* **50**, 014003 (2017).
- ¹⁴ P. Mehta, P. Barboun, F. A. Herrera, J. Kim, P. Rumbach, D.B. Go, J.C. Hicks, and W.F. Schneider, Overcoming ammonia synthesis scaling relations with plasma-enabled catalysis, *Nature Cat.* **1**, 269 (2018).
 - ¹⁵ G.A. Olah, Electrophilic methane conversion, *Acc. Chem. Res.* **20**, 422 (1987).
 - ¹⁶ J.H. Lunsford, Catalytic oxidative coupling of methane, *Angew. Chem., Int. Ed.* **34**, 970 (1995).
 - ¹⁷ J. Kim, D. B. Go, and J. C. Hicks, Synergistic effects of plasma-catalyst interactions for CH₄ activation, *Phys. Chem. Chem. Phys.* **19**, 13010 (2017).
 - ¹⁸ P. Rumbach, R. Xu, and D. B. Go, Electrochemical production of oxalate and formate from CO₂ by solvated electrons produced using an atmospheric-pressure plasma, *J. Electrochem. Soc.* **163**, F1157 (2016).
 - ¹⁹ A. Studer and D. P. Curran, The electron is a catalyst, *Nat. Chem.* **6**, 765 (2014).
 - ²⁰ A. Houmam, Electron transfer initiated reactions: Bond formation and bond dissociation, *Chem. Rev.* **108**, 2180 (2008).
 - ²¹ W. P. Reinhardt, Complex coordinates in the theory of atomic and molecular structure and dynamics, *Annu. Rev. Phys. Chem.* **33**, 223 (1982).
 - ²² N. Moiseyev, Quantum theory of resonances: Calculating energies, widths and cross-sections by complex scaling, *Phys. Rep.* **302**, 212 (1998).
 - ²³ N. Moiseyev, *Non-Hermitian quantum mechanics*. Cambridge University Press, 2011.
 - ²⁴ T.-C. Jagau, K. B. Bravaya, and A. I. Krylov, Extending quantum chemistry of bound states to electronic resonances, *Annu. Rev. Phys. Chem.* **68**, 525 (2017).
 - ²⁵ A. I. Krylov, Equation-of-motion coupled-cluster methods for open-shell and electronically excited species: The hitchhiker’s guide to Fock space, *Annu. Rev. Phys. Chem.* **59**, 433 (2008).
 - ²⁶ K. Sneskov and O. Christiansen, Excited state coupled cluster methods, *WIREs: Comput. Mol. Sci.* **2**, 566 (2012).
 - ²⁷ R. J. Bartlett, Coupled-cluster theory and its equation-of-motion extensions, *WIREs: Comput. Mol. Sci.* **2**, 126 (2012).
 - ²⁸ S. Klaiman and I. Gilary, On resonance: A first glance into the behavior of unstable states, *Adv. Quantum Chem.* **63**, 1 (2012).
 - ²⁹ M. Ehara and T. Sommerfeld, CAP/SAC-CI method for calculating resonance states of

- metastable anions, *Chem. Phys. Lett.* **537**, 107 (2012).
- ³⁰ T.-C. Jagau, D. B. Dao, N. S. Holtgrewe, A. I. Krylov, and R. Mabbs, Same but different: Dipole-stabilized shape resonances in CuF^- and AgF^- , *J. Phys. Chem. Lett.* **6**, 2786 (2015).
- ³¹ J. Lyle, T.-C. Jagau, and R. Mabbs, Spectroscopy of temporary anion states: Renner-Teller coupling and electronic autodetachment in copper difluoride anion, *Faraday Discuss.* , 533 (2019).
- ³² S. Gulania, T.-C. Jagau, A. Sanov, and A. I. Krylov, The quest to uncover the nature of benzonitrile anion, *Phys. Chem. Chem. Phys.* (2020), submitted.
- ³³ W. Skomorowski, S. Gulania, and A. I. Krylov, Bound and continuum-embedded states of cyanopolyynes anions, *Phys. Chem. Chem. Phys.* **20**, 4805 (2018).
- ³⁴ Z. Benda and T.-C. Jagau, Understanding processes following resonant electron attachment: Minimum-energy crossing points between anionic and neutral potential energy surfaces, *J. Chem. Theory Comput.* **14**, 4216 (2018).
- ³⁵ A. A. Kunitsa and K. B. Bravaya, First-principles calculations of the energy and width of the 2A_u shape resonance in p-benzoquinone: A gateway state for electron transfer, *J. Phys. Chem. Lett.* **6**, 1053 (2015).
- ³⁶ G. Jolicard and E. J. Austin, Optical potential stabilisation method for predicting resonance levels, *Chem. Phys. Lett.* **121**, 106 (1985).
- ³⁷ U. V. Riss and H.-D. Meyer, Calculation of resonance energies and widths using the complex absorbing potential method, *J. Phys. B* **26**, 4503 (1993).
- ³⁸ E. J. D. Mahoney, B. S. Truscott, M. N. R. Ashfold, and Yu. A. Mankelevich, Optical emission from C_2^- anions in microwave-activated CH_4/H_2 plasmas for chemical vapor deposition of diamond, *J. Phys. Chem. A* **121**, 2760 (2017).
- ³⁹ M. C. McCarthy, C. A. Gottlieb, H. Gupta, and P. Thaddeus, Laboratory and astronomical identification of the negative molecular ion C_6H^- , *Astrophys. J. Lett.* **652**, L141 (2006).
- ⁴⁰ S. Brünken, H. Gupta, C. A. Gottlieb, M. C. McCarthy, and P. Thaddeus, Detection of the carbon chain negative ion C_8H^- in TMC-1, *Astrophys. J. Lett.* **664**, L43 (2007).
- ⁴¹ P. Thaddeus, C. A. Gottlieb, H. Gupta, S. Brünken, M. C. McCarthy, M. Agúndez, M. Guelin, and J. Cernicharo, Laboratory and astronomical detection of the negative molecular ion C_3N^- , *Astrophys. J.* **677**, 1132 (2008).
- ⁴² Cernicharo, J., Guélin, M., Agúndez, M., Kawaguchi, K., McCarthy, M., and Thaddeus, P.,

- Astronomical detection of C_4H^- , the second interstellar anion, *Astronomy & Astrophysics* **467**, L37 (2007).
- ⁴³ J. Cernicharo, M. Guélin, M. Agúndez, M. C. McCarthy, and P. Thaddeus, Detection of C_5N^- and vibrationally excited C_6H in IRC+10216, *Astrophys. J. Lett.* **688**, L83 (2008).
- ⁴⁴ M. Agúndez, J. Cernicharo, M. Guélin, C. Kahane, E. Roueff, J. Klos, F.J. Aoiz, F. Lique, N. Marcelino, J. R. Goicoechea, M. González-García, C.A. Gottlieb, M.C. McCarthy, and P. Thaddeus, Astronomical identification of CN^- , the smallest observed molecular anion, *Astronomy & Astrophysics* **517**, L2 (2010).
- ⁴⁵ B. A. McGuire, A. M. Burkhardt, S. Kalenskii, C. N. Shingledecker, A. J. Remijan, E. Herbst, and M. C. McCarthy, Detection of the aromatic molecule benzonitrile $\text{c-C}_6\text{H}_5\text{CN}$ in the interstellar medium, *Science* **359**, 202 (2018).
- ⁴⁶ W. H. A Wollaston, Method of examining refractive and dispersive powers, by prismatic reflection, *Philos. Trans. R. Soc. London* **92**, 365 (1802).
- ⁴⁷ A. N. Goyette, J. E. Lawler, L. W. Anderson, D. M. Gruen, T. G. McCauley, D. Zhou, and A. R. Krauss, Spectroscopic determination of carbon dimer densities in $\text{Ar-H}_2\text{-CH}_4$ $\text{Ar-H}_2\text{-C}_{60}$ and plasmas, *J. Phys. D: Appl. Phys.* **31**, 1975 (1998).
- ⁴⁸ N. J. Reilly, T. W. Schmidt, and S. H. Kable, Two-dimensional fluorescence (excitation/emission) spectroscopy as a probe of complex chemical environments, *J. Phys. Chem. A* **110**, 12355 (2006).
- ⁴⁹ E. Szymańska, I. Cadez, E. Krishnakumar, and N. J. Mason, Electron impact induced anion production in acetylene, *Phys. Chem. Chem. Phys.* **16**, 3425 (2014).
- ⁵⁰ K. Emrich, An extension of the coupled-cluster formalism to excited states (I), *Nucl. Phys. A* **351**, 379 (1981).
- ⁵¹ H. Sekino and R. J. Bartlett, A linear response, coupled-cluster theory for excitation energy, *Int. J. Quant. Chem.* **26**, 255 (1984).
- ⁵² H. Koch and P. Jørgensen, Coupled cluster response functions, *J. Chem. Phys.* **93**, 3333 (1990).
- ⁵³ H. Koch, H.J.Aa. Jensen, P. Jørgensen, and T. Helgaker, Excitation energies from the coupled clusters singles and doubles linear response functions (CCSDLR). Applications to Be , CH^+ , CO , and H_2O , *J. Chem. Phys.* **93**, 3345 (1990).
- ⁵⁴ J. F. Stanton and R. J. Bartlett, The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited

- state properties, *J. Chem. Phys.* **98**, 7029 (1993).
- ⁵⁵ M. Nooijen and R. J. Bartlett, Description of core-excitation spectra by the open-shell electron-attachment equation-of-motion coupled cluster method, *J. Chem. Phys.* **102**, 6735 (1995).
- ⁵⁶ S. V. Levchenko and A. I. Krylov, Equation-of-motion spin-flip coupled-cluster model with single and double substitutions: Theory and application to cyclobutadiene, *J. Chem. Phys.* **120**, 175 (2004).
- ⁵⁷ A. I. Krylov, The quantum chemistry of open-shell species, in *Reviews in Comp. Chem.*, edited by A. L. Parrill and K. B. Lipkowitz, volume 30, pages 151–224. J. Wiley & Sons, 2017.
- ⁵⁸ D. Zuev, T.-C. Jagau, K. B. Bravaya, E. Epifanovsky, Y. Shao, E. Sundstrom, M. Head-Gordon, and A. I. Krylov, Complex absorbing potentials within EOM-CC family of methods: Theory, implementation, and benchmarks, *J. Chem. Phys.* **141**, 024102 (2014).
- ⁵⁹ T.-C. Jagau, D. Zuev, K. B. Bravaya, E. Epifanovsky, and A. I. Krylov, A fresh look at resonances and complex absorbing potentials: Density matrix based approach, *J. Phys. Chem. Lett.* **5**, 310 (2014).
- ⁶⁰ T.-C. Jagau and A. I. Krylov, Complex absorbing potential equation-of-motion coupled-cluster method yields smooth and internally consistent potential energy surfaces and lifetimes for molecular resonances, *J. Phys. Chem. Lett.* **5**, 3078 (2014).
- ⁶¹ T.-C. Jagau and A. I. Krylov, Characterizing metastable states beyond energies and lifetimes: Dyson orbitals and transition dipole moments, *J. Chem. Phys.* **144**, 054113 (2016).
- ⁶² W. Skomorowski and A. I. Krylov, Real and imaginary excitons: Making sense of resonance wavefunctions by using reduced state and transition density matrices, *J. Phys. Chem. Lett.* **9**, 4101 (2018).
- ⁶³ R. Santra and L. S. Cederbaum, Non-Hermitian electronic theory and applications to clusters, *Phys. Rep.* **368**, 1 (2002).
- ⁶⁴ A. I. Krylov, From orbitals to observables and back, *J. Chem. Phys.* **153**, 080901 (2020).
- ⁶⁵ J. V. Ortiz, Dyson-orbital concepts for description of electrons in molecules, *J. Chem. Phys.* **153**, 070902 (2020).
- ⁶⁶ A. V. Luzanov, A. A. Sukhorukov, and V. E. Umanskii, Application of transition density matrix for analysis of excited states, *Theor. Exp. Chem.* **10**, 354 (1976), Russian original: *Teor. Eksp. Khim.*, 10, 456 (1974).
- ⁶⁷ A. V. Luzanov and V. F. Pedash, Interpretation of excited states using charge-transfer number,

- Theor. Exp. Chem. **15**, 338 (1979).
- ⁶⁸ A. V. Luzanov and O. A. Zhikol, Excited state structural analysis: TDDFT and related models, in *Practical aspects of computational chemistry I: An overview of the last two decades and current trends*, edited by J. Leszczynski and M.K. Shukla, pages 415–449. Springer, 2012.
- ⁶⁹ F. Plasser, M. Wormit, and A. Dreuw, New tools for the systematic analysis and visualization of electronic excitations. I. Formalism, J. Chem. Phys. **141**, 024106 (2014).
- ⁷⁰ F. Plasser, S. A. Bppler, M. Wormit, and A. Dreuw, New tools for the systematic analysis and visualization of electronic excitations. II. Applications, J. Chem. Phys. **141**, 024107 (2014).
- ⁷¹ S. Mewes, F. Plasser, A. Krylov, and A. Dreuw, Benchmarking excited-state calculations using exciton properties, J. Chem. Theory Comput. **14**, 710 (2018).
- ⁷² S. Matsika, X. Feng, A. V. Luzanov, and A. I. Krylov, What we can learn from the norms of one-particle density matrices, and what we can’t: Some results for interstate properties in model singlet fission systems, J. Phys. Chem. A **118**, 11943 (2014).
- ⁷³ A. I. Krylov and P. M. W. Gill, Q-Chem: An engine for innovation, WIREs: Comput. Mol. Sci. **3**, 317 (2013).
- ⁷⁴ Y. Shao, Z. Gan, E. Epifanovsky, A.T.B. Gilbert, M. Wormit, J. Kussmann, A.W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P.R. Horn, L.D. Jacobson, I. Kaliman, R.Z. Khaliullin, T. Kus, A. Landau, J. Liu, E.I. Proynov, Y.M. Rhee, R.M. Richard, M.A. Rohrdanz, R.P. Steele, E.J. Sundstrom, H.L. Woodcock III, P.M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G.J.O. Beran, Y.A. Bernard, E. Berquist, K. Brandhorst, K.B. Bravaya, S.T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S.H. Chien, K.D. Closser, D.L. Crittenden, M. Diedenhofen, R.A. DiStasio Jr., H. Do, A.D. Dutoi, R.G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M.W.D. Hanson-Heine, P.H.P. Harbach, A.W. Hauser, E.G. Hohenstein, Z.C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyayev, J. Kim, J. Kim, R.A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C.M. Krauter, K.U. Laog, A. Laurent, K.V. Lawler, S.V. Levchenko, C.Y. Lin, F. Liu, E. Livshits, R.C. Lochan, A. Luenser, P. Manohar, S.F. Manzer, S.-P. Mao, N. Mardirossian, A.V. Marenich, S.A. Maurer, N.J. Mayhall, C.M. Oana, R. Olivares-Amaya, D.P. O’Neill, J.A. Parkhill, T.M. Perrine, R. Peverati, P.A. Pieniazek, A. Prociuk, D.R. Rehn, E. Rosta, N.J. Russ, N. Sergueev, S.M. Sharada, S. Sharma, D.W. Small, A. Sodt, T. Stein, D. Stuck, Y.-C. Su, A.J.W. Thom, T. Tsuchimochi, L. Vogt, O. Vydrov, T. Wang, M.A. Watson, J. Wenzel, A. White, C.F. Williams, V. Vanovschi, S.

- Yeganeh, S.R. Yost, Z.-Q. You, I.Y. Zhang, X. Zhang, Y. Zhou, B.R. Brooks, G.K.L. Chan, D.M. Chipman, C.J. Cramer, W.A. Goddard III, M.S. Gordon, W.J. Hehre, A. Klamt, H.F. Schaefer III, M.W. Schmidt, C.D. Sherrill, D.G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A.T. Bell, N.A. Besley, J.-D. Chai, A. Dreuw, B.D. Dunietz, T.R. Furlani, S.R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D.S. Lambrecht, W.Z. Liang, C. Ochsenfeld, V.A. Rassolov, L.V. Slipchenko, J.E. Subotnik, T. Van Voorhis, J.M. Herbert, A.I. Krylov, P.M.W. Gill, and M. Head-Gordon, Advances in molecular quantum chemistry contained in the Q-Chem 4 program package, *Mol. Phys.* **113**, 184 (2015).
- ⁷⁵ S. Gulania, T.-C. Jagau, and A. I. Krylov, EOM-CC guide to Fock-space travel: The C₂ edition, *Faraday Discuss.* **217**, 514 (2019).
- ⁷⁶ B. K. Janousek, J. I. Brauman, and J. Simons, An experimental and theoretical determination of the electron affinity of the ethynyl radical, HC₂·, *J. Chem. Phys.* **71**, 2057 (1979).
- ⁷⁷ K. M. Ervin and W. C. Lineberger, Photoelectron spectra of C₂⁻ and C₂H⁻, *J. Phys. Chem.* **95**, 1167 (1991).
- ⁷⁸ T. R. Taylor and C. S. Xu, Photoelectron spectra of the C_{2n}H⁻ (n=1–4) and C_{2n}D⁻ (n=1–3) anions, *J. Chem. Phys.* **108**, 10018 (1998).
- ⁷⁹ S. Harrison and J. Tennyson, Bound and continuum states of molecular anions C₂H⁻ and C₃N⁻, *J. Phys. B* **44**, 045206 (2011).
- ⁸⁰ M. L. Senent and M. Hochlaf, Reactivity of anions in interstellar media: Detectability and applications, *Astrophys. J.* **768**, 59 (2013).
- ⁸¹ M. N. R. Ashfold, G. A. King, D. Murdock, M. G. D. Nix, T. A. A. Oliver, and A. G. Sage, $\pi - \sigma^*$ excited states in molecular photochemistry, *Phys. Chem. Chem. Phys.* **12**, 1218 (2010).