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

Bound and continuum-embedded states of cyanopolyyne anions

Supporting Information

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I. $\eta-$TRAJECTORIES FOR RESONANCES DOMINATED BY VALENCE $\pi \to \pi^*$ OR $\sigma \to \pi^*$ EXCITATIONS

All η-trajectories were calculated using the aug-cc-VTZ+3s3p basis set. Table SI shows CAP onset parameters in these calculation. The CAP onset parameters were chosen as square root of the expectation value $\langle R^2 \rangle$, calculated for the anion's ground-state wave function. Left panels in all figures show zero-order energies $E(\eta)$, right panels show corresponding first-order corrected energies $U(\eta)$.

TABLE SI: CAP onset parameters (in bohr).

Molecule	r_x^0	r_y^0	r_z^0
CN^-	3.35	3.35	5.55
C_3N^-	4.39	4.39	14.79
C_5N^-	5.27	5.27	26.82
C_7N^-	6.00	6.00	40.72

A. CN$^-$

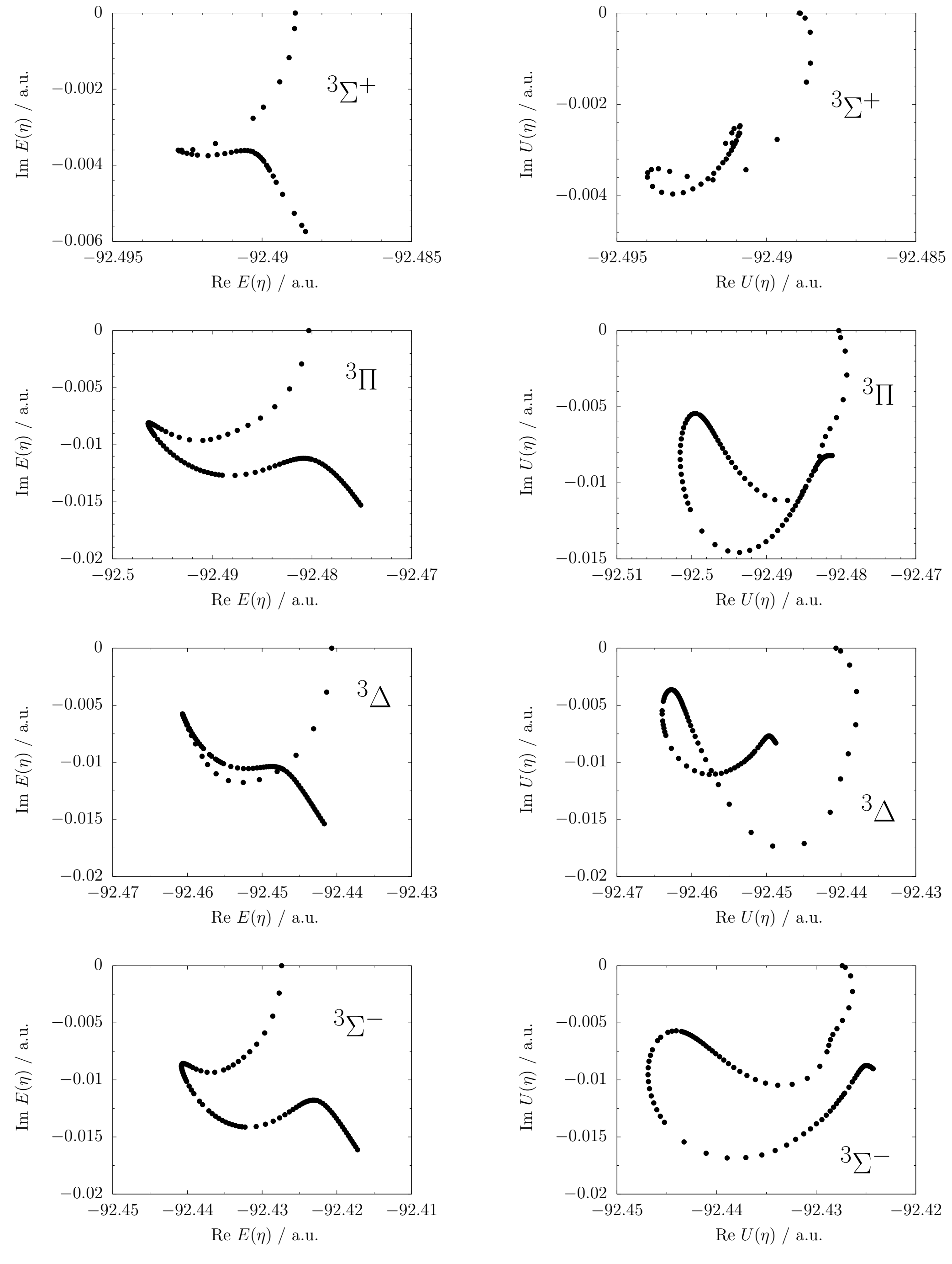


FIG. S1: $E(\eta)$ and $U(\eta)$ trajectories for resonances in CN$^-$ of triplet spin symmetry. η varies from to 0 to 0.01 a.u. for $^3\Sigma^+$, and from 0 to 0.15 a.u. for $^3\Pi$, $^3\Delta$ and $^3\Sigma^-$.

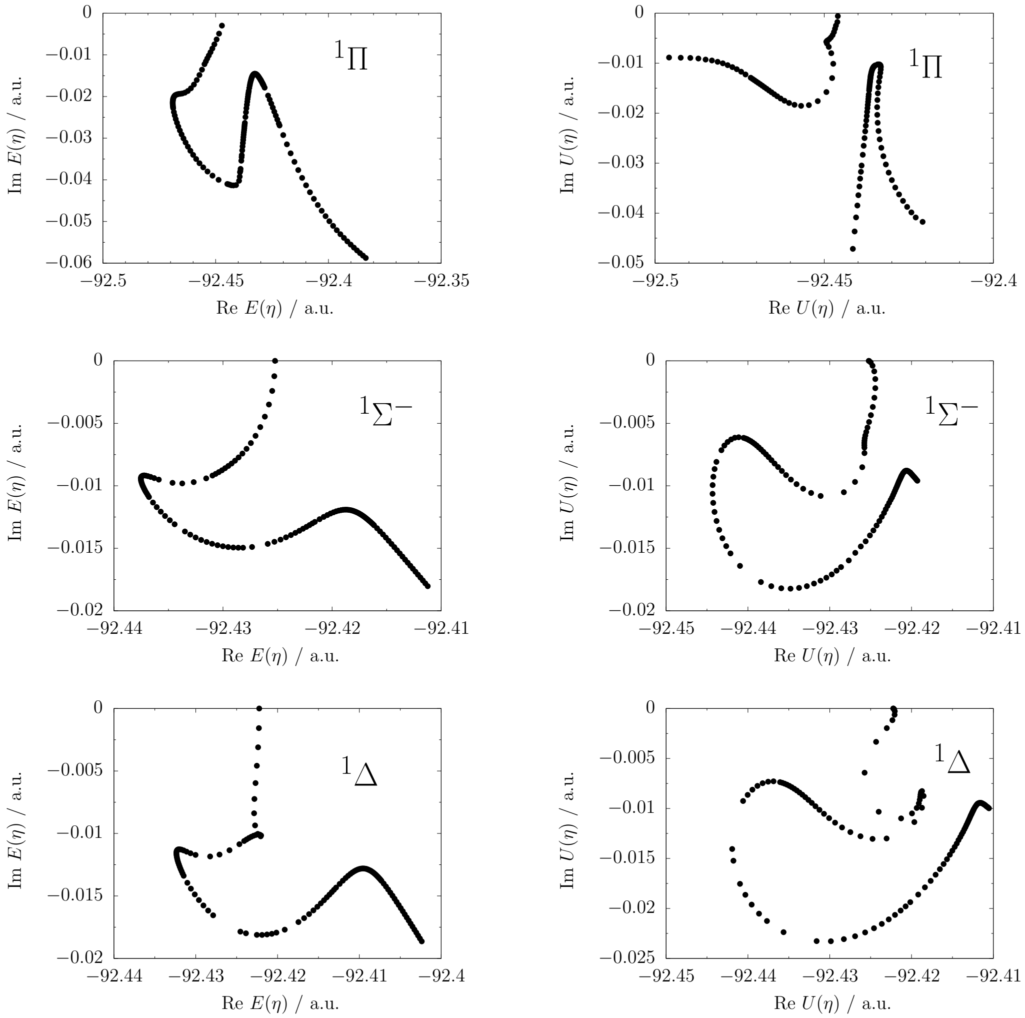


FIG. S2: $E(\eta)$ and $U(\eta)$ trajectories for resonances in CN$^-$ of singlet spin symmetry. η varies from 0 to 0.19 a.u. for $^1\Delta$ and $^1\Sigma^-$ and from 0 to 1.5 a.u. for $^1\Pi$.

B. C_3N^-

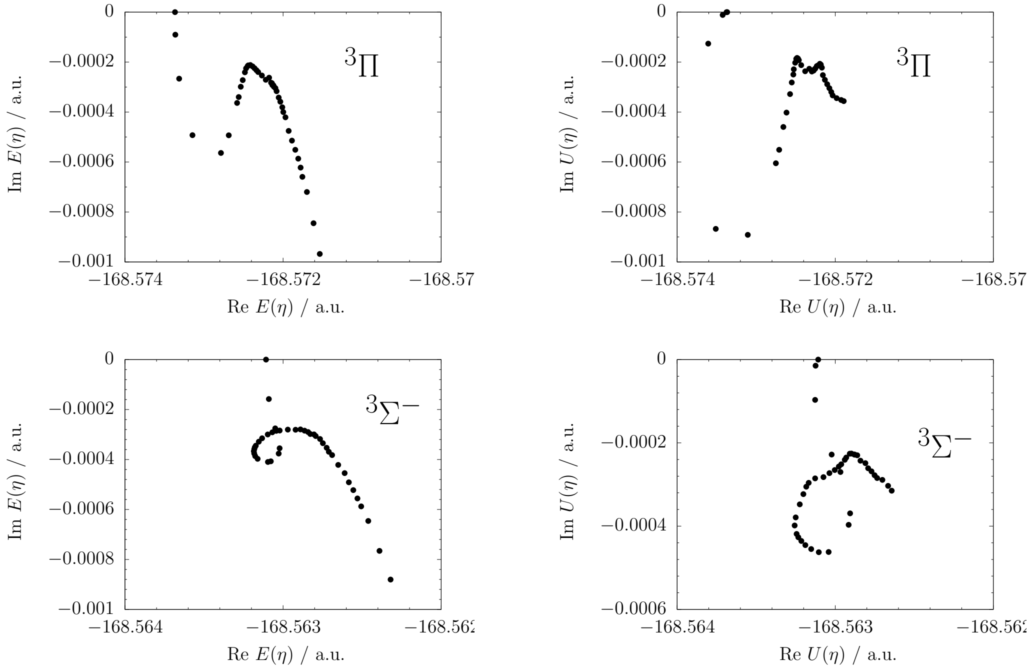
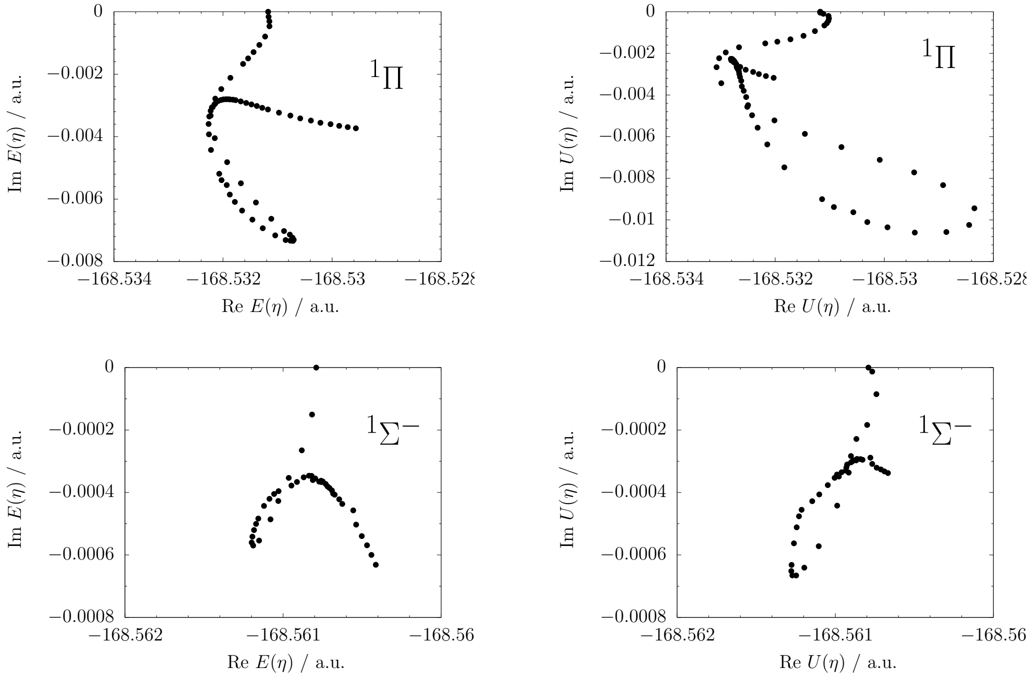


FIG. S3: $E(\eta)$ and $U(\eta)$ trajectories for resonances in C_3N^- of triplet spin symmetry. η varies from 0 to 0.01 a.u.



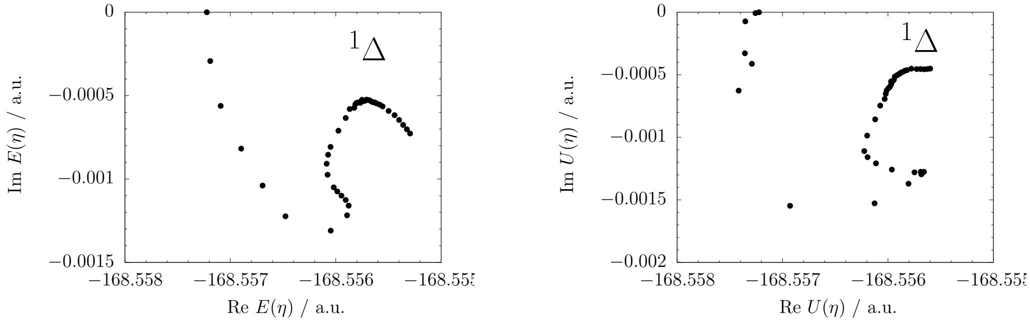


FIG. S4: $E(\eta)$ and $U(\eta)$ trajectories for resonances in C_3N^- of singlet spin symmetry. η varies from 0 to 0.005 a.u. for $^1\Delta$ and $^1\Sigma^-$, and from 0 to 0.034 for $^1\Pi$.

C. C_5N^-

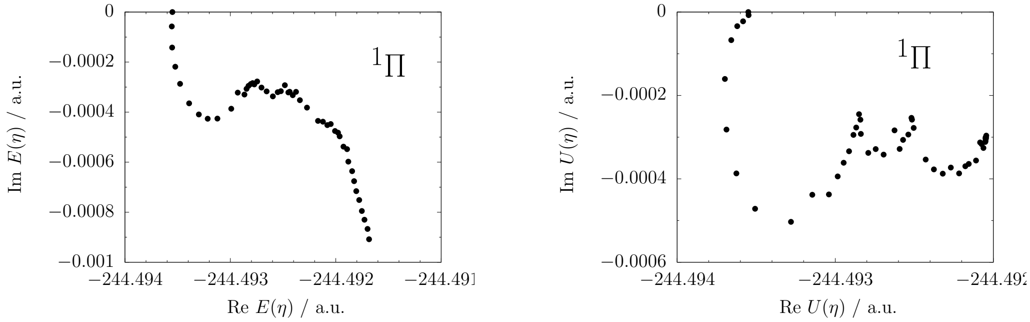


FIG. S5: $E(\eta)$ and $U(\eta)$ trajectories for $^1\Pi$ resonance in C_5N^-. η varies from 0 to 0.03 a.u.

II. η–TRAJECTORIES FOR POSSIBLE DIPOLE-STABILIZED RESONANCES, WITH SIGNIFICANT CONTRIBUTION OF EXCITATION FROM σ TO DIFFUSE σ^* ORBITAL

Trajectories were calculated using the aug-cc-VDZ+3s3p basis set. CAP onset parameters as in Table SI. In the figures below left panels show zero-order energies $E(\eta)$, right panels show corresponding first-order corrected energies $U(\eta)$.

A. C_5N^-

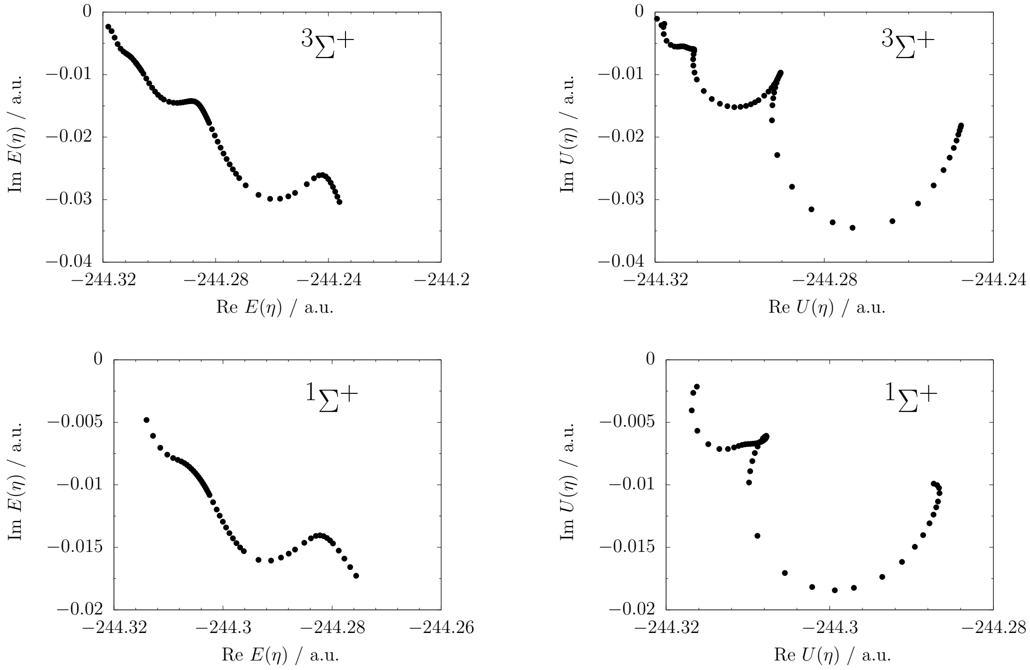


FIG. S6: $E(\eta)$ and $U(\eta)$ trajectories for resonances in C_5N^- of triplet spin symmetry. η varies from 0.00005 to 0.75 a.u. for $^3\Sigma^+$ state and from 0.0002 to 0.04 a.u. for $^1\Sigma^+$ state.

B. C_7N^-

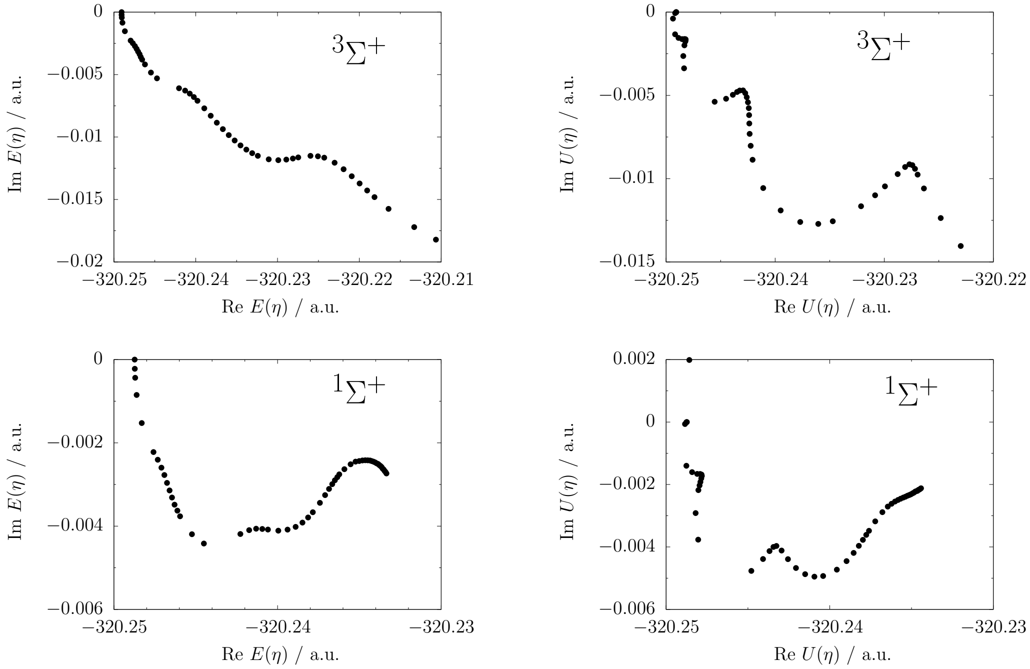


FIG. S7: $E(\eta)$ and $U(\eta)$ trajectories for $^1\Pi$ resonance in C_7N^-. η varies from 0 to 0.1 a.u.

III. RESONANCES IN CN^- FROM COMPLEX BASIS FUNCTIONS METHOD

To reaffirm our conclusions on the basis of the CAP augmented calculations, we carried out additional calculations by means of the complex basis function (CBF) method. We employed here the most recent implementation of the CBF method combined with the EOM-EE-CCSD approach[1]. As described in the main paper, the calculation were performed with the aug-cc-pVTZ+3s3p basis set in which the Gaussian exponents of the additional diffuse functions (3s3p) were scaled by the complex number $e^{-2i\theta}$ with θ going from 0° to 35° in intervals of 1°. Figure S8 shows all θ trajectories obtained for excited states in CN^- of triplet spin symmetry. The identification of resonance trajectories and their corresponding stationary points is straightforward. Table SII shows the extracted parameters of CN^- resonances, which can be compared with the results of the CAP calculations (Table IV in the main paper).

TABLE SII: Positions E_R and widths Γ of the triplet resonances in CN^- obtained with complex basis function method.

	E_R / eV	Γ / eV
$^3\Sigma^+$	6.30	0.28
$^3\Pi$	6.24	0.74
$^3\Delta$	7.16	0.50
$^3\Sigma^-$	7.78	0.76

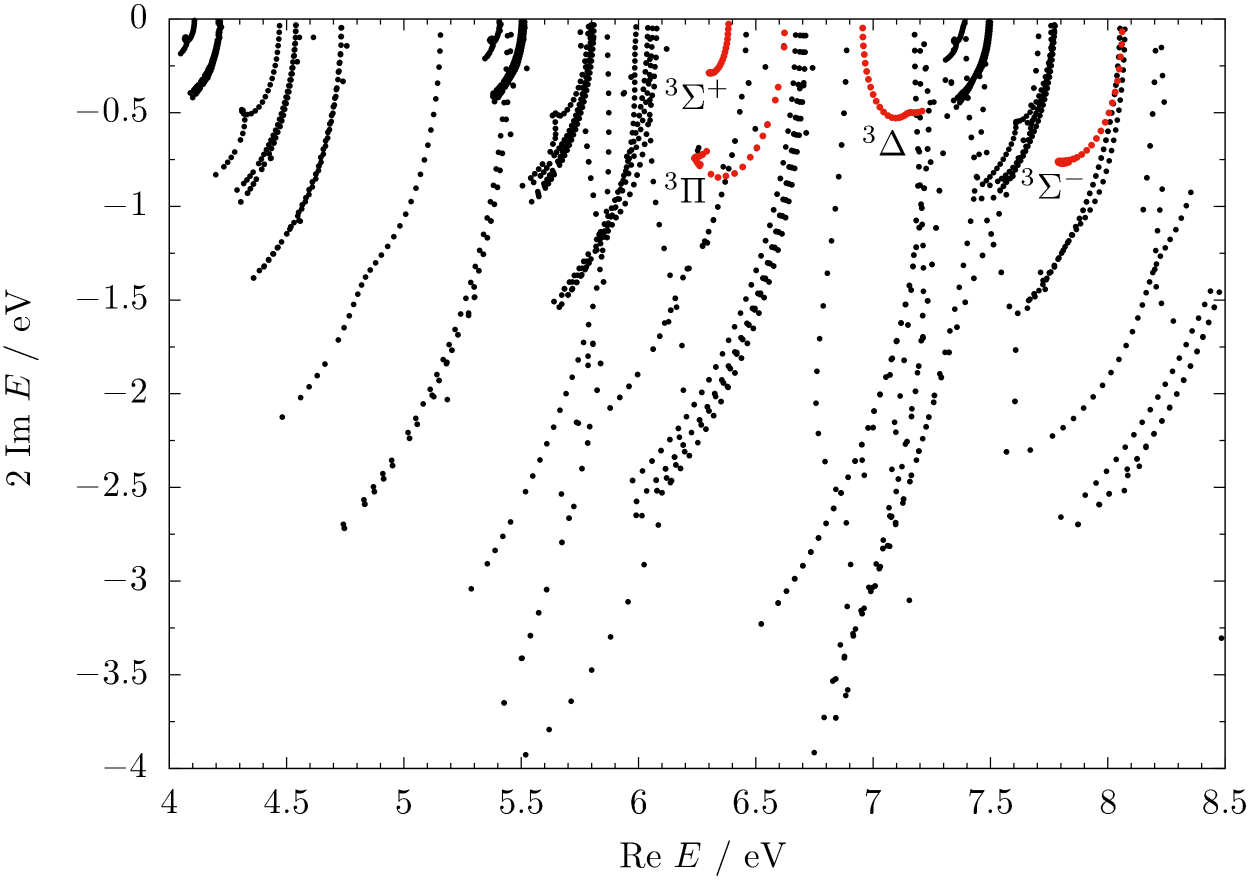


FIG. S8: θ trajectories for triplet excited states in CN^-. The plot shows real part versus twice the imaginary part of excitation energies obtained from the EOM-EE-CCSD calculations. θ varies from 0° to 35°. Trajectories corresponding to the identified resonances are marked in red.

IV. CALCULATION OF PHOTODETACHMENT CROSS SECTIONS

The total photodetachment cross section σ_{tot} was calculated as a sum of two terms: background cross section (σ_{bg}) due to direct detachment into the continuum and resonance cross section ($\sigma_{\rm res}$) due to transitions into the anion's metastable states,

$$\sigma_{\rm tot} = \sigma_{\rm bg} + \sigma_{\rm res}. \tag{1}$$

Background cross section $\sigma_{\rm bg}$ is a sum of independent terms describing electron detachment from the anionic ground state X into final electronic states F of the radical:

$$\sigma_{\rm bg} = \sum_F \sigma_{X\to F}. \tag{2}$$

Each term $\sigma_{X\to F}$ was calculated using the respective Dyson orbital $\phi^{\rm Dys}_{X\to F}$ and a plane wave representing the outgoing electron[2]. Based on detachment energies, we included the contributions from detachment into the radical lowest $^2\Sigma^+$ and $^2\Pi$ states (for each of the anions), and, additionally, into the second $^2\Sigma^+$ state (for CN$^-$ only).

The resonance contribution $\sigma_{\rm res}$ is a sum of terms describing optical transitions from anionic ground state X into each of metastable states f of the anion with non-vanishing transition dipole moment:

$$\sigma_{\rm res} = \sum_f \sigma_{X\to f}. \tag{3}$$

We computed the individual terms $\sigma_{X\to f}$ for each of the relevant states f using the formula for the absorption cross section for bound-to-bound transition[3]:

$$\sigma_{i\to f}(\omega) = \frac{1}{4}\frac{g_f}{g_i}\lambda^2_{fi}A_{fi}g(\omega) = \frac{4\pi^2}{3}\frac{g_f}{g_i}\frac{\omega_{if}e^2}{4\pi\epsilon_0\hbar c}|\mu_{i\to f}|^2 g(\omega), \tag{4}$$

or in atomic units:

$$\sigma_{i\to f}(\omega) = \frac{g_f}{g_i}\frac{4\pi^2\omega_{if}}{3c}|\mu_{i\to f}|^2 g(\omega), \tag{5}$$

where g_f and g_i are degeneracies of upper and lower levels, λ_{if} and ω_{if} are the wavelength and the frequency of the resonance transition, A_{fi} is the Einstein coefficient, $\mu_{i\to f}$ is the transition dipole moment, and $g(\omega)$ is the lineshape function. We assumed the line shape function $g(\omega)$ to be Lorentzian with a full-width-at-half-maximum equal to the resonance width Γ:

$$g(\omega) = \frac{\Gamma/2\pi}{(\omega-\omega_{if})^2 + (\Gamma/2)^2}. \tag{6}$$

Transition dipole moments $\mu_{i\to f}$ from the anion ground state $X^1\Sigma^+$ to the resonance state f were calculated at the optimal $\eta^{(0)}$ for each of the optically active metastable state, using the recent implementation[4]. Since in the CAP-augmented calculation, $\mu_{i\to f}\mu_{f\to i}$ is a complex number, we assumed that the observable cross section is due to real part of the transition strength:

$$|\mu_{i\to f}|^2 = \mathrm{Re}(\mu_{i\to f}\mu_{f\to i}). \tag{7}$$

Calculated transition dipole moments are shown in Table SIII.

TABLE SIII: Transition dipole moments from the anionic ground state $X^1\Sigma^+$ to metastable excited states (left and right: $\mu_{X\to f}$ and $\mu_{f\to X}$, respectively), and corresponding CAP strength η at which the dipole moments were calculated (in atomic units).

Anion	State f	$\mu_{X\to f}$	$\mu_{f\to X}$	η
CN^-	$^1\Pi$	$0.35 + 0.07i$	$0.36 + 0.07i$	0.064
C_3N^-	$^1\Pi$	$0.62 + 0.09i$	$0.65 + 0.08i$	0.0085
	$2^1\Sigma^+$	0.08	0.09	0.0
C_5N^-	$^1\Pi$	$-0.47 - 0.02i$	$-0.49 - 0.02i$	0.001
	$2^1\Sigma^+$	$-2.04 + 0.79i$	$-2.21 + 0.83i$	0.018
C_7N^-	$^1\Pi$	0.37	0.39	0.0
	$2^1\Sigma^+$	$4.60 - 0.14i$	$4.95 - 0.13i$	0.030

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[1] A. F. White, E. Epifanovsky, C. W. McCurdy, and M. Head-Gordon, *J. Chem. Phys.*, 2017, **146**, 234107.

[2] S. Gozem, A. O. Gunina, T. Ichino, D. L. Osborn, J. F. Stanton, and A. I. Krylov, *J. Phys. Chem. Lett.*, 2015, **6**, 4532–4540.

[3] R. C. Hilborn, *arXiv*, 2002, p. 0202029.

[4] T.-C. Jagau and A. I. Krylov, *J. Chem. Phys.*, 2016, **144**, 054113.

Relevant Cartesian geometries

Anions geometries employed in the resonance calculations:

```
CN- (anion)
Nuclear Repulsion Energy =  18.8831290175 hartrees
Total CCSD Energy = -92.72330279 hartrees

                  Coordinates (Angstroms)
    ATOM           X           Y            Z
    1 C       0.000000     0.000000    -0.633769
    2 N       0.000000     0.000000     0.543230

C3N- (anion)
Nuclear Repulsion Energy = 70.0417347661 hartrees
Total  CCSD Energy = -168.75034755 hartrees

                  Coordinates (Angstroms)
     ATOM          X            Y            Z
    1 C       0.000000     0.000000     1.989631
    2 C       0.000000     0.000000     0.738201
    3 C       0.000000     0.000000    -0.628428
    4 N       0.000000     0.000000    -1.799488

C5N- (anion)
Nuclear Repulsion Energy = 135.9210880765 hartrees
Total CCSD Energy = -244.68048977 hartrees

                   Coordinates (Angstroms)
     ATOM           X           Y            Z
    1 N       0.000000     0.000000    -3.068059
    2 C       0.000000     0.000000    -1.898259
    3 C       0.000000     0.000000    -0.541259
    4 C       0.000000     0.000000     0.690040
    5 C       0.000000     0.000000     2.035340
    6 C       0.000000     0.000000     3.293540

C7N- (anion)
Nuclear Repulsion Energy = 211.5329017291 hartrees
Total CCSD Energy = -320.82118474 hartrees

                   Coordinates (Angstroms)
     ATOM           X           Y            Z
    1 N       0.000000     0.000000    -4.344000
    2 C       0.000000     0.000000    -3.175900
    3 C       0.000000     0.000000    -1.816700
    4 C       0.000000     0.000000    -0.588000
    5 C       0.000000     0.000000     0.749400
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```
   6 C        0.000000      0.000000      1.987300
   7 C        0.000000      0.000000      3.325400
   8 C        0.000000      0.000000      4.586500
```

Basis set details

Calculations were primarily done using the aug-cc-pVTZ+3s3p basis set, in which the standard aug-cc-pVTZ basis set [R.A. Kendall, T.H. Dunning, and R.J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992)] was augmented by an extra set of diffuse functions (3s3p) centered on each atom. The exponents of these additional functions were generated in an even-tempered manner with a spacing of 2.0, starting at the most diffuse function in the original basis set.

```
C     0
S   8   1.00
   8236.0000000         0.0005310
   1235.0000000         0.0041080
    280.8000000         0.0210870
     79.2700000         0.0818530
     25.5900000         0.2348170
      8.9970000         0.4344010
      3.3190000         0.3461290
      0.3643000        -0.0089830
S   8   1.00
   8236.0000000        -0.0001130
   1235.0000000        -0.0008780
    280.8000000        -0.0045400
     79.2700000        -0.0181330
     25.5900000        -0.0557600
      8.9970000        -0.1268950
      3.3190000        -0.1703520
      0.3643000         0.5986840
S   1   1.00
      0.9059000         1.0000000
S   1   1.00
      0.1285000         1.0000000
S   1   1.00
      0.0440200         1.0000000
S   1   1.00
      0.0220200         1.0000000
S   1   1.00
      0.0110200         1.0000000
S   1   1.00
      0.0055100         1.0000000
```

```
P   3   1.00
     18.7100000         0.0140310
      4.1330000         0.0868660
      1.2000000         0.2902160
P   1   1.00
      0.3827000         1.0000000
P   1   1.00
      0.1209000         1.0000000
P   1   1.00
      0.0356900         1.0000000
P   1   1.00
      0.0175000         1.0000000
P   1   1.00
      0.0088000         1.0000000
P   1   1.00
      0.0044000         1.0000000
D   1   1.00
      1.0970000         1.0000000
D   1   1.00
      0.3180000         1.0000000
D   1   1.00
      0.1000000         1.0000000
F   1   1.00
      0.7610000         1.0000000
F   1   1.00
      0.2680000         1.0000000
```

```
N     0
S   8   1.00
  11420.0000000          0.0005230
   1712.0000000          0.0040450
    389.3000000          0.0207750
    110.0000000          0.0807270
     35.5700000          0.2330740
     12.5400000          0.4335010
      4.6440000          0.3474720
      0.5118000         -0.0085080
S   8   1.00
  11420.0000000         -0.0001150
   1712.0000000         -0.0008950
    389.3000000         -0.0046240
    110.0000000         -0.0185280
     35.5700000         -0.0573390
     12.5400000         -0.1320760
      4.6440000         -0.1725100
      0.5118000          0.5999440
S   1   1.00
      1.2930000          1.0000000
S   1   1.00
      0.1787000          1.0000000
S   1   1.00
      0.0576000          1.0000000
S   1   1.00
      0.0288000          1.0000000
S   1   1.00
      0.0144000          1.0000000
S   1   1.00
      0.0072000          1.0000000
```

```
P   3   1.00
     26.6300000          0.0146700
      5.9480000          0.0917640
      1.7420000          0.2986830
P   1   1.00
      0.5550000          1.0000000
P   1   1.00
      0.1725000          1.0000000
P   1   1.00
      0.0491000          1.0000000
P   1   1.00
      0.0245000          1.0000000
P   1   1.00
      0.0122000          1.0000000
P   1   1.00
      0.0061000          1.0000000
D   1   1.00
      1.6540000          1.0000000
D   1   1.00
      0.4690000          1.0000000
D   1   1.00
      0.1510000          1.0000000
F   1   1.00
      1.0930000          1.0000000
F   1   1.00
      0.3640000          1.0000000
```