Supplementary online information

This is a supplementary material to paper "Resonances and dissociative electron attachment to HNCO" by Zawadzki et al. First we give the complete list of parameters of the nonlocal resonance model for calculation of dissociative electron attachment

$$\mathrm{e}^- + \mathrm{HNCO} \rightarrow \mathrm{H} + \mathrm{NCO}^-.$$

Second we show additional potential energy curves for relaxed geometry of the CNO-part of the molecule. This information is presented to support the modification of the discrete-state potential by shifting its asymptotic energy according to the experimentally observed DEA threshold. Finally we present the DEA cross sections for different values of this shift to show that the shape of the cross section curve is really independent of this modification, apart from the fact that the lowering of the threshold reveals the low-energy part of the cross section curve.

1 Model parameters

As described in the main text the nonlocal resonance model parameters were fitted to reproduce the R and E dependence of the calculated fixed-nuclei eigenphase sums for equilibrium geometry of HNCO molecule and the NH bond stretched between 1.5 and 3.0 bohr with step 0.1 and the electron energy between 1 meV to 5 eV. The eigenphase function is fitted to the generalized Breit-Wigner formula

$$\delta(R,\epsilon) = \delta_{\mathrm{BG}}(R,\epsilon) + \arctan \frac{\Gamma(R,\epsilon)/2}{E - V_d(R) - \Delta(R,\epsilon)}$$

with

$$\begin{aligned} \delta_{\mathrm{BG}} &= A(R) - B(R)\ln E + C(R)\sqrt{E}, \\ \Gamma &= 2\pi |V_{dE}(R)|^2, \\ \Delta &= p.v. \int \frac{|V_{d\epsilon}(R)|^2}{E-\epsilon} \mathrm{d}\epsilon. \end{aligned}$$

The energy dependence of the background phase shift shape δ_{BG} is in accordance with low-energy behavior of phase shifts for molecules with supercritical dipole moment. Furthermore we assume the linear form of R-dependence. The fitting procedure gives (all values of model parameters are given in atomic units)

$$\begin{aligned} A(R) &= 2.2527 - 1.1936R, \\ B(R) &= 0.22327R - 0.37938, \\ C(R) &= 1.9347R - 7.8098. \end{aligned}$$

The following form of the discrete-state-continuum coupling function consisting of two separable terms is assumed

$$V_{dE}(R) = g_1(R)[1 + g_2(R)\sqrt{E}]e^{-\beta E},$$

value of $\beta = 8.0035$ and the functions $g_i(R)$ were obtained by fitting the eigenphases for each calculated value of R separately. Then the shape of functional dependence was guessed and parameterized in final global fit. The resulting functions are

$$\begin{aligned} g_1(R) &= 0.09198 \exp[-0.43584(R - 1.7017)^2], \\ g_2(R) &= 14.984 - 14.061 \cos[1.0634(R - 1.7655)]. \end{aligned}$$

The discrete-state potential

$$V_d(R) = 4260e^{-7.34R} + 0.1199e^{-0.86883R} - \frac{2.25}{(r-3)^4 + 57.62(R-3)^2 + 408.2}$$

was fitted in two steps. The last term was obtained in the first step fitting the long-range polarization behavior with the nominator determined by dipole polarizability of the hydrogen atom. The first two terms, describing the position of the resonance, were obtained by fitting the R-matrix eigephase sums together with the parameters of background and discrete-state-continuum coupling since $V_d(R)$ enters the fitting formula.

2 NCO-geometry relaxation

The threshold for the dissociative attachment channel in the original model as described in the previous section is too high. This is not surprising since the one-dimensional model takes into account only the NH stretch coordinate. In reality the geometry of the NCO group relaxes from the equilibrium configuration in the neutral HNCO molecule to equilibrium geometry in the NCO^- anion, which lowers the energy of the DA threshold. To map the way how fast this relaxation takes place we performed series of calculation using the same CCSD-T/aug-cc-pVTZ approach as described in the main text with different geometries of the NCO group. The results are shown in Figure 1. We can conclude that the potential energy relaxes by approximately $\Delta E = 200$ meV in the interval of NH bond length $R = 2.5 - 3.5$. To include this relaxation in the 1D calculation we added the following term simulating this relaxation to the potential $V_d(R)$

$$\tilde{V}_d(R) = V_d(R) - \frac{\Delta E}{1 + e^{-3(R-3)}}.$$

3 Cross section dependence on the relaxation

The relaxation energy $\Delta E \simeq 0.2$ eV is not large enough to yield the correct DEA threshold. This is likely a consequence of the accuracy of the quantum chemistry

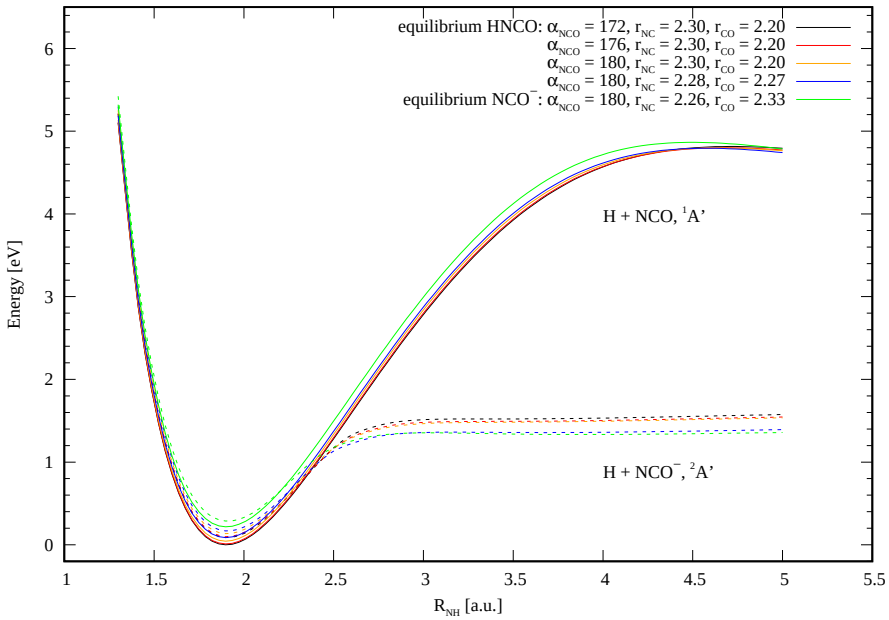

Figure 1: Dependence of potential surfaces on NCO geometry for neutral molecule (solid lines) and the anion (dashed lines).

calculations. Furthermore, it is possible that geometry of the fragment anion NCO^- is not fully relaxed in our test calculation. We therefore checked how the DEA cross section curve depends on ΔE. The resulting cross sections for different values of the relaxation shift ΔE are shown in Figure 2.

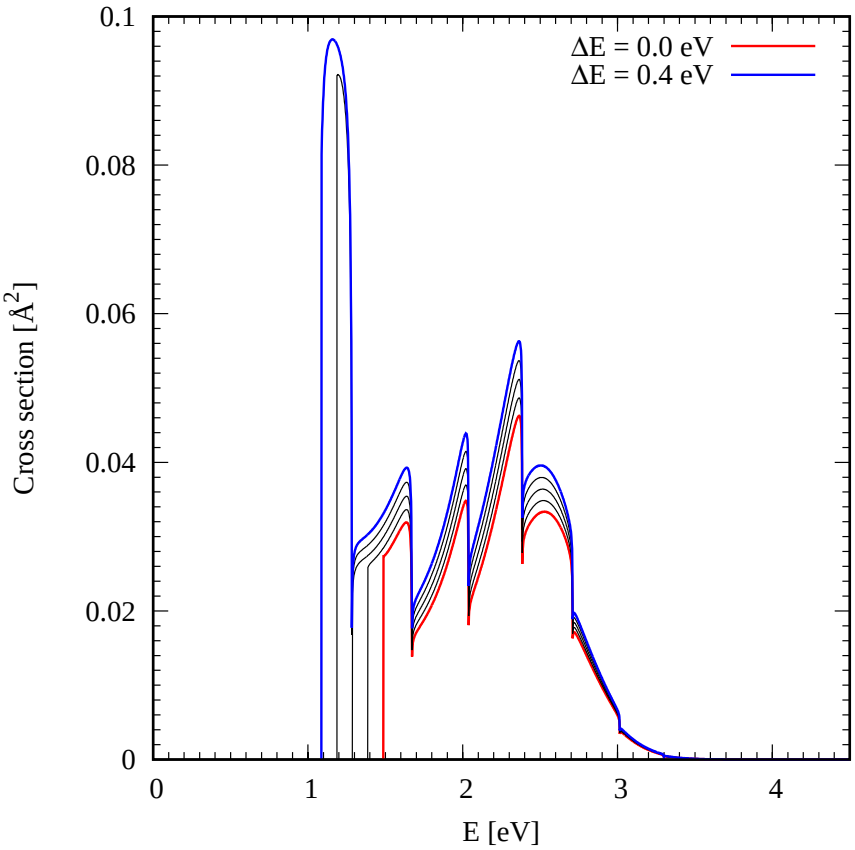

Figure 2: Resulting cross sections for $\Delta E = 0, 0.1, 0.2, 0.3$ and 0.4 eV.