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

Supporting Information: Dissociative electron attachment to 5-bromo-uracil: non-adiabatic dynamics on complex-valued potential energy surfaces

Lucas M. Cornetta,[*,†] Todd J. Martinez[¶,‡] and Márcio T. do N. Varella[§]

[†] *Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, Rua Sérgio Buarque de Holanda, 777 - Cidade Universitária, Campinas, São Paulo, Brazil*

[‡] *Department of Chemistry and PULSE Institute, Stanford University, Stanford, California 94305, United States*

[¶] *SLAC National Accelerator Laboratory, Menlo Park, CA 94025*

[§] *Instituto de Física, Universidade de São Paulo, Rua do Matão 1371, 05508-090, São Paulo, São Paulo, Brazil*

E-mail: lucascor@unicamp.br

Scattering calculations

The Schwinger Multicannel method implemented with pseudopotentials (SMCPP) was recently reviewed,[S1] we therefore only present a few relevant aspects. The SMCPP scattering electronic wave function is resolved as

$$|\Psi_{\mathbf{k}_i}^{(\pm)}\rangle = \sum_{\mu} c_{\mu}^{(\pm)}(\mathbf{k}_i)|\chi_{\mu}\rangle, \tag{1}$$

where $\mathbf{k}_i$ is the wave vector of the incident electron, ± denote the ingoing (-) and the outgoing (+) boundary conditions and $|\chi_{\mu}\rangle$ are spin-adapted Slater determinants of $N+1$ particles called configuration space functions (CSF). The Schwinger variational principle leads to a working expression for the scattering amplitude, from which we evaluate the integral cross section, given by

$$f(\mathbf{k}_f, \mathbf{k}_i) = -\frac{1}{2\pi}\sum_{\mu,\nu}\langle S_{\mathbf{k}_f}|V|\chi_{\mu}\rangle \left(d^{-1}\right)_{\mu\nu} \langle \chi_{\nu}|V|S_{\mathbf{k}_i}\rangle \ , \tag{2}$$

with

$$d_{\mu\nu} = \langle \chi_{\mu}|A^{(+)}|\chi_{\nu}\rangle \ , \tag{3}$$

and

$$A^{(+)} = \frac{\hat{H}}{N+1} - \frac{(\hat{H}P + P\hat{H})}{2} + \frac{(VP + PV)}{2} - VG_P^{(+)}V \ . \tag{4}$$

In the above expressions, V is the electron-target interaction, $\mathbf{k}_f$ is the outgoing projectile wave vector, $|S_{\mathbf{k}}\rangle$ is an eigenstate of the interaction-free Hamiltonian (H_0), given by the product of a target state and a plane wave, $\hat{H} = (E - H)$ is the difference between the collision energy and the scattering Hamiltonian, $H = (H_0 + V)$, P is a projector onto the open (energetically allowed) electronic states of the target, $G_P^{(+)}$ is the free-particle Green's operator projected on the P space. Since we only report elastic (single-channel) calculations, the P projector is given by $P = |\Phi_0\rangle\langle\Phi_0|$, where Φ_0 is the target ground state. We performed calculations in the static-exchange plus polarization (SEP) approximations for the CSF space. In this approximation the functions are given by $|\chi_\mu\rangle \rightarrow |\chi_{\mu\nu}\rangle = \mathcal{A}[|\Phi_\nu\rangle \otimes |\varphi_\mu\rangle]$, where $|\Phi_\nu\rangle$ is used to label the electronic state of the target with either singlet or triplet spin coupling. The SEP takes single excitations of the neutral BrU into account with the additional electron occupying an additional orbital (scattering orbital), taking electronic polarization effects into account.

The orbitals are built from a pseudopotential[S2] Hartee-Fock calculation of the neutral BrU. Besides, we have employed modified virtual orbitals[S3] generated from positively charged structures with charge +10 (MVO+10). The cartesian gaussian basis sets used along with the pseudopotentials for the heavy atoms (all but hydrogens) are given in Tab. S1. For hydrogen atoms, we have employed a $4s1p$ basis set proposed by Dunning.[S4]

Table S1: Exponents of the basis functions.

Type	Carbon	Nitrogen	Oxygen	Bromine
s	12.496280	17.56987	16.05878	6.779740
s	2.470286	3.423613	5.920242	1.071059
s	0.614028	0.884301	1.034907	0.748707
s	0.184028	0.259045	0.316843	0.202254
s	0.039982	0.053066	0.065203	0.036220
s	-	-	-	0.009055
p	5.228869	7.050692	10.14120	4.789276
p	1.592058	1.910543	2.782999	1.856547
p	0.568612	0.579261	0.841004	0.664700
p	0.210326	0.165395	0.232939	0.265909
p	0.072250	0.037192	0.077646	0.098552
d	0.603592	0.403039	0.756793	0.477153
d	0.156753	0.091192	0.180759	0.139024

We performed scattering calculations for five BrU geometries and the molecule is planar in all of them. Because of the C_s symmetry point group, the integral cross section (ICS) was decomposed in two contributions. As usual, the A' and A'' subgroups relate to the reflection operation of the scattering wave function through the molecule symmetry plane. The energy criteria[S5] was used for the CSFs collection, in which we include all configurations satisfying $\epsilon_{particle} + \epsilon_{scattering} - \epsilon_{hole} < \Delta_c$, where the ϵ's correspond to the orbitals/MVOs eigenvalues and Δ_c is an energy cutoff. The calibration of Δ_c aimed to allow a balanced description between anion and neutral species, and all calculations used the same value $\Delta_c = -2.40$ Hartree. In Table S2 we show the number of CSFs used for each calculation.

Table S2: Number of CSFs

$R - R_{\text{eq}}$ (Å)	A'	A''
-0.2	18627	17469
-0.1	18009	17243
0	17659	16861
+0.1	17815	16325
+0.2	16627	15763

Electronic structure

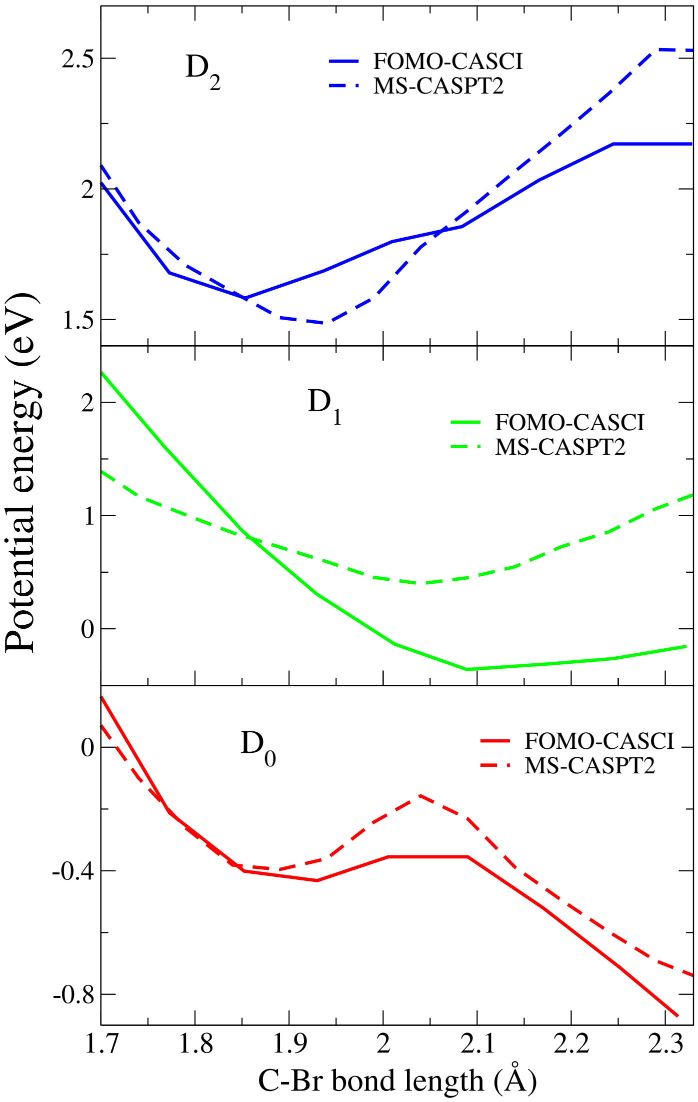

Figure S1: Comparison between FOMO-CASCI potential energy curves of D_0 (top), D_1 (middle) and D_2 (bottom) states with those obtained with the multistate CASPT2(7,6) level of theory. The curves were vertically shifted for the comparison.

DEA model sensitivity

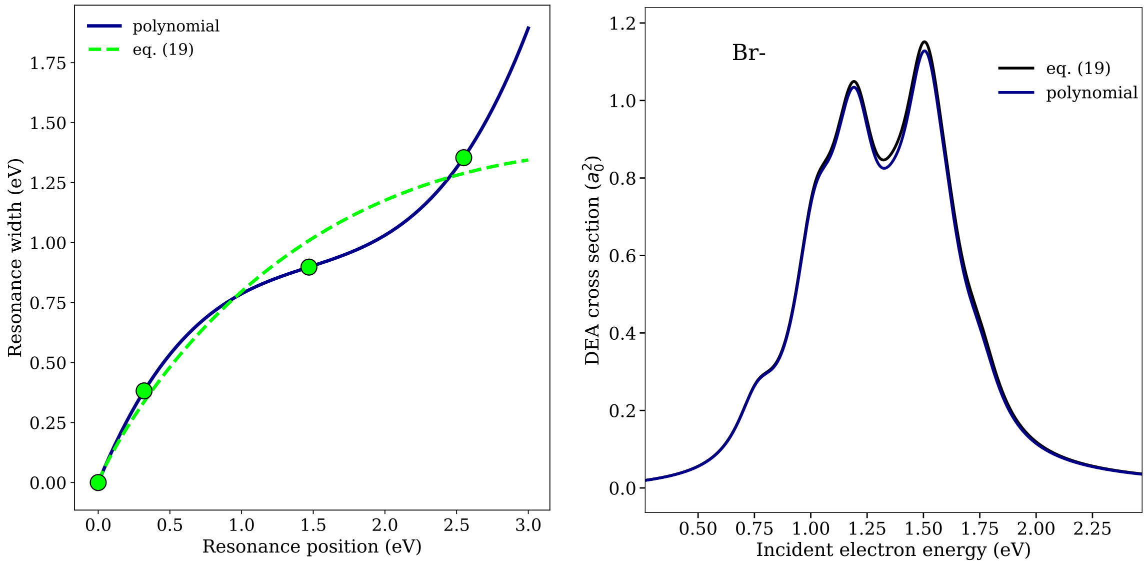

Figure S2: (Left) Comparison between eq. (19) (main text) and the alternative third order polynomial fit $\Gamma_L^{\sigma^*_{\mathrm{CBr}}}(\mathbf{R}) = 1.4461 E_{\mathrm{res}}^{\sigma^*_{\mathrm{CBr}}}(\mathbf{R}) - 0.8530(E_{\mathrm{res}}^{\sigma^*_{\mathrm{CBr}}}(\mathbf{R}))^2 + 0.1938(E_{\mathrm{res}}^{\sigma^*_{\mathrm{CBr}}}(\mathbf{R}))^3$. (Right) DEA curves, in a_0^2, as a function of the incident electron energy, in eV, for the two Γ_L models. The curves were obtained with $\lambda = 0.22$ and $\delta = 5.34$ eV.

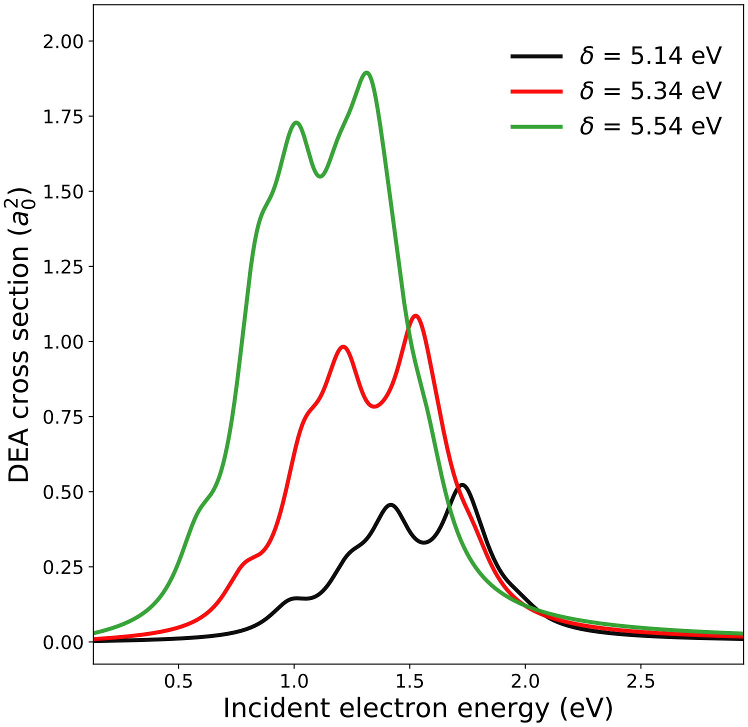

Figure S3: DEA curves, in a_0^2, as a function of the incident electron energy, in eV, for three different δ values. The curves were obtained with $\lambda = 0.22$.

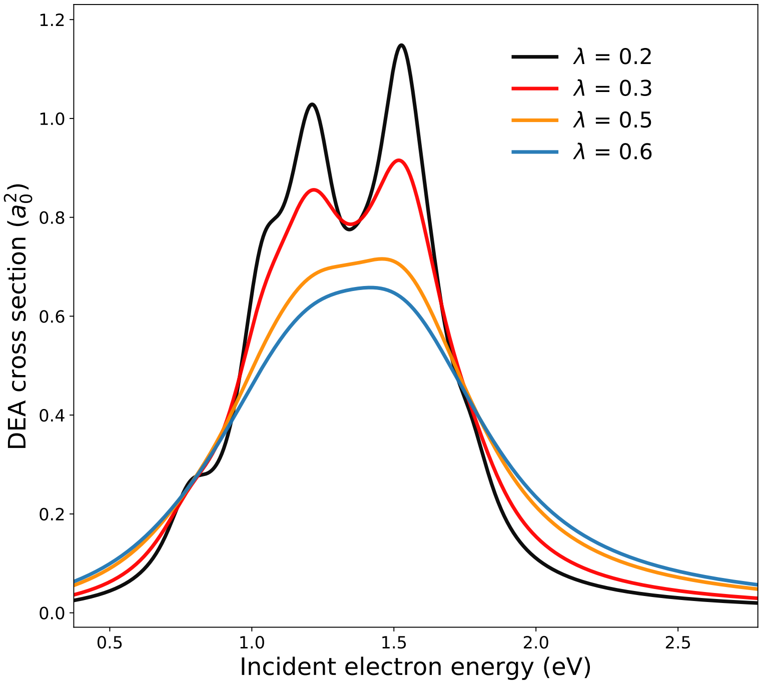

Figure S4: DEA curves, in a_0^2, as a function of the incident electron energy, in eV, for four different λ values. The curves were obtained with $\delta = 5.34$ eV.

References

(S1) M. H. F. Bettega M. A. P. Lima R. F. da Costa, M. T. do N. Varella. Eur. Phys. J. D, **69**: 159, 2015.

(S2) Bell Laboratories, M. Hill, G. B. Bachelet, D. R. Hamann, and M. Schluter. Pseudopotentials that work: From H to Pu. Physical Review B, **26(8)**:41994228, 1982.

(S3) C. W. Bauschlicher. The construction of modified virtual orbitals (MVOs) which are suited for configuration interaction calculations. The Journal of Chemical Physics, **72**:880, 1980.

(S4) T. H. Dunning. Gaussian basis functions for use in molecular calculations. Contraction of (12s9p) atomic basis sets for the second row atoms. Chemical Physics Letters, **7**:423427, 1970.

(S5) F. Kossoski and M. H F Bettega. Low-energy electron scattering from the aza-derivatives of pyrrole, furan, and thiophene. Journal of Chemical Physics, **138**, 2013.