

Supplementary Material

Non-adiabatic Coupling in the Potential Energy Surfaces of SO₂ Molecule

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S.1 Adiabatic to diabatic transformation (ADT) equations for Four state

One way to obtain the ADT matrix for a 4-state sub-Hilbert space is by considering a specific order of multiplication for the elementary rotation matrices as following:

$A(\gamma_{12}, \gamma_{13}, \gamma_{14}, \gamma_{23}, \gamma_{24}, \gamma_{34}) =$

$$\begin{pmatrix} \cos \gamma_{14}(Q) & 0 & 0 & \sin \gamma_{14}(Q) \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -\sin \gamma_{14}(Q) & 0 & 0 & \cos \gamma_{14}(Q) \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos \gamma_{24}(Q) & 0 & \sin \gamma_{24}(Q) \\ 0 & 0 & 1 & 0 \\ 0 & -\sin \gamma_{24}(Q) & 0 & \cos \gamma_{24}(Q) \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos \gamma_{23}(Q) & \sin \gamma_{23}(Q) & 0 \\ 0 & \sin \gamma_{23}(Q) & \cos \gamma_{23}(Q) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \\ \cdot \begin{pmatrix} \cos \gamma_{13}(Q) & 0 & \sin \gamma_{13}(Q) & 0 \\ 0 & 1 & 0 & 0 \\ -\sin \gamma_{13}(Q) & 0 & \cos \gamma_{13}(Q) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \cos \gamma_{12}(Q) & \sin \gamma_{12}(Q) & 0 & 0 \\ -\sin \gamma_{12}(Q) & \cos \gamma_{12}(Q) & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos \gamma_{34}(Q) & \sin \gamma_{34}(Q) \\ 0 & 0 & -\sin \gamma_{34}(Q) & \cos \gamma_{34}(Q) \end{pmatrix} \quad (S1)$$

Numerical stability can be challenging to achieve when multiplying matrices as shown in Eq. (S1), as there are multiple possible orders for the matrices. Typically, the most stable solution involves transforming the strongest coupling term, (such as τ_{34}) such that γ_{34} appears in the last matrix of the product.

For a four-dimensional Hilbert space with the four states, antisymmetric non-adiabatic coupling matrix τ is given in the form

$$\tau = \begin{pmatrix} 0 & \tau_{12} & \tau_{13} & \tau_{14} \\ -\tau_{12} & 0 & \tau_{23} & \tau_{24} \\ -\tau_{13} & -\tau_{23} & 0 & \tau_{34} \\ -\tau_{14} & -\tau_{24} & -\tau_{34} & 0 \end{pmatrix} \quad (S2)$$

After substituting Eqs. (S1) and (S2) into adiabatic-to-diabatic transformation (ADT) condition (Eq. (S3)),

$$\nabla \cdot A(Q) + \tau \cdot A(Q) = 0 \quad (S3)$$

We obtain explicit coupled first-order differential equations for the various elements of matrix A:

$$\nabla \gamma_{12} = -\sec \gamma_{13} (\tau_{24} \cos \gamma_{23} \sec \gamma_{24} \sin \gamma_{14} - 0.5 \tau_{13} \sin \gamma_{23} \sec \gamma_{14} - \tau_{34} \sin \gamma_{14} \sin \gamma_{23} - \\ 0.5 \tau_{34} \sec \gamma_{14} \sin \gamma_{24} \tan \gamma_{13} + \tau_{13} \sin \gamma_{24} \tan \gamma_{13} \sin \gamma_{14} + \cos \gamma_{14} (\tau_{12} \sec \gamma_{24} \cos \gamma_{23} - 0.5 \tau_{13} \sin \gamma_{23} -$$

$$0.5 \tau_{34} \sin\gamma_{24} \tan\gamma_{13}) + \tau_{13} \sin\gamma_{23} \sin\gamma_{14} \tan\gamma_{14} + \tau_{34} \sin\gamma_{14} \sin\gamma_{24} \tan\gamma_{13} \tan\gamma_{14} + \tau_{23} \sin\gamma_{24} \tan\gamma_{13} \tan\gamma_{24}) \quad (\text{S4.a})$$

$$\begin{aligned} \nabla\gamma_{13} = & -\tau_{34} \cos\gamma_{23} \sin\gamma_{14} - \tau_{24} \sin\gamma_{23} \sec\gamma_{24} \sin\gamma_{14} + \frac{7}{8} \tau_{23} \tan\gamma_{23} \tan\gamma_{13} \cos\gamma_{24} - \\ & \frac{7}{8} \tau_{23} \tan\gamma_{23} \tan\gamma_{13} \sec\gamma_{24} - \tau_{13} \sin\gamma_{14} \sin\gamma_{24} \tan\gamma_{13} \tan\gamma_{23} - \cos\gamma_{14} (\tau_{13} \cos\gamma_{23} + \tau_{12} \sin\gamma_{23} \sec\gamma_{24} - \\ & \tau_{34} \sin\gamma_{24} \tan\gamma_{13} \tan\gamma_{23}) - \frac{1}{8} \tau_{23} \sin\gamma_{24} \tan\gamma_{24} \tan\gamma_{13} \tan\gamma_{23} \end{aligned} \quad (\text{S4.b})$$

$$\nabla\gamma_{14} = -\tau_{14} + \sec\gamma_{23} (\tau_{34} \cos\gamma_{14} - \tau_{13} \sin\gamma_{14}) \tan\gamma_{13} - (\tau_{12} \cos\gamma_{14} + \tau_{24} \sin\gamma_{14} + \tau_{23} \sec\gamma_{23} \tan\gamma_{13}) \tan\gamma_{24} \quad (\text{S4.c})$$

$$\begin{aligned} \nabla\gamma_{23} = & -(\sec\gamma_{13})^2 (\tau_{23} \sec\gamma_{24} (\cos 2\gamma_{13} + \cos 2\gamma_{24}) + \sin\gamma_{24} (\tau_{34} \cos\gamma_{14} - \tau_{13} \sin\gamma_{14})) + \\ & (\sec\gamma_{24} \cos\gamma_{23} (\tau_{12} \cos\gamma_{14} + \tau_{24} \sin\gamma_{14}) - \sin\gamma_{23} (\tau_{12} \cos\gamma_{14} + \tau_{34} \sin\gamma_{14})) \tan\gamma_{13} \end{aligned} \quad (\text{S4.d})$$

$$\nabla\gamma_{24} = -\tau_{24} \cos\gamma_{14} + \tau_{12} \sin\gamma_{14} + (\cos\gamma_{24} (\tau_{34} \cos\gamma_{14} - \tau_{13} \sin\gamma_{14}) - \tau_{23} \sin\gamma_{24}) \tan\gamma_{23} \quad (\text{S4.e})$$

$$\nabla\gamma_{34} = \sec\gamma_{13} \sec\gamma_{23} (\cos\gamma_{24} (-\tau_{34} \cos\gamma_{14} + \tau_{13} \sin\gamma_{14}) + \tau_{23} \sin\gamma_{24}) \quad (\text{S4.f})$$

The presence of a conical intersection can be tested by integrating the circular non adiabatic coupling terms (NACTs) around a closed loop and examining the resulting phase change. It is important to note that the contours we have considered specially surround a conical intersection (CI), such as CIs (1,2) or (3,4) if they exist. When a contour surrounds a CI, the corresponding ADT angle is π , indicating the presence of a CI within the contour. However, if a closed contour does not surround a CI, then the NACT matrix elements between the corresponding adiabatic electronic states will be significantly small or close to zero. Therefore, if the contour surrounds the conical intersection of electronic states 1 and 2 (between two A'), and the interaction with other states in this region is negligible, then the NACT matrix elements between these two states will be dominant, while the matrix elements between other electronic states may be significantly smaller or close to zero. Since the DDR method implemented in the MOLPRO package can only determine NACTs between electronic states with the same symmetry, such as between two states with A' symmetry (states 1 and 2) or between two states with A'' symmetry (states 3 and 4), we were unable to calculate NACTs between states with different symmetries, such as states 1 and 3, 1 and 4, 2 and 3, 2 and 4. However, our analysis confirms that these interactions may be significantly small or almost zero because the adiabatic states 1 and 2 are separated from states 3 and 4 in the regions we have considered, as shown in the configurations of the SO₂ molecule in **Fig. 7** with $q=0.30 \text{ \AA}$ and **Fig. 11** with $q=0.35 \text{ \AA}$ in the manuscript.

Fig. S1 and **Fig. S2** display the adiabatic potential energies for states 1 ¹A₁, 1 ¹B₂ in C_{2v}, (¹A' in C_s), 1 ¹B₁, 1 ¹A₂ in C_{2v}, (¹A'' in C_s), and the NACTs for states 1,2 ($\tau_{\varphi 12}$ coupling between states 1 ¹A₁ and 1 ¹B₂ in C_{2v}/ 1 ¹A' and 2 ¹A' in C_s) and 3,4 ($\tau_{\varphi 34}$ coupling between states 1 ¹B₁ and 1 ¹A₂ in C_{2v}/ 1 ¹A'' and 2 ¹A'' in C_s) along the φ coordinate for the configurations shown in **Figs. 7** and **11** in the manuscript, respectively. Our results in **Fig. S1**, considering the intersection between states 1 ¹A₁ and 1 ¹B₂ ($\tau_{\varphi 12}$) show that the circle contour with a radius of $q=0.30 \text{ \AA}$ approaches the (2,3) conical intersection. Therefore, we cannot expect very small values

of NACTs between states 2 and 3 in this region. However, it is possible to neglect the effect of $\tau_{\phi 23}$ on γ_{12} for $q = 0.30 \text{ \AA}$, since $\tau_{\phi 23}$ can be directly found in one of terms of Eq. (S4.a) which multiplies $\sin\gamma_{24} \tan\gamma_{13} \tan\gamma_{24}$, and these trigonometric functions are nearly zero. Consequently, NACTs between these electronic states may be significantly small or close to zero. Considering $\tau_{13} = \tau_{14} = \tau_{23} = \tau_{24} = 0$, Eqs. (S4) can be simplified as follows:

$$\nabla\gamma_{12} = -\sec\gamma_{13}(-\tau_{34} \sin\gamma_{14} \sin\gamma_{23} - 0.5 \tau_{34} \sec\gamma_{14} \sin\gamma_{24} \tan\gamma_{13} + \cos\gamma_{14}(\tau_{12} \sec\gamma_{24} \cos\gamma_{23} - 0.5 \tau_{34} \sin\gamma_{24} \tan\gamma_{13})) + \tau_{34} \sin\gamma_{14} \sin\gamma_{24} \tan\gamma_{13} \tan\gamma_{14} \quad (\text{S5.a})$$

$$\nabla\gamma_{13} = -\tau_{34} \cos\gamma_{23} \sin\gamma_{14} - \cos\gamma_{14}(\tau_{12} \sin\gamma_{23} \sec\gamma_{24} - \tau_{34} \sin\gamma_{24} \tan\gamma_{13} \tan\gamma_{23}) \quad (\text{S5.b})$$

$$\nabla\gamma_{14} = \sec\gamma_{23} \tau_{34} \cos\gamma_{14} \tan\gamma_{13} - \tau_{12} \cos\gamma_{14} \tan\gamma_{24} \quad (\text{S5.c})$$

$$\nabla\gamma_{23} = -(\sec\gamma_{13})^2 \sin\gamma_{24} \tau_{34} \cos\gamma_{14} + (\tau_{12} \sec\gamma_{24} \cos\gamma_{23} \cos\gamma_{14} - \sin\gamma_{23}(\tau_{12} \cos\gamma_{14} + \tau_{34} \sin\gamma_{14})) \tan\gamma_{13} \quad (\text{S5d})$$

$$\nabla\gamma_{24} = \tau_{12} \sin\gamma_{14} + (\tau_{34} \cos\gamma_{24} \cos\gamma_{14} - \tau_{23} \sin\gamma_{24}) \tan\gamma_{23} \quad (\text{S5e})$$

$$\nabla\gamma_{34} = -\tau_{34} \sec\gamma_{13} \sec\gamma_{23} \cos\gamma_{24} \cos\gamma_{14} \quad (\text{S5f})$$

Since the coupling between states 1 and 2 with the other states is weak, $\gamma_{13} = \gamma_{14} = \gamma_{23} = \gamma_{24} = 0$, Eqs. (S5) can be written by

$$\nabla\gamma_{12} = -\tau_{12} \quad (\text{S6.a})$$

$$\nabla\gamma_{13} = 0 \quad (\text{S6.b})$$

$$\nabla\gamma_{14} = 0 \quad (\text{S6.c})$$

$$\nabla\gamma_{23} = 0 \quad (\text{S6.d})$$

$$\nabla\gamma_{24} = 0 \quad (\text{S6.e})$$

$$\nabla\gamma_{34} = -\tau_{34} \quad (\text{S6.f})$$

$\gamma_{12}(\mathbf{Q})$ and $\gamma_{34}(\mathbf{Q})$ are evaluated by integration over open path nuclear coordinates:

$$\gamma_{12}(\mathbf{Q}) = -\int_{Q_0}^Q d\mathbf{Q} \tau_{12}(\mathbf{Q}) \quad (\text{S7.a})$$

$$\gamma_{34}(\mathbf{Q}) = -\int_{Q_0}^Q d\mathbf{Q} \tau_{34}(\mathbf{Q}) \quad (\text{S7.b})$$

Eq. (S7.a) corresponds to Eq. (22) in the manuscript for a two-state system. Therefore, to calculate $\gamma_{12}(\mathbf{Q})$, $\gamma_{34}(\mathbf{Q})$, it is not necessary to integrate coupled Eqs. (S4.a-S4.f). It is worth noting that our numerical study is based on a specific set of two-state NACTs.

The same rationale can be applied to the conical intersection of electronic states 3 and 4 (between two A''). We can also derive the aforementioned equations for the conical intersection of electronic states 3 and 4

(between two A''). It is crucial to ensure accuracy when transitioning from a four-state calculation to two calculations for a two-state system.

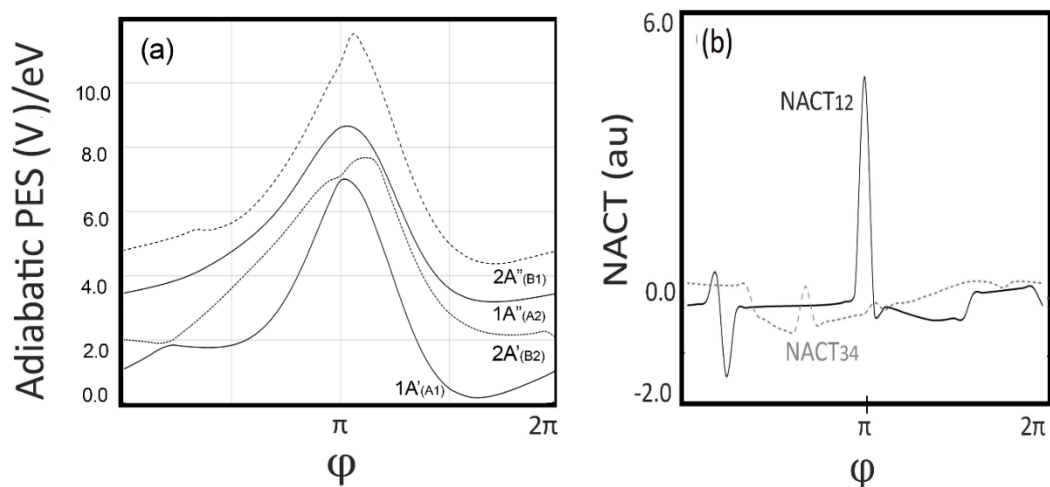


Fig. S1 (a) adiabatic potential energies for the 1^1A_1 , 1^1B_2 in C_{2v} , ($^1A'$ in C_s), 1^1B_1 , 1^1A_2 in C_{2v} , ($^1A''$ in C_s), states and (b) NACT for states 1,2($\tau_{\varphi_{12}}$ coupling between states 1^1A_1 and 1^1B_2 in C_{2v} / $1^1A'$ and $2^1A'$ in C_s) and 3,4($\tau_{\varphi_{34}}$ coupling between states 1^1B_1 and 1^1A_2 in C_{2v} / $1^1A''$ and $2^1A''$ in C_s) are plotted along φ coordinate for the configuration shown of SO_2 in Fig. 7 in the manuscript and $q=0.30 \text{ \AA}$

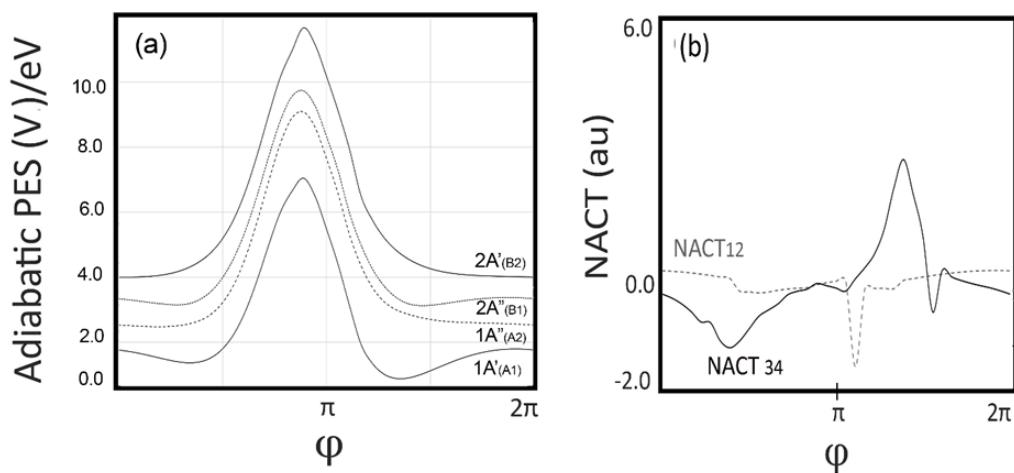


Fig. S2 (a) adiabatic potential energies for the 1^1A_1 , 1^1B_2 in C_{2v} , ($^1A'$ in C_s), 1^1B_1 , 1^1A_2 in C_{2v} , ($^1A''$ in C_s), states and (b) NACT for states 1,2($\tau_{\varphi_{12}}$ coupling between states 1^1A_1 and 1^1B_2 in C_{2v} / $1^1A'$ and $2^1A'$ in C_s) and 3,4($\tau_{\varphi_{34}}$ coupling between states 1^1B_1 and 1^1A_2 in C_{2v} / $1^1A''$ and $2^1A''$ in C_s) are plotted along φ coordinate for the configuration shown of SO_2 in Fig. 11 in the manuscript and $q=0.35 \text{ \AA}$

S.2 Subroutine for calculating diabatic potentials and couplings for any point of the nuclear configuration space of SO₂ molecule

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***,SO2 Diabatization and NACME calculation

gprint,orbitals,civector
memory,800,m
symmetry,x
orient,noorient          !noorient should always be used for diabatization
geometry={s;
          o1,s,r1;
          o2,s,r2,o1,theta}

basis=aug-cc-pvqz        !basis set

r1=2.7063                !Reference geometry
theta=[121.25]

r=[3.0463]               !Displaced geometries
dr=[0,0.01,-0.01]       !Small displacements for finite difference NACME calculation

reforb1=2140.2           !Orbital dumprecord at reference geometry
refci=6000.2             !MRCI record at reference geometry
savci=6100.2             !MRCI record at displaced geometries

text,compute wavefunction at reference geometry (C2v)
r2=r1

{hf;occ,14,4;wf,32,2,4;orbital,2100.2}

{multi;occ,14,4;closed,6,1;
 wf,32,2;state,2;          !1B1(1A") and 1A2(2A") states
 natorb,reforb1           !Save reference orbitals on reforb1
 noextra}                  !Dont use extra symmetries

{ci;occ,14,4;closed,6,1;   !MRCI at reference geometry
 wf,32,2,0;state,2;       !1B1(1A") and 1A2(2A") states
 orbital,reforb1          !Use orbitals from previous CASSCF
 save,refci}              !Save MRCI wavefunction

Text,Displaced geometries

do i=1,#r                  !Loop over different r values
 data,truncate,savci+1    !truncate dumpfile after reference
 reforb=reforb1

do j=1,3                    !Loop over small displacements for NACME
 r2=r(i)+dr(j)           !Set current r2

{multi;occ,14,4;closed,6,1;
 wf,32,2,0;state,2;       !Wavefunction definition
 start,reforb             !Starting orbitals
 orbital,3140.2+j;        !Dumprecord for orbitals
 diab,reforb              !Generate diabatic orbitals relative to reference geometry
 noextra}                 !Dont use extra symmetries

reforb=3141.2              !Use orbitals for j=1 as reference for j=2,3

{ci;occ,14,4;closed,6,1;
 wf,32,2,0;state,2;       !Use diabatic orbitals
 save,savci+j}            !Save MRCI for displaced geometries

eadia=energy              !Save adiabatic energies for use in ddr
if(j.eq.1) then
 e1(i)=energy(1)          !Save adiabatic energies for table printing
 e2(i)=energy(2)
end if

{ci;trans,savci+j,savci+j; !Compute transition densities at R2+DR(j)
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```

dm,7000.2+j}          !Save transition densities on this record
{ci;trans,savci+j,refci; !Compute transition densities between R2+DR(j) and R1
dm,7100.2+j}          !Save transition densities on this record
{ci;trans,savci+j,savci+1; !Compute transition densities between R and R2+DR(j)
dm,7200.2+j}          !Save transition densities on this record

{ddr
density,7000.2+j,7100.2+j !Densities for <R2+DR||R2+DR> and <R2+DR||R1>
orbital,3140.2+j,2140.2 !Orbitals for <R2+DR||R2+DR> and <R2+DR||R1>
energy,eadia(1),eadia(2) !Adiabatic energies
mixing,1.2,2.2}        !Compute mixing angle and diabatic energies

if(j.eq.1) then       !Store diabatic energies for R2 (DR(1)=0)
  mixci(i)=mixangci(1) !Mixing angle obtained from ci vectors only
  h11ci(i)=hdiaci(1)  !Diabatic energies obtained from ci vectors only
  h21ci(i)=hdiaci(2)  !HDIA contains the lower triangle of the diabatic hamiltonian
  h22ci(i)=hdiaci(3)
  mixtot(i)=mixang(1) !Mixing angle from total overlap (including first-order correction)
  h11(i)=hdia(1)      !Diabatic energies obtained from total overlap
  h21(i)=hdia(2)
  h22(i)=hdia(3)
end if

mix(j)=mixang(1)      !Store mixing angles for R2+DR(j)

enddo                 !End loop over j

dchi(i)=(mix(3)-mix(2))/(dr(2)-dr(3))*pi/180 !Finite difference derivative of mixing angle

{ddr
density,7201.2,7202.2,7203.2 !Compute NACME using 3-point formula
orbital,3141.2,3142.2,3143.2
states,2.2,1.2}
nacmec(i)=nacme

{table,r,mixci,mixtot,dchi,nacmec(i)
Title,Mixing angles and non-adiabatic coupling matrix elements for SO2
format,'(f10.2,4f14.4) '
sort,1
}

{table,r,e1,e2,h11ci,h22ci,h21ci
Title,Diabatic energies for SO2, obtained from CI-vectors
format,'(f10.2,5f16.8) '
sort,1}

{table,r,e1,e2,h11,h22,h21
title,Diabatic energies for SO2, obtained from CI-vectors and orbital correction
format,'(f10.2,5f16.8) '
sort,1}

enddo

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