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ºSupplementary Information for

Nitrosodisulfide $[S_2NO]^-$ (perthionitrite) is a true intermediate during the "cross-talk" of nitrosyl and sulfide

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1. Force Field parameters for acetone and dichloromethane

1- Acetone Force Field:

AMBER12 Preparation File:

```
    0    0    2

This is a remark line
molecule.res
ACE   INT  0
CORRECT     OMIT DU   BEG
  0.0000
   1  DUMM  DU    M    0  -1  -2     0.000      .0        .0      .00000
   2  DUMM  DU    M    1   0  -1     1.449      .0        .0      .00000
   3  DUMM  DU    M    2   1   0     1.523   111.21       .0      .00000
   4  C1    CT    M    3   2   1     1.540   111.208  -180.000 -0.267278
   5  H1    HC    E    4   3   2     1.081   155.459    40.754  0.070586
   6  H2    HC    E    4   3   2     1.087    46.671    57.234  0.070586
   7  H3    HC    E    4   3   2     1.086    86.938   174.442  0.070586
   8  C2    C     M    4   3   2     1.514    79.458   -74.171  0.667582
   9  O1    O     E    8   4   3     1.192   121.661   156.463 -0.556545
  10  C3    CT    M    8   4   3     1.514   116.633   -23.542 -0.267278
  11  H4    HC    E   10   8   4     1.087   110.326   -59.178  0.070586
  12  H5    HC    E   10   8   4     1.085   110.381    59.116  0.070586
  13  H6    HC    E   10   8   4     1.081   109.781  -179.982  0.070586


LOOP

IMPROPER
   C1   C3   C2   O1

DONE
STOP
```

AMBER12 Parameters File:

```
remark goes here
MASS
CT 12.010        0.878
HC 1.008         0.135
C  12.010        0.616
O  16.000        0.434

BOND
CT-HC  337.30   1.092
CT-C   328.30   1.508
C -O   648.00   1.214

ANGLE
CT-C -O    68.030     123.110
CT-C -CT   62.820     116.050
HC-CT-HC   39.430     108.350
```

```
HC-CT-C    47.200     109.680

DIHE
CT-C -CT-HC   1    0.000      180.000          2.000
HC-CT-C -O    1    0.800        0.000         -1.000
HC-CT-C -O    1    0.080      180.000          3.000

IMPROPER
CT-CT-C -O          1.1          180.0         2.0

NONBON
  CT          1.9080  0.1094
  HC          1.4870  0.0157
  C           1.9080  0.0860
  O           1.6612  0.2100
```

2- Dichloromethane Force Field:

AMBER12 Preparation File:

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This is a remark line
molecule.res
DCM   INT  0
CORRECT     OMIT DU   BEG
  0.0000
   1  DUMM  DU    M    0  -1  -2     0.000      .0        .0      .00000
   2  DUMM  DU    M    1   0  -1     1.449      .0        .0      .00000
   3  DUMM  DU    M    2   1   0     1.523   111.21       .0      .00000
   4  Cl1   Cl    M    3   2   1     1.540   111.208  -180.000 -0.069987
   5  C1    CT    M    4   3   2     1.790    94.068    96.011 -0.305330
   6  H1    H2    E    5   4   3     1.088   108.056    65.063  0.225987
   7  H2    H2    E    5   4   3     1.087   108.062   -55.715  0.220075
   8  Cl2   Cl    M    5   4   3     1.792   113.320  -175.306 -0.070744


LOOP

IMPROPER

DONE
STOP
```

AMBER12 Parameters File:

```
remark goes here
MASS
Cl 35.450        1.910
CT 12.010        0.878
H2 1.008         0.135

BOND
```

```
Cl-CT  279.00   1.786
CT-H2  337.30   1.092

ANGLE
Cl-CT-H2   40.330     107.650
Cl-CT-Cl   54.230     111.030
H2-CT-H2   39.430     108.350

DIHE

IMPROPER

NONBON
  Cl          1.9480  0.2650
  CT          1.9080  0.1094
  H2          1.4870  0.0157
```

2. Details of the real time TD-DFT simulations

In order to obtain an absorption spectrum from an electron dynamics simulation, we followed the same procedure as in reference 1. The system was subjected to an initial δ function like electric-field kick, narrow enough to homogeneously excite all electronic frequencies. This was achieved using a linearly polarized Gaussian type perturbation $(\vec{E}(t))$ imposed to the ground state density

$$\vec{E}(t) = E_0 \exp\left[\frac{-t^2}{2\omega^2}\right]\hat{r} \quad \text{(S3)}$$

The values utilized for the maximum (E_0) and width (ω) of the gaussian perturbation where 0.01 au and $2.24.10^{-3}$ fs respectively. By performing a real time simulation in each polarization of the perturbation (symmetries in the system may alleviate this need), the polarizability tensor $\alpha(\omega)$ was constructed from the Fourier transforms of the time dependent dipole moment $\mu(t)$

$$\alpha_{ik}(\omega) = \frac{\mu_k^{ind}(\omega)}{E_i(\omega)} = \frac{\int dte^{i\omega t}\mu_k^{ind}(t)e^{-\gamma t}}{\int dte^{i\omega t}E_i(t)} \quad \text{(S4)}$$

The damping factor γ introduces a broadening in the absorption spectrum peaks emulating the lifetime of the excited states. Values in the order of 0.2 fs^{-1} were adopted for this parameter to compute the spectra. Finally, the absorption cross section ($\sigma(\omega)$) was obtained from the trace of the frequency domain polarizability tensor

$$\sigma(\omega) = \frac{4\pi\omega}{c}\operatorname{Im}[\alpha(\omega)] \quad \text{(S5)}$$

And the dipole strength function $S(\omega)$ was calculated as:

$$S(\omega) = \frac{1}{3}Tr[\alpha(\omega)] \quad \text{(S6)}$$

Absorption spectra presented in this work were calculated by performing this real-time calculations at different geometries derived from the nuclear QM/MM dynamics, averaging the spectra obtained for each configuration until the absorption maximum was stabilized at a certain value. Depending on the flexibility showed by the molecule across the simulations, the process took between 10 and 100 snapshots to reach convergence, as shown in the example presented in Figure S1.

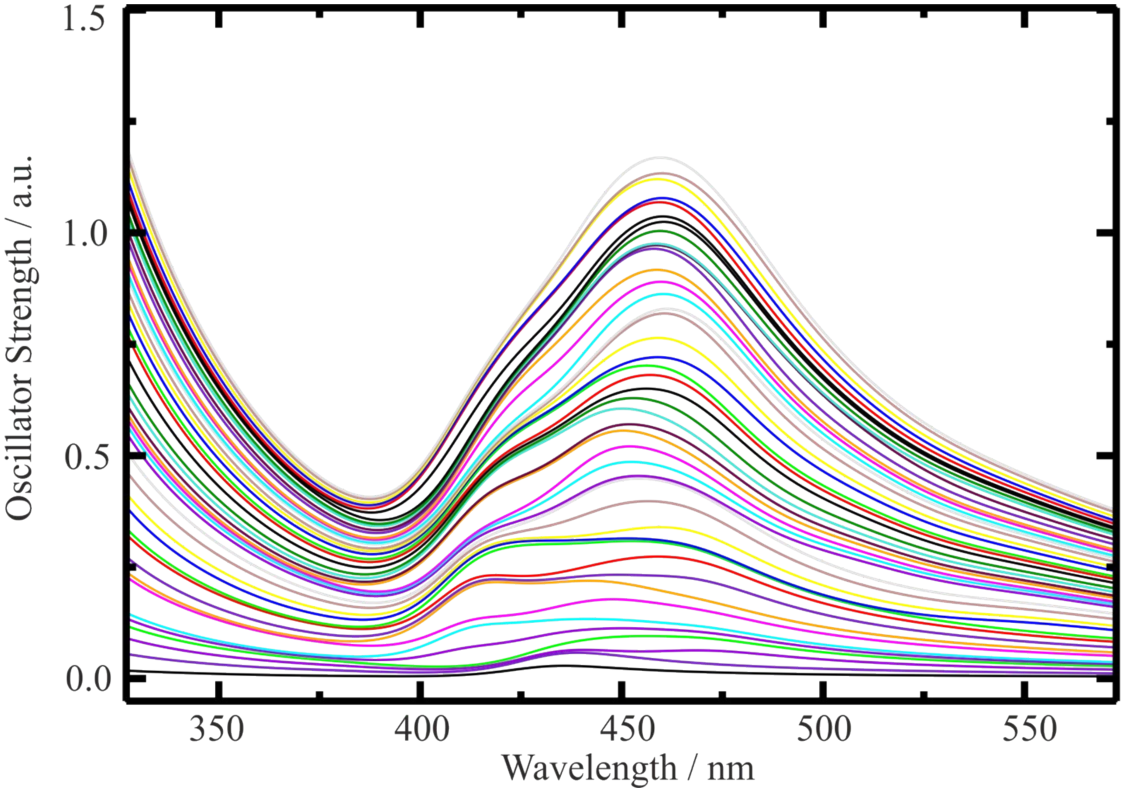


Figure S1. Convergence process for the spectrum of S_2NO^- in acetone (N = 42). Each spectrum $E_i(\lambda)$ is calculated as $E_i(\lambda)=\sum_{j=1}^{i} e_j(\lambda)$, where $e_j(\lambda)$ represents a single spectrum for a given geometry. All spectra presented in this work were calculated as $E(\lambda)=\frac{E_N(\lambda)}{N}$.

3. Calculated spectra for the species presented in Table 1

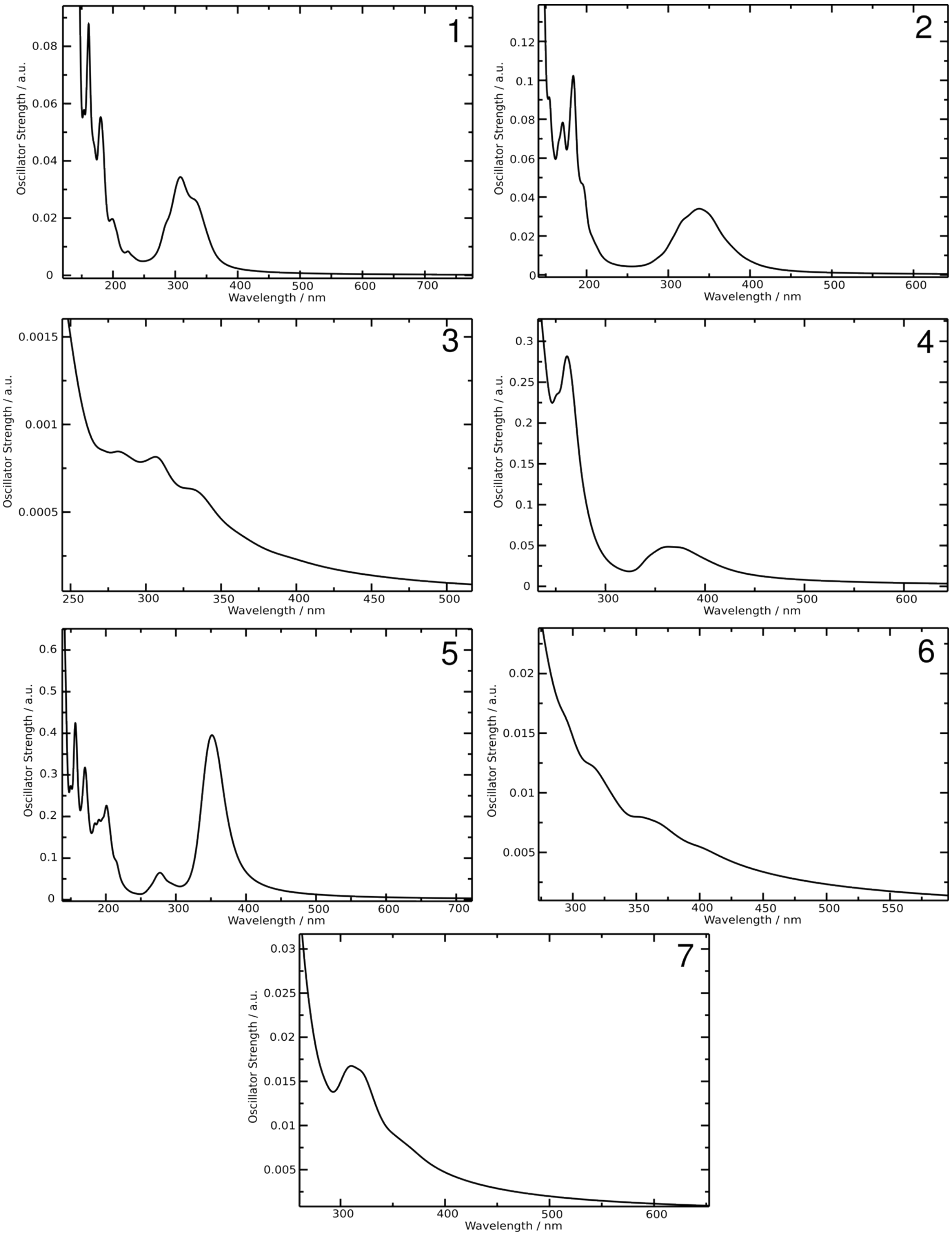


Figure S2. Calculated spectra for 1- *cis*-$ONOO^-$ in H_2O, 2- *cis*-$ONOO^-$ in CH_2Cl_2, 3- EtSNO in H_2O, 4- SN(SH)O in MeCN, 5- SN(OH)S in MeCN, 6- HSNO in H_2O and 7- SNO^- in MeCN.

4. Optimized geometrical parameters for S_2NO^- using PCM model.

The parameters presented in Table S1 were obtained by geometry optimization with Gaussian 09[2] at PBE/dzvp level of theory. The solvent was modeled as a polarizable continuum characterized by its dielectric constant ε. The absorption maxima corresponding to these geometries were calculated using *linear response* TD-DFT as implemented in Gaussian 09.

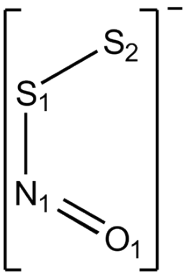
Parameter	Water	Acetone	Acetonitrile	
ε	78.3553	20.493	35.688	
$d(N_1\text{-}O_1)$ / Å	1.24	1.24	1.24	
$d(N_1\text{-}S_1)$ / Å	1.79	1.79	1.79	
$d(S_1\text{-}S_2)$ / Å	2.04	2.04	2.04	
$\theta(O_1\text{-}N_1\text{-}S_1)$ / º	118.8	119.0	118.9	
$\theta(N_1\text{-}S_1\text{-}S_2)$ / º	113.6	114.2	113.8	
λ_{max} / nm	434.26	435.74	434.88	

Table S1. Geometry Optimization parameters and absorption maxima for S_2NO^- calculated with PCM approximation and *linear response* TD-DFT.

5. ***Spectroscopic properties of S_2NO^- employing different xc-functionals and basis.***

Functional / basis	λ_{max} /nm (Water)	λ_{max} / nm (Acetone)
PBE / dzvp	425.22	448.42
PBE / aug-cc-pvtz	430.88	454.74
B3LYP / dzvp	420.26	448.37
B3LYP / aug-cc-pvtz	427.28	455.64
B3P86 / dzvp	415.74	443.45
B3P86 / aug-cc-pvtz	421.74	449.58
PW91 / dzvp	426.96	450.28
PW91 / aug-cc-pvtz	432.73	456.66
TPSSh / dzvp	417.76	444.20
TPSSh / aug-cc-pvtz	423.48	450.40

Table S2.Absorption maximum of selected structures extracted from the MD in acetone and water for S_2NO^- calculated with PCM approximation at different levels of theory.

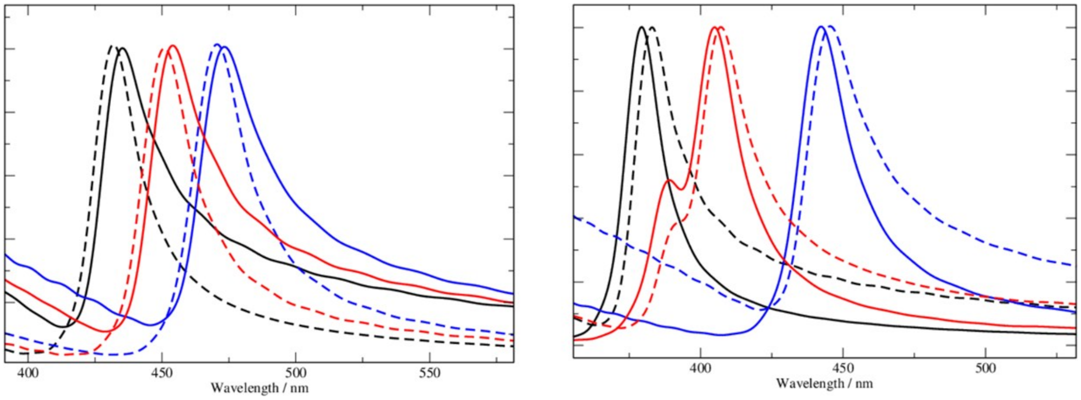
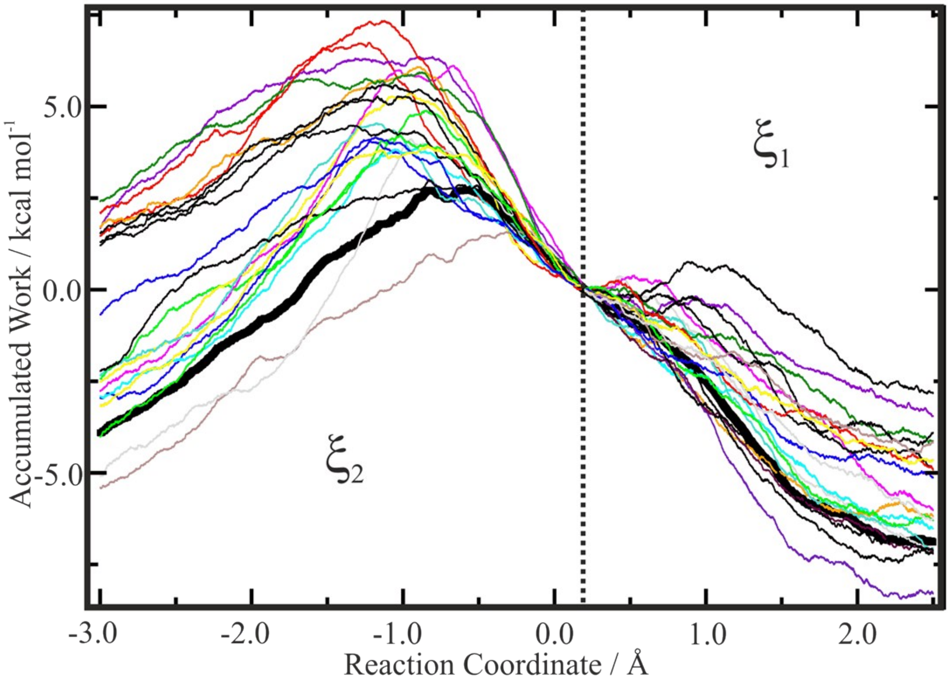


Figure S3. Calculated sprectra for selected geometries (black, red and blue lines) of $SSNO^-$ in acetone (left) and water (right). Dashed lines were calculated using tzvp basis set and thick lines were calculated using dzvp basis set.

6. Accumulated Work obtained in the free energy profile



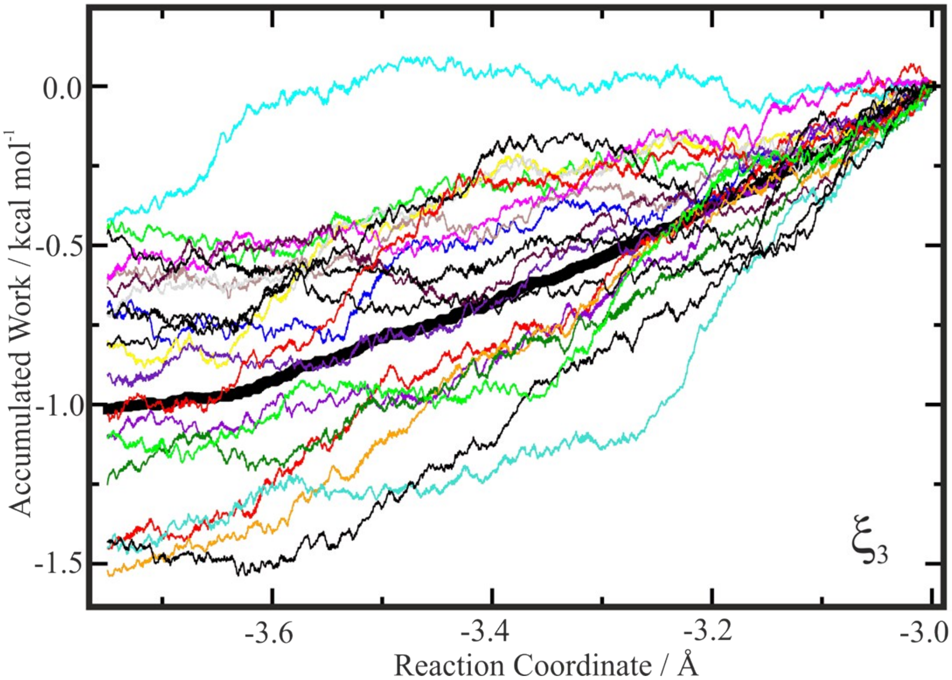


Figure S4. Accumulated work obtained in the free energy profile simulations across ξ_1+ξ_2 (top) and ξ_3 (bottom). The thick line represents the Jarzynski estimator for the free energy of the process across the coordinates.

7. References

1. U. N. Morzan, F. F. Ramírez, M. B. Oviedo, C. G. Sánchez, D. A. Scherlis and M. C. González Lebrero, *J. Chem. Phys.*, 2014, **140**, 164105.
2. Gaussian 09, Revision **E.01**, M. J. Frisch et al., *Gaussian, Inc.*, Wallingford CT, 2009.