Multidimensional Potential Energy Surfaces
resolved at the RASPT2 level for accurate
photoinduced isomerization dynamics of
azobenzene

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Supporting Information Available

1 Active space orbitals

1.1 \textit{trans}-azobenzene

Occupied orbitals:

Virtual orbitals:
1.2 *cis*-azobenzene

Occupied orbitals:

Virtual orbitals:

Orbitals involved in the $n\pi^*$ transition:

\[
\begin{align*}
\text{trans-azobenzene} & \quad \rightarrow \\ 
\text{cis-azobenzene} & \quad \rightarrow
\end{align*}
\]

Orbitals involved in the $\pi\pi^*$ transition:

\[
\begin{align*}
\text{trans-azobenzene} & \quad \rightarrow \\ 
\text{cis-azobenzene} & \quad \rightarrow
\end{align*}
\]
2 SS-RASPT2 vs MS-RASPT2

For the points of the rigid scan in which CNNC < 82° or CNNC > 102° the $S_0$ and $S_1$ PESs are well separated in energy, and the results of SS-RASPT2 and MS-RASPT2 are exactly the same, as shown in Figure S1 (a). However, for $82° \leq \text{CNNC} \leq 102°$, the results of the two methods differ significantly. Here, the SS-RASPT2 PESs show double or triple crossings (see Figure S1 (b)), which disappear after MS-RASPT2 correction. These SS-RASPT2 CIs are not accompanied by a sudden change in the wavefunction, as expected in a real crossing point, but rather the two wavefunctions show a multiconfigurational nature in which the closed shell and $n\pi^*$ configurations mix. This is consequence of the strong wavefunction mixing at the RASSCF level in this region, that is not properly fixed by the SS-RASPT2 correction. However, the scenario is more balanced at MS-RASPT2 level, where the wavefunction mixing is also corrected and the nature of two states is better defined.

**Figure S1:** Comparison between SS-RASPT2 (red line) and MS-RASPT2 (blue line) energy at CNNC = 60° (a) and at CNNC = 90° (b).
3 Rigid bidimensional scan starting from the trans $S_0$ minimum (torsion + symmetric bending)

Figure S2: Side views ((a) and (b)) and top view ($S_0$ (c) and $S_1$ (d)) of the PESs in the coordinates of CNNC torsion and symmetric CNN bending for the rigid scan starting from the trans $S_0$ minimum; cuts through the PESs for a selected symmetric bending (e-h) and torsion (i-l) values ($S_0$ red line, $S_1$ blue line).
4 Rigid bidimensional scan starting from the *cis* $S_0$ minimum (torsion + symmetric bending)

**Figure S3:** Side ((a) and (b)) and top views ($S_0$ (c) and $S_1$ (d)) of the PESs in the space of CNNC torsion and symmetric CNN bending for the rigid scan starting from the *cis* $S_0$ minimum; cuts through the PESs for a selected symmetric bending (e-h) and torsion (i-l) values ($S_0$ red line, $S_1$ blue line).
5 Bidimensional CNN/NNC bending scans

Figure S4: Top views of $S_0$ and $S_1$ PESs (isolines every 0.1 eV) and energy gap $E_{S_1 - S_0}$ in the space of CNN and NCC bending angles for fixed torsion 150°, 98°, 90°, 86° and 30° at the RASPT2 level (see computational methods); the diagonal connects symmetric structures. For 98°, 90° and 86° torsion the NAC vector module (in atomic units) is also displayed, for the points where $E_{S_1 - S_0} \leq 0.3$ eV.

For CNNC $\leq 60^\circ$ the PESs are affected by the change from trans- to cis-derived structures, which produces some ridges. This is much visible in the case of CNNC = 10°, where $S_1$ displays two minima (T10-$S_1$ min trans and T10-$S_1$ min cis see main text): the trans-derived structure is the absolute minimum but this is likely to be an artifact of merging the two rigid scans, while the real minimum is more probably the cis-derived one, which is more coherent with the $n\pi^*$ minima from the other scans.
5.1 Relevant structures from the rigid scan

Table S1: Structures and energies* of $S_0$, $S_1$ and $S_2$ at significant points (minima, saddle points, relevant CIs) obtained with the rigid scan (in the space of CNNC torsion and CNN/NNC bending) and with unconstrained optimizations. (* $a$=SS-RASPT2, $b$=MS-RASPT2)

|               | CNNC (°) | CNN (°) | NNC (°) | $E_{S_0}$ (eV) | $E_{S_1}$ (eV) | $E_{S_2}$ (eV) |
|---------------|----------|---------|---------|----------------|----------------|----------------|
| $S_0$ trans min | 180      | 112-114 | 112-114 | 0.00$^a$       | 2.66$^a$       | 3.86$^a$       |
| $S_0$ cis min  | 0        | 120     | 120     | 0.37$^a$       | 3.15$^a$       | -              |
| $S_0$ TS       | 90       | 118     | 118     | 1.57$^a$       | 2.14$^a$       | -              |
| $S_1$ trans min| 180      | 126     | 126     | 0.51$^a$       | 2.21$^a$       | -              |
| $S_1$ cis min  | 0        | 126     | 126     | 0.53$^a$       | 3.03$^a$       | -              |
| $S_1$ symm min | 100      | 120     | 120     | 1.60$^a$       | 2.06$^a$       | -              |
| $S_2$ min      | 180      | 108-110 | 108-110 | 0.11$^a$       | 2.99$^a$       | 3.84$^a$       |
| $S_1/S_0$ CI-bend1 | 180  | 150     | 150     | 3.04$^a$       | 3.08$^a$       | -              |
| $S_1/S_0$ CI-bend2 | 0  | 156     | 156     | 3.22$^a$       | 3.24$^a$       | -              |
| T120-S0 min    | 120      | 114     | 114     | 1.03$^a$       | 2.27$^a$       | -              |
| T120-S1 min    | 120      | 122     | 122     | 1.19$^a$       | 2.10$^a$       | -              |
| T102-S0 min    | 102      | 116     | 116     | 1.51$^b$       | 2.13$^b$       | -              |
| T102-S1 min    | 102      | 120     | 122     | 1.55$^b$       | 2.15$^b$       | -              |
| T94-S0 min     | 94       | 116     | 116     | 1.54$^b$       | 2.42$^b$       | -              |
| T94-S1 min     | 94       | 116     | 132     | 1.74$^b$       | 2.16$^b$       | -              |
| T82-S0 min     | 82       | 116     | 116     | 1.45$^b$       | 2.42$^b$       | -              |
| T82-S1 min     | 82       | 116     | 134     | 1.70$^b$       | 2.17$^b$       | -              |
| T60-S0 min     | 60       | 122     | 122     | 1.15$^a$       | 2.22$^a$       | -              |
| T60-S1 min     | 60       | 124     | 124     | 1.16$^a$       | 2.20$^a$       | -              |
| T10-S0 min     | 10       | 118     | 118     | 0.37$^a$       | 3.16$^a$       | -              |
| T10-S1 min trans | 10     | 144     | 146     | 2.01$^a$       | 2.85$^a$       | -              |
| T10-S1 min cis | 10       | 126     | 126     | 0.57$^a$       | 3.01$^a$       | -              |
| T98-S1/S0 CI   | 98       | 116     | 146     | 2.12$^b$       | 2.22$^b$       | -              |
| T94-S1/S0 CI   | 94       | 114     | 146     | 2.16$^b$       | 2.19$^b$       | -              |
| T90-S1/S0 CI   | 90       | 114     | 146     | 2.13$^b$       | 2.20$^b$       | -              |
| opt-S1 min     | 96       | 115     | 145     | 1.98$^b$       | 1.98$^b$       | -              |
| opt-S1/S0 CI   | 95       | 115     | 146     | 1.98$^b$       | 1.99$^b$       | -              |
### opt-S\(_1\) min

|   |   |   |
|---|---|---|
| C | -0.006985 | -0.232103 |
| C | 0.030078  | -0.003127  |
| C | 1.252379  | 0.190744   |
| C | 2.455494  | 0.155297   |
| C | 2.430874  | -0.074810  |
| C | 1.199922  | -0.272303  |
| N | -1.137080 | -0.012100  |
| N | -2.234636 | -0.056160  |
| C | -3.214394 | -0.852850  |
| C | -4.430584 | -0.308318  |
| C | -5.409036 | -1.155837  |
| C | -5.216724 | -2.555787  |
| N | -4.010619 | -3.095529  |
| C | -3.004798 | -2.269254  |
| H | -4.581059 | 0.781159   |
| H | -6.339916 | -0.723865  |
| H | -5.991023 | -3.210603  |
| H | -3.47685 | -4.177693  |
| H | -2.066231 | -2.680039  |
| H | 1.234137  | 0.364557   |
| H | 3.408451  | 0.308962   |
| H | 3.366423  | -0.100028  |
| H | 1.188202  | -0.452524  |
| H | -0.968334 | -0.375943  |

### opt-S\(_1\)/S\(_0\) CI

|   |   |   |
|---|---|---|
| C | -0.017837 | -0.210072 |
| C | 0.027308  | 0.004079  |
| C | 1.254511  | 0.182461  |
| C | 2.454150  | 0.143350  |
| C | 2.421296  | -0.075909 |
| C | 1.185289  | -0.254775 |
| N | -1.135888 | -0.012378 |
| N | -2.235221 | -0.059299 |
| C | -3.212787 | -0.854912 |
| C | -4.19818  | -0.302452 |
| C | -5.94479  | -1.158673 |
| C | -5.206229 | -2.559044 |
| C | -4.090656 | -3.097953 |
| C | -3.008775 | -2.270912 |
| H | -5.67254  | 0.779766  |
| H | -6.318479 | -0.720204 |
| H | -5.975899 | -3.214502 |
| H | -3.848851 | -4.180497 |
| H | -2.077584 | -2.681470 |
| H | 1.243646  | 0.343627  |
| H | 3.410745  | 0.282156  |
| H | 3.353962  | -0.108282 |
| H | 1.166523  | -0.425297 |
| H | -0.981816 | -0.342961 |
Figure S5: NAC vector coordinates (expressed as x,y,z respectively for each atom) for selected test geometries. The blue color refers to nitrogen atoms while the green color refers to carbon atoms. The x,y,z NAC value for all the hydrogen atoms was always close to 0,0,0 (not reported)

(a) CNNC = 90°
CN = 116°-132°
ΔE1-S0 = 0.42 eV

(b) CNNC = 90°
CN = 116°-146°
ΔE1-S0 = 0.08 eV

(c) CNNC = 90°
CN = 150°-150°
ΔE1-S0 = 0.15 eV
8 Semiclassical dynamics

8.1 PES fit details

The function $\Delta U_{tbb}$ used to reproduce the QM PES is a combination of sixth order cosine and sixth order polynomial approximations

$$\Delta U_{tbb} = U_{tbb0} + U_t(\phi) + \sum_{i=1}^{2} U_{b,i}(\theta_i) + U_{bb}^{II}(\theta_1, \theta_2) +$$

$$+ \sum_{i=1}^{2} U_{tb,i}^{II}(\phi, \theta_i) + U_{bhb}^{II}(\phi, \theta_1, \theta_2).$$

The term $U_{tbb0}$ is a shift constant, while

$$U_t(\phi) = \sum_{n=1}^{6} k_n \cos (n \phi - \gamma_n)$$

is the expression used to calculate the classical torsional potential energy. The third and the fourth terms,

$$U_{b,i}(\theta_i) = \sum_{m=1}^{6} k_i^m \theta_i^m,$$

$$U_{bb}^{II}(\theta_1, \theta_2) = \sum_{l=1}^{3} \sum_{m=l}^{6-l} (k_l^m \theta_1^l \theta_2^m + k_l^m \theta_1^m \theta_2^l),$$

are the diagonal and off-diagonal terms of the 2D polynomial approximation and describe the anharmonicity and the coupling (denoted by the superscript II) between the two bending angles $\theta_1$ and $\theta_2$. The last terms,

$$U_{tb,i}^{II}(\phi, \theta_i) = \sum_{m=1}^{6} \theta_i^m \sum_{n=1}^{6} k_{i,n}^m \cos (n \phi - \gamma_n^m),$$

$$U_{bhb}^{II}(\phi, \theta_1, \theta_2) = \sum_{l=1}^{3} \sum_{m=l}^{6-l} \sum_{n=1}^{6} (k_n^{l,m} \theta_1^l \theta_2^m + k_n^{l,m} \theta_1^m \theta_2^l) \cos (n \phi - \gamma_n^{l,m}),$$

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are combinations of cosine and polynomial expressions, describing the coupling between the
dihedral angle $\phi$ and the two bending angles $\vartheta_1$ and $\vartheta_2$. Thus, rewriting equation (1), we
get

$$
\Delta U_{tbb} = U_{tbb0} + \sum_{n=1}^{6} k_n \cos (n \phi - \gamma_n) + \\
+ \sum_{i=1}^{2} \sum_{m=1}^{6} k_i^m \vartheta_i^m + \sum_{m=1}^{6} \sum_{n=m}^{6-m} \left( k_{l,m}^l \vartheta_1^l \vartheta_2^m + k_{m,l}^m \vartheta_1^m \vartheta_2^l \right) + \\
+ \sum_{i=1}^{6} \vartheta_i^m \sum_{n=1}^{6} k_{i,n}^m \cos (n \vartheta - \gamma_n^m) + \\
+ \sum_{l=1}^{6} \sum_{m=1}^{6-l} \left( k_{l,m}^l \vartheta_1^l \vartheta_2^m + k_{m,l}^m \vartheta_1^m \vartheta_2^l \right) \cos (n \vartheta - \gamma_{l,m}^l),
$$

(7)

Equation (7) presents 277 parameters, but those to be calculated through the fit procedure can be drastically reduced if applied to our specific problem. Phases $\gamma_n$, $\gamma_n^m$ and $\gamma_{n,m}^l$ can assume the value of 0 or $\pi/2$, but after few tests, we noted that better results were reached keeping all the phases equal to zero. Furthermore, $\Delta U_{tbb}$ must be symmetric upon exchange of $\vartheta_1$ and $\vartheta_2$, therefore $k_1^m = k_2^m \equiv k^m$, $k_{l,m}^l = k_{m,l}^m \equiv k_{l,m}^l$, $k_{1,n}^m = k_{2,n}^m \equiv k_n^m$ and $k_{l,m}^l = k_{n,l}^m \equiv k_{l,m}^l$. Thus, we obtain

$$
\Delta U_{tbb} = U_{tbb0} + \sum_{n=1}^{6} k_n \cos (n \phi) + \sum_{m=1}^{6} k^m (\vartheta_1^m + \vartheta_2^m) + \\
+ \sum_{l=1}^{6} \sum_{m=1}^{6-l} \left( \vartheta_1^l \vartheta_2^m + \vartheta_1^m \vartheta_2^l \right) + \\
+ \sum_{m=1}^{6} (\vartheta_1^m + \vartheta_2^m) \sum_{n=1}^{6} k_n^m \cos (n \phi) + \\
+ \sum_{l=1}^{6} \sum_{m=1}^{6-l} \left( \vartheta_1^l \vartheta_2^m + \vartheta_2^l \vartheta_1^m \right) \sum_{n=1}^{6} k_{l,m}^l \cos (n \phi),
$$

(8)
in which the parameters to fit are 112.

The fit has been carried out with the scipy.optimize.curve_fit function of Python
(which uses the non linear least squares method), obtaining satisfactory results. Figure S6 shows the fitted surfaces of $S_0$ and $S_1$, as well as the comparison between the fitting function and the computed points for selected cuts of the 3D surfaces.

**Table S2:** Root Mean Square Absolute Error (RMSAE) and Root Mean Square Relative Error (RMSRE) for the fit of $S_0$ and $S_1$ PESs

|          | RMSAE (eV) | RMSRE (%) |
|----------|------------|-----------|
| $S_0$    | 0.049      | 2.4       |
| $S_1$    | 0.042      | 1.6       |

8.2 **Velocity scaling factor**

Since the molecule has only three non-frozen degrees of freedom, the atoms velocities will be significantly smaller with respect to a fully unconstrained simulation. This implies a smaller decay probability, due to the presence of a dot product between NAC and velocity in its formula. For this reason, we compared our average velocity of the four central C, N, N, C atoms ($\bar{v}_R$) with that of a Wigner sampling in the full coordinate space ($\bar{v}_F$), finding that

$$\frac{\bar{v}_F}{\bar{v}_R} \approx 4.5$$

(9)

This material is available free of charge via the Internet at [http://pubs.acs.org/](http://pubs.acs.org/).
Figure S6: Side views of the fitted $S_0$ (a) and $S_1$ (b) PESs in the space of CNNC torsion and symmetric CNN bending; selected cuts through the PESs showing both the computed points and the fit.