PCCP

ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Resonant states in cyanogen NCCN—Supplementary Information

Pamir Nag,[a] Roman Čurík,[a*] Michal Tarana,[a] Miroslav Polášek,[a] Masahiro Ehara,[b] Thomas Sommerfeld,[c*] and Juraj Fedor[a*]

1 One-dimensional model for the CC stretch excitation cross section

This supplement discusses the details of the one-dimensional pseudodihalogen model used to compute the contribution of the CC-mode to the vibrational excitation cross section. Here, the focus is on technical aspects of the model. The computed cross section as such is discussed is the main text.

To be specific, we model the cross section for electron-impact excitation of the CC stretch mode (ν_2)

$$\mathrm{e}^-(E)+\mathrm{NCCN}(\nu_2^{(0)}) \longrightarrow \mathrm{e}^-(E')+\mathrm{NCCN}(\nu_2^{(1)}) \qquad (1)$$

with a one-dimensional pseudodihalogen picture. In oher words, we assume that the $0 \to 1$ excitation of $\nu_2; c.f.Tab.1$ decouples from all other vibrational degrees of freedom; only CC-stretch excitations of the resonance can contribute to the CC-stretch excitation cross section of the neutral.

In this one-dimensional picture the cross section can be approximated as

$$\sigma_{0\to 1}(E) = 2\pi\sqrt{\frac{E-\varepsilon_1}{E}} \left| \left\langle \nu_2^{(1)} \middle| f \left[E - (\hat{T}+V_0+E_r-\frac{i}{2}\Gamma) \right]^{-1} f \middle| \nu_2^{(0)} \right\rangle \right|^2 \qquad (2)$$

see eq.(46) of Ref. [1]. The cross section σ depends on the energy of the incoming electron, E. To compute it, we have to evaluate the matrix element of a resolvent with respect to the initial and final vibrational states $\left|\nu_2^{(0)}\right\rangle$ and $\left|\nu_2^{(1)}\right\rangle$ of the target, where ε_1 is the excitation energy corresponding to the first excited state. The vibrational states are associated with the potential energy curve (PEC) of the neutral, $V_0(q_2)$, and both states are dressed by an entry or exit amplitude, f, defined as $|f|^2 = \Gamma/\sqrt{E_r}$ before the matrix element of the resolvent is taken. The resolvent itself depends on E, the nuclear kinetic energy operator, $\hat{T}$, and the complex potential energy curve (PEC) of the resonance $V_0+E_r-\frac{i}{2}\Gamma$.

As an input, the model needs the neutral PEC. After computing minimal energy structure and harmonic frequency using CCSD(T) and the cc-pVTZ basis set, the PEC was evaluated using the same computational method at eleven displacements along the CC stretch mode (q_2 values in the range -0.15 to 0.08 Å). The results were then fit to a Morse oscillator.

At the same geometries, the resonance parameters E_r and Γ of the $^2\Pi_u$ resonance were computed using the CAP/SAC-CI method[2,3] and the AUG-cc-pVTZ basis augmented with an even-scaled (4p1d) set of additional diffuse functions. The resonance position turns out to be almost a linear function of q_2, and it was fit to a quadratic function. In the q_2 range investigated, the resonance width is small (between 5 and 0.2 meV) and, in particular, for very small widths, the results are noisy owing to limitations of our Gaussian basis set representing a long-lived state close to threshold. Guided by the highly robust results for the resonance position, we first identified the crossing point, $q_2^{(c)}$, of the neutral and anion PECs, where $\Gamma(q_2)$ must vanish. Using this information, $\Gamma(q_2)$ was modeled as a function rising exponentially from threshold

$$\Gamma(q_2) = c\left(e^{-k(q_2-q_2^{(c)})}-1\right) \qquad (3)$$

where c and k are free parameters that were fit to our *ab initio* data. The resulting PEC of the CC stretch and the associated complex PEC of the $^2\Pi_u$ resonances are displayed in Fig. 1.

Note the seemingly different behavior of the $1^2\Pi_u$ curve shown in Fig. 1 here and Fig. 4 of the main text. The $1^2\Pi_u$ PEC shown in the main text shows a minimum at a shorter bond length than the neutral. Moreover, in the RAC calculations, no crossing of the $1^2\Pi_u$ resonance with the neutral ground state is observed, while Fig. 1 shows a clear crossing.

We would like to point out that these differences are not caused by the different quantum chemistry methods, nor by the different approaches for the determination of the resonance parameters, but are due to the different choices of the nuclear coordinates. In the RAC calculations the independent variable is the C–C bond length while the remaining geometry parameters are fixed. Such a coordinate is more suitable for larger C–C bond distances since the equilibrium and the asymptotic C–N distances are similar. In contrast to this, the data in Fig. 1 employ the C–C stretch normal mode coordinate, which is more is suitable for the region around

---

[a] *J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 3, 18223 Prague, Czech Republic*
[b] *SOKENDAI, The Graduate University for Advanced Studies, Nishigonaka, Myodaiji, Okazaki 444-8585, Japan*
[b] *Department of Chemistry and Physics, Southeastern Louisiana University, SLU 10878, Hammond, LA 70402, USA*
[*] Corresponding authors. Emails: roman.curik@jh-inst.cas.cz, thomas.sommerfeld@selu.edu, juraj.fedor@jh-inst.cas.cz

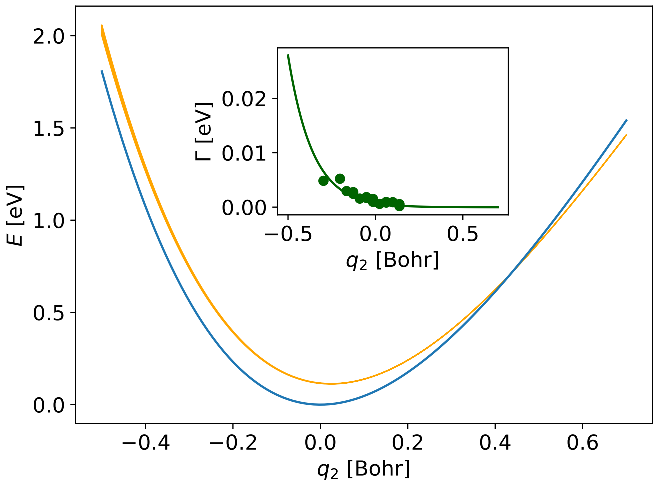

Fig. 1 Potential energy surfaces along the CC stretch mode of neutral NCCN (blue) and the $^2\Pi_u$ resonance (orange). The resonance width, Γ, is indicated as the width of the potential energy curve and it is also given in the inset (green) together with the original noisy CAP results (see text). For the resonance position, E_r, the CAP results show no discernable noise on the scale of the plot and are omitted.

the equilibrium geometry. The C–C stretch normal mode simultaneously stretches the C–C and C–N bond lengths in a ratio of roughly 4:1.

To evaluate the cross section, we employed a discreet variable representation (DVR) of all relevant quantities[4]. In the kinetic energy operator, the reduced mass associated with the harmonic frequency v_2 from neutral NCCN was used (13.33 amu).

The computed cross section for exciting the CC stretching mode from its ground to the first excited state, $\sigma_{0\rightarrow 1}(E)$, is shown in Fig. 5 of the main text. In the model, the excitation cross section shows a three-peak boomerang structure that is dominated by its central peak (note the logarithmic intensity scale). Each peak can be interpreted as $0 \rightarrow 1$ vibrational excitation of the neutral proceeding through a particular vibrational state of the resonance (see below). Thus, according to the computed peak at at 0.21 eV, vibrational excitation is predicted to be most efficient, if it proceeds *via* the first excited state of the resonance.

In order to arrive at this interpretation, we slightly rewrite the expression for the cross section eq.(2). Suppose the Hamiltonian in the resolvent, $\hat{H}_r = \hat{T} + V_0 + E_r - \frac{i}{2}\Gamma$, which describes the motion on the complex PEC of the resonance, is expressed in term of its eigenstates, $\left|v_r^{(n)}\right\rangle$, and complex eigenvalues $\varepsilon_r^{(n)}$ (the complex vibrational levels of the resonance)

$$\left[E - (\hat{T} + V_0 + E_r - \frac{i}{2}\Gamma)\right]^{-1} = \sum_n \frac{\left|v_r^{(n)}\right\rangle \left\langle v_r^{(n)}\right|}{E - \varepsilon_r^{(n)}} \tag{4}$$

Then the cross section in eq.(2) can be written as an energy-dependent prefactor, $\sqrt{(E-\varepsilon_1)/E}$, as before, times a sum of terms that consist of the product of two Franck-Condon-like factors, $\langle v_2^{(1)} f | v_r^{(n)} \rangle$ and $\langle v_r^{(n)} | f v_2^{(0)} \rangle$, devided by an energy denominator $(E - \varepsilon_r^{(n)})^{-1}$.

As the $^2\Pi_u$ resonance is very narrow and $\Gamma(q_2)$ remains very small in and beyond the Franck-Condon zone, the energy denominators cause the sharp lines of the boomerang structure, and each energy denominator—or each vibrational level of the resonance—can be associated with a particular line. Yet, the denominators have little impact on the relative intensities.

In contrast, the prefactor has a marked effect on the low energy region. At the first peak ($E = 105$ meV) it is less than 0.25 suppressing a potentially intensive peak. However, then it reaches very quickly its asymptotic value. At the second peak ($E = 210$ meV) the prefactor is about 0.7, and for the third peak the prefactor is almost 1.

Thus, the intensity pattern of the boomerang structure as such is determined by the product of Franck-Condon-like factors. For both excitation through the ground and second excited state of the resonance one of these factors is large while the other is much smaller resulting in a relatively small product and therefore a small intensity. In contrast, for excitation through the first excited state, both factors are reasonably large making for a substantially larger intensity.

Notes and references

1 M. Berman, H. Estrada, L. S. Cederbaum and W. Domcke, *Phys. Rev. A*, 1983, **28**, 1363.

2 M. Ehara and T. Sommerfeld, *Chem. Phys. Lett.*, 2012, **537**, 107–112.

3 T. Sommerfeld and M. Ehara, *J. Chem. Theoy. Comput.*, 2015, **11**, 4627–4633.

4 D. T. Colbert and W. H. Miller, *J. Chem. Phys.*, 1992, **96**, 1982.