

## Supplementary Information

Dynamics of Photodissociation of Nitric Oxide From S-Nitrosylated Cysteine  
and N-Acetylated Cysteine Derivatives in Water.

*Hojeong Yoon, Seongchul Park, and Manho Lim\**

Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National  
University, Busan 46241, Korea

Molecules		TgSNO		CysNO		NacSNO		NapSNO	
		$\bar{\nu}/\text{cm}^{-1}$	$\epsilon (\times 10^4 \text{ M}^{-1}\text{cm}^{-2})$	$\bar{\nu}/\text{cm}^{-1}$	$\epsilon (\times 10^4 \text{ M}^{-1}\text{cm}^{-2})$	$\bar{\nu}/\text{cm}^{-1}$	$\epsilon (\times 10^4 \text{ M}^{-1}\text{cm}^{-2})$	$\bar{\nu}/\text{cm}^{-1}$	$\epsilon (\times 10^4 \text{ M}^{-1}\text{cm}^{-2})$
RSNO	<sup>Am</sup> CO					1635	3.3	1640	3.2
	<sup>Ac</sup> CO <sub>a</sub>	1618	8.5	1633	6.6	1623	9.2	1621	9.3
	NO	1509	6.8	1541	8.3	1546	8.3	1507	7.3
	CN					1452	6.1	1448	7
	<sup>Ac</sup> CO <sub>s</sub>	1317	5.4	1311	2.4	1350	3.8	1341	4.7
RSNO*	NO	1826	14	1784	15	1842	17		
	<sup>Am</sup> CO					1627	3.3		
	<sup>Ac</sup> CO <sub>a</sub>	1657	7.2	1675	9	1591	7.3		
	CN					1467	7.3		
	<sup>Ac</sup> CO <sub>s</sub>	1303	5.8	1457	1.4	1372	4.2		
RS	<sup>Am</sup> CO					1633	3.1	1639	3.9
	<sup>Ac</sup> CO <sub>a</sub>	1579	11	1596	9	1589	13	1583	12
	CN					1463	6.5	1457	6.2
	<sup>Ac</sup> CO <sub>s</sub>	1278	1.4	1315	1.6	1344	3.2	1341	3.8
RSSR	<sup>Am</sup> CO					1632	6.2	1633	7.1
	<sup>Ac</sup> CO <sub>a</sub>	1602	16	1629	15	1618	21	1615	19
	CN					1454	13	1455	14
	<sup>Ac</sup> CO <sub>s</sub>	1358	7.1	1314	5.1	1352	7.8		

**Table S1.** Calculated vibrational frequencies ( $\bar{\nu}$ ) and the oscillator strengths ( $\epsilon$ ) of the C=O and C–N stretching modes of the amide group (<sup>Am</sup>CO and CN), NO stretching mode (NO), and asymmetric and symmetric C=O stretching modes of the acetate group (<sup>Ac</sup>CO<sub>a</sub> and <sup>Ac</sup>CO<sub>s</sub>) for TgSNO, CysNO, NacSNO, and NapSNO. Each frequency is assigned to the major mode of vibration. The calculated vibrational frequency is adjusted to match with the observed bands using the scale factor of 0.929–0.950 for the ground state (RSNO, RS, and RSSR) and 0.950–0.996 for the excited state, RSNO\*. The DFT method is less reliable for the excited electronic state of ionic molecule, and thus, the charge is neutralised using Na<sup>+</sup> in the calculation of RSNO\*.

Molecules		TgSNO			CySNO			NacSNO			NapSNO		
		$\bar{\nu}$ /cm <sup>-1</sup>	$\Delta\bar{\nu}_{1/2}$ /cm <sup>-1</sup>	$\epsilon (\times 10^4)$ M <sup>-1</sup> cm <sup>-2</sup>	$\bar{\nu}$ /cm <sup>-1</sup>	$\Delta\bar{\nu}_{1/2}$ /cm <sup>-1</sup>	$\epsilon (\times 10^4)$ M <sup>-1</sup> cm <sup>-2</sup>	$\bar{\nu}$ /cm <sup>-1</sup>	$\Delta\bar{\nu}_{1/2}$ /cm <sup>-1</sup>	$\epsilon (\times 10^4)$ M <sup>-1</sup> cm <sup>-2</sup>	$\bar{\nu}$ /cm <sup>-1</sup>	$\Delta\bar{\nu}_{1/2}$ /cm <sup>-1</sup>	$\epsilon (\times 10^4)$ M <sup>-1</sup> cm <sup>-2</sup>
RSNO	<sup>Am</sup> CO							1628	28	2.4	1630	31	2.4
	<sup>Ac</sup> CO <sub>a</sub>	1592	30	3.7	1626	24	5.4	1603	30	9.2	1601	29	9.0
	NO	1486	74	1.5	1535	85	3.3	1523	65	4.1	1502	73	4.0
	CN							1479	30	2.4	1474	33	2.4
	<sup>Ac</sup> CO <sub>s</sub>	1378	23	1.3	1419	28	1.7	1388	17	1.2	1385	20	2.0
RSNO*	NO	1830	6.4	0.44	1830	7.4	0.89	1828	8.1	1.0			
	<sup>Am</sup> CO							1630	29	1.5			
	<sup>Ac</sup> CO <sub>a</sub>	1587	24	1.8	1626	24	3.4	1604	38	5.5			
	CN							1479	30	1.9			
	<sup>Ac</sup> CO <sub>s</sub>	1388	21	1.0									
RS	<sup>Am</sup> CO							1624	21	2.0	1628	34	2.5
	<sup>Ac</sup> CO <sub>a</sub>	1572	60	3.9	1613	17	2.3	1592	28	6.6	1583	38	8.6
	CN							1485	42	3.2	1479	41	1.3
	<sup>Ac</sup> CO <sub>s</sub>												
RSSR	<sup>Am</sup> CO							1632	24	2.9	1633	28	3.3
	<sup>Ac</sup> CO <sub>a</sub>	1585	30	8.9	1625	25	9.7	1605	33	12	1601	30	12
	CN							1472	36	2.6	1472	41	3.9
	<sup>Ac</sup> CO <sub>s</sub>	1384	24	2.8									

**Table S2.** Fitted spectral parameters of basis spectra used to fit the TRIR spectra of TgSNO, CySNO, NacSNO, and NapSNO in the spectral region of 1850–1350 (1450) cm<sup>-1</sup>. <sup>Am</sup>CO, CN, NO, <sup>Ac</sup>CO<sub>a</sub>, and <sup>Ac</sup>CO<sub>s</sub> represent C=O and C–N stretching modes of the amide group, NO stretching mode, and asymmetric and symmetric C=O stretching modes of the acetate group, respectively. Parameters for RSNO and RSSR are obtained by fitting their equilibrium spectra. The position, full width at half maximum, and integrated extinction coefficient of the band are represented by  $\bar{\nu}$ ,  $\Delta\bar{\nu}_{1/2}$ , and  $\epsilon$ , respectively.

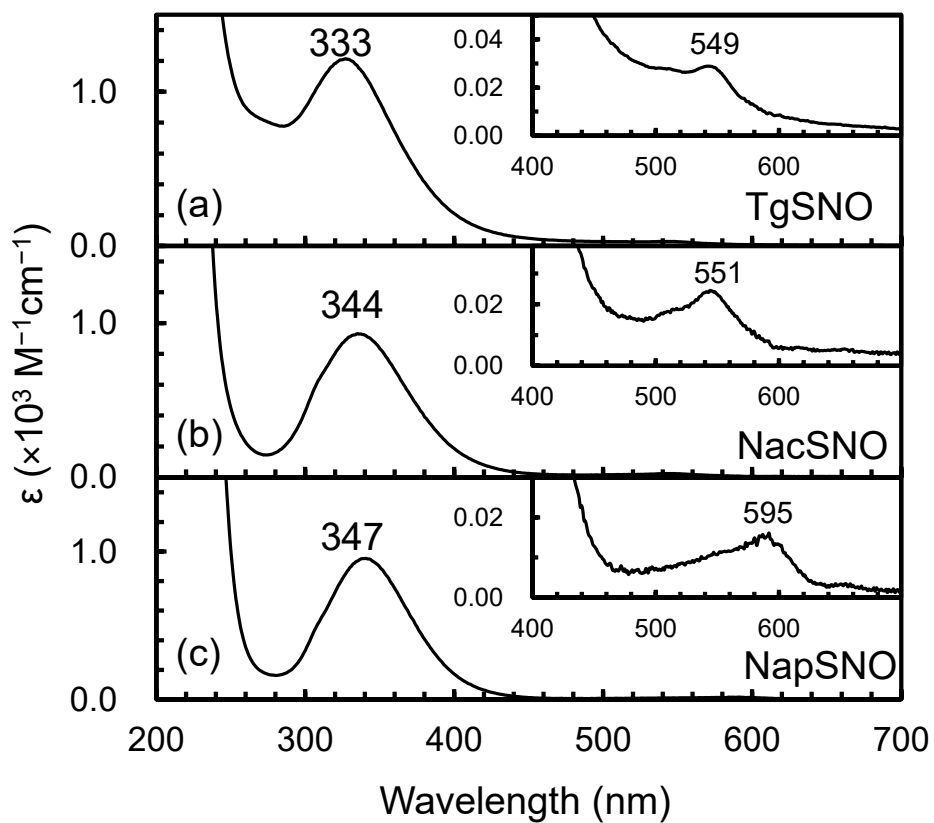
(a)

Cis-conformer	TgSON (29.9)		CySON (27.6)		NacSON (26.6)		NapSON (37.0)	
	$\bar{\nu}/\text{cm}^{-1}$	$\epsilon (\times 10^4 \text{ M}^{-1}\text{cm}^{-2})$	$\bar{\nu}/\text{cm}^{-1}$	$\epsilon (\times 10^4 \text{ M}^{-1}\text{cm}^{-2})$	$\bar{\nu}/\text{cm}^{-1}$	$\epsilon (\times 10^4 \text{ M}^{-1}\text{cm}^{-2})$	$\bar{\nu}/\text{cm}^{-1}$	$\epsilon (\times 10^4 \text{ M}^{-1}\text{cm}^{-2})$
NO	1842	18	1830	18	1851	16	1829	28
<sup>Am</sup> CO					1638	3.8	1633	4.5
<sup>Ac</sup> CO <sub>a</sub>	1624	6.7	1636	5.5	1578	13	1605	9.6
CN					1452	6.2	1460	7.7
<sup>Ac</sup> CO <sub>s</sub>	1292	5.9	1300	1.7	1316	3.3	1343	4.4

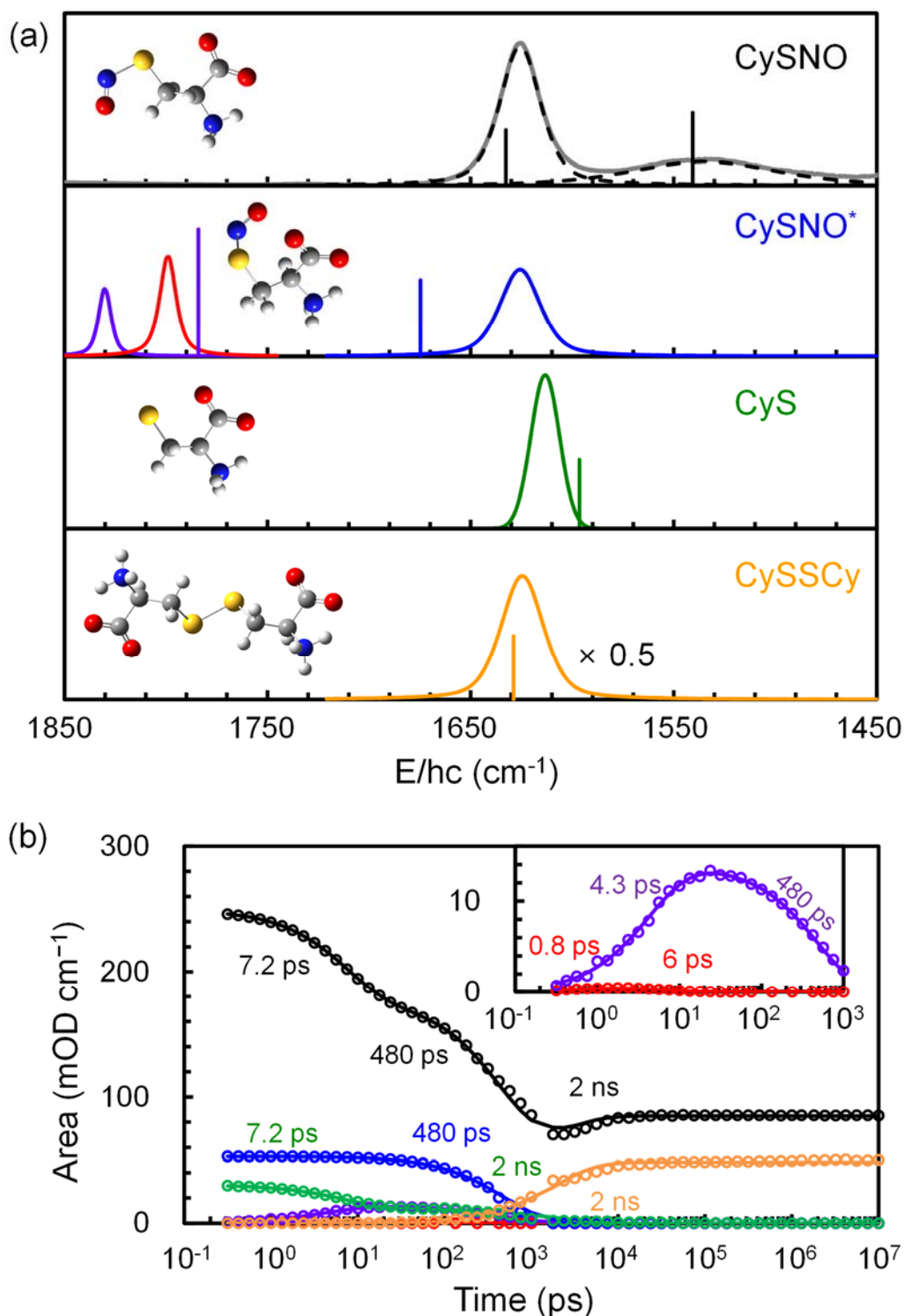
(b)

Trans-conformer	TgSON (39.4)		CySON (34.4)		NacSON (38.2)		NapSON (37.1)	
	$\bar{\nu}/\text{cm}^{-1}$	$\epsilon (\times 10^4 \text{ M}^{-1}\text{cm}^{-2})$	$\bar{\nu}/\text{cm}^{-1}$	Int	$\bar{\nu}/\text{cm}^{-1}$	$\epsilon (\times 10^4 \text{ M}^{-1}\text{cm}^{-2})$	$\bar{\nu}/\text{cm}^{-1}$	$\epsilon (\times 10^4 \text{ M}^{-1}\text{cm}^{-2})$
NO	1831	30	1839	27	1849	29	1807	32
<sup>Am</sup> CO					1628	2.3	1634	3.6
<sup>Ac</sup> CO <sub>a</sub>	1605	8.3	1627	7.2	1615	11	1599	15
CN					1452	6.8	1449	8.5
<sup>Ac</sup> CO <sub>s</sub>	1373	7.9	1304	2.6	1346	3.5	1341	4

**Table S3.** Calculated vibrational frequencies ( $\bar{\nu}$ ) and their oscillator strengths ( $\epsilon$ ) of the NO stretching mode (NO), C=O and C–N stretching modes of the amide group (<sup>Am</sup>CO and CN), and asymmetric and symmetric C=O stretching modes of the acetate group (<sup>Ac</sup>CO<sub>a</sub> and <sup>Ac</sup>CO<sub>s</sub>) for (a) cis- and (b) trans-conformer of TgSON, CySON, NacSON, and NapSON. Each frequency is assigned to the major mode of vibration. The calculated vibrational frequency is adjusted by the scale factor of 0.929–0.950 used for RSNO in the ground state. RSON has 27.6–39.4 kcal/mol higher energy than the corresponding RSNO and the energy value in kcal/mol is given in parenthesis.

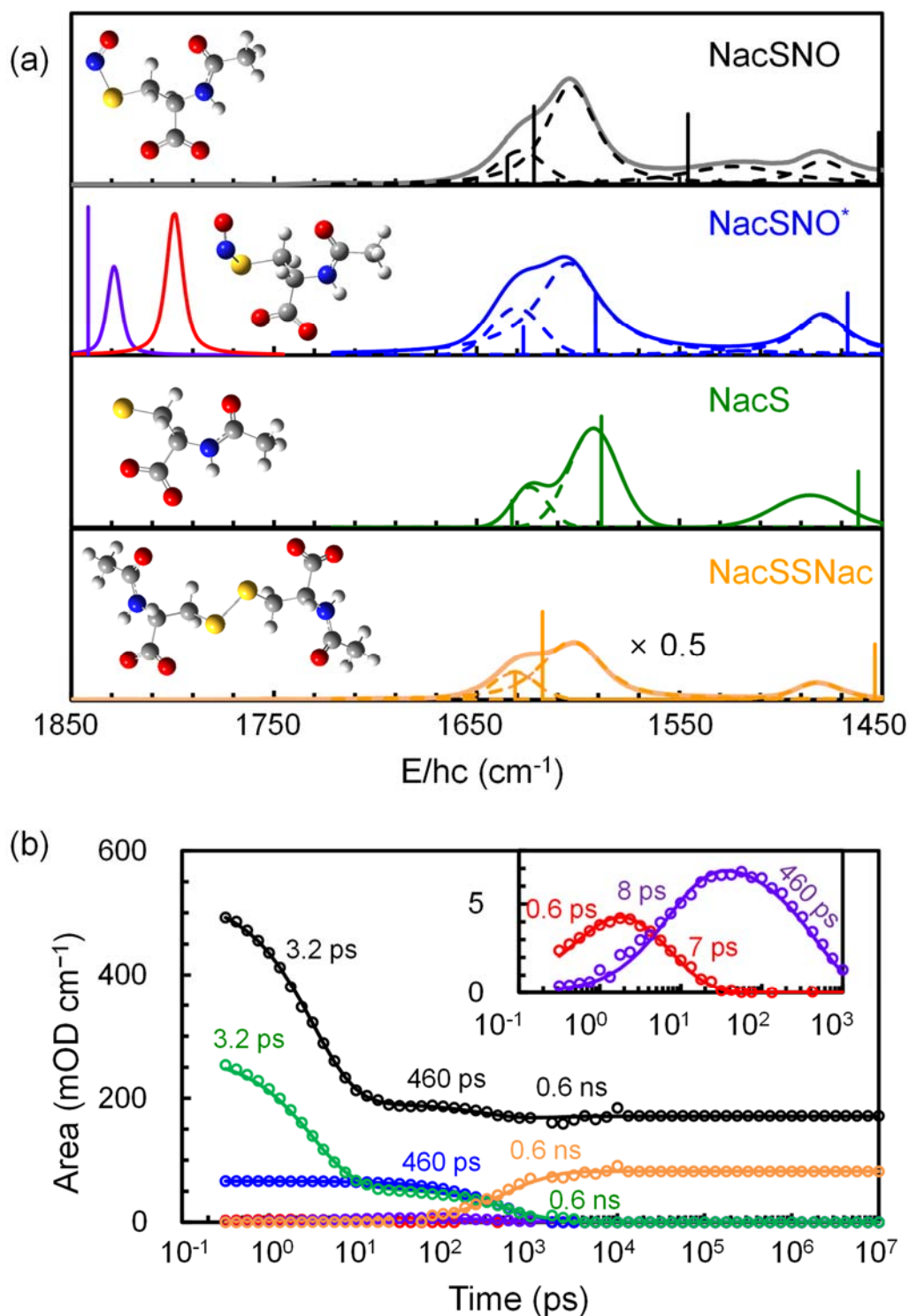


**Figure S1.** Equilibrium UV-Vis spectra of (a) TgSNO, (b) NacSNO, and (c) NapSNO in D<sub>2</sub>O with the peak positions of the absorption bands. The inset shows the expanded view for the band around 550 nm.



**Figure S2.** (a) Basis absorption spectra used to fit TRIR spectra of CySNO with optimised molecular structures and calculated frequencies shown as sticks. Spectrum of CySNO is the equilibrium IR spectrum of CySNO and the spectra of CyS, CySNO\*, and CySSCy are obtained by the global fitting of TRIR spectra of CySNO. Equilibrium IR spectrum of CySNO (thick grey line) is fitted with two bands (dashed black lines). The calculated NO frequency of CySNO\* (purple stick) is for the fundamental NO band but the fitted spectrum includes the

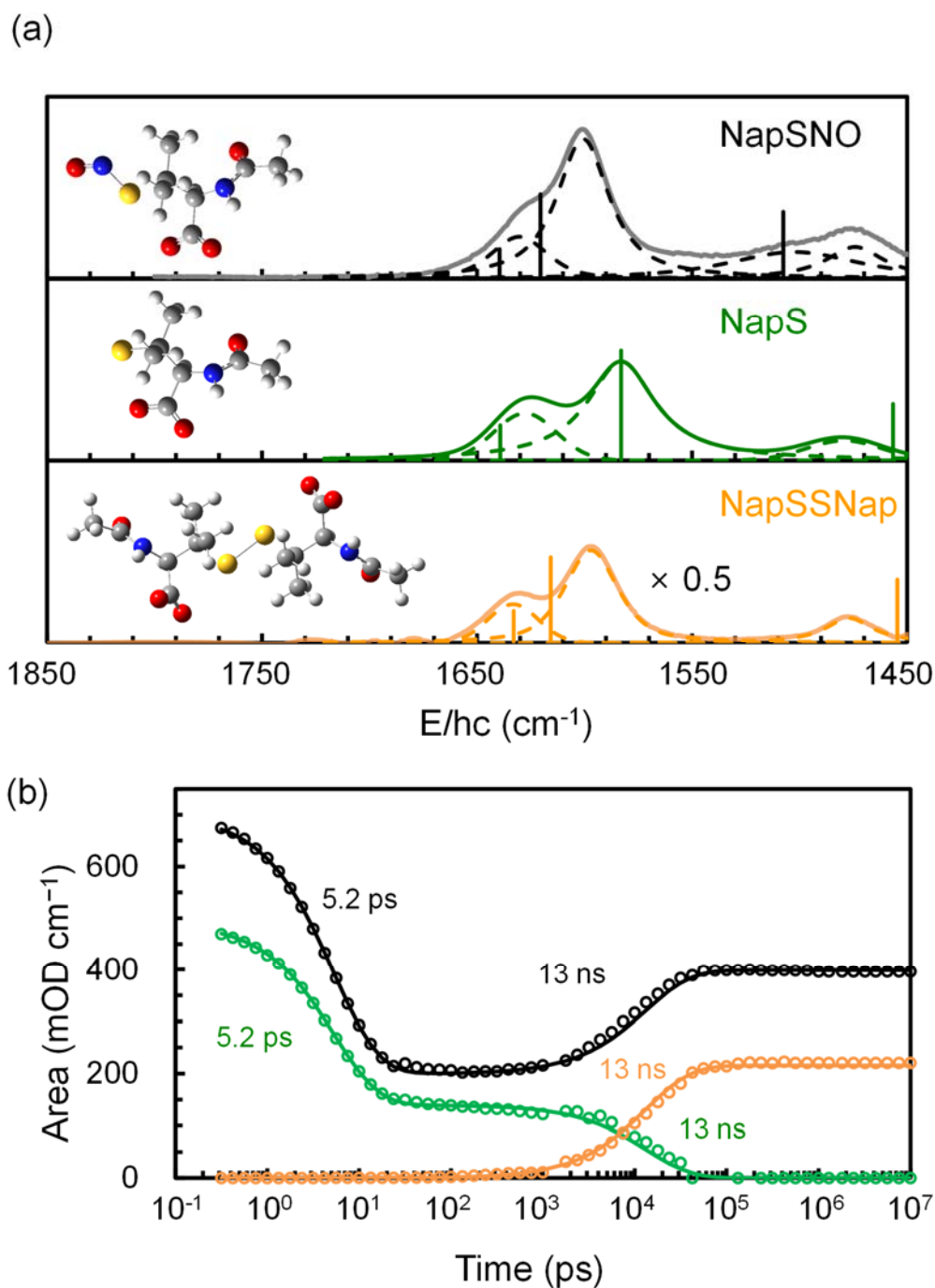
fundamental (purple line) and hot (red line) NO bands. In the ball-and-stick molecular model, white, grey, blue, red, and yellow spheres depict hydrogen, carbon, nitrogen, oxygen, and sulfur atoms, respectively. (b) The time-dependent amplitude changes of basis spectra for CySNO (black circles), CyS (green circles), CySSCy (orange circles), and bands for the acetate group of CySNO\* (blue circles). The value represents the magnitude of sum of the integrated areas of new absorptions for CySNO\*, CyS, and CySSCy; however, it indicates that of the bleach (negative-going feature) for CySNO. The time-dependent amplitude changes of the bands at 1830 (purple circles) and 1802 (red circles)  $\text{cm}^{-1}$  are shown in the inset. Time constants for the exponential decay or grow are shown in the figure with colour coding. The time-dependent amplitude changes are well reproduced by Scheme 1 (solid lines).



**Figure S3.** (a) Basis absorption spectra used to fit TRIR spectra of NacSNO with optimised molecular structures and calculated frequencies shown as sticks. Spectra of NacSNO and NacSSNac are the equilibrium IR spectra and those of NacS and NacSNO\* are obtained by global fitting of the TRIR spectra of NacSNO. Equilibrium IR spectrum of NacSNO (thick grey line) was fitted with four bands (dashed black lines) and that of NacSSNac (thick light orange line) was fitted with three bands (dashed orange lines). The calculated NO frequency

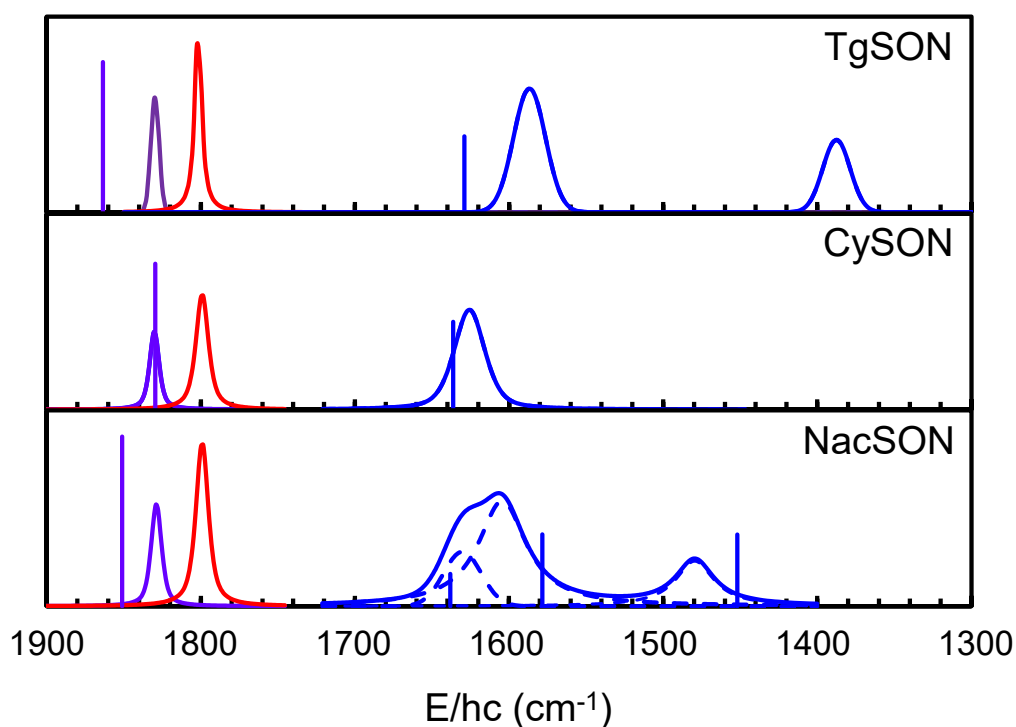


of NacSNO\* (purple stick) is for the fundamental NO band; however, the fitted spectrum includes the fundamental (purple line) and hot (red line) NO bands. In the ball-and-stick molecular model, white, grey, blue, red, and yellow spheres depict hydrogen, carbon, nitrogen, oxygen, and sulfur atoms, respectively. (b) The time-dependent amplitude changes of basis spectra for NacSNO (black circles), NacS (green circles), NacSSNac (orange circles), and bands for the acetate group of NacSNO\* (blue circles). The value represents the magnitude of sum of the integrated areas of new absorptions for NacSNO\*, NacS, and NacSSNac and it represents that of the bleach (negative-going feature) for NacSNO. The time-dependent amplitude changes of the bands at 1828 (purple circles) and 1800 (red circles)  $\text{cm}^{-1}$  are shown in the inset. Time constants for the exponential decay or grow are shown in the figure with colour coding. The time-dependent amplitude changes are well reproduced by Scheme 1 (solid lines).

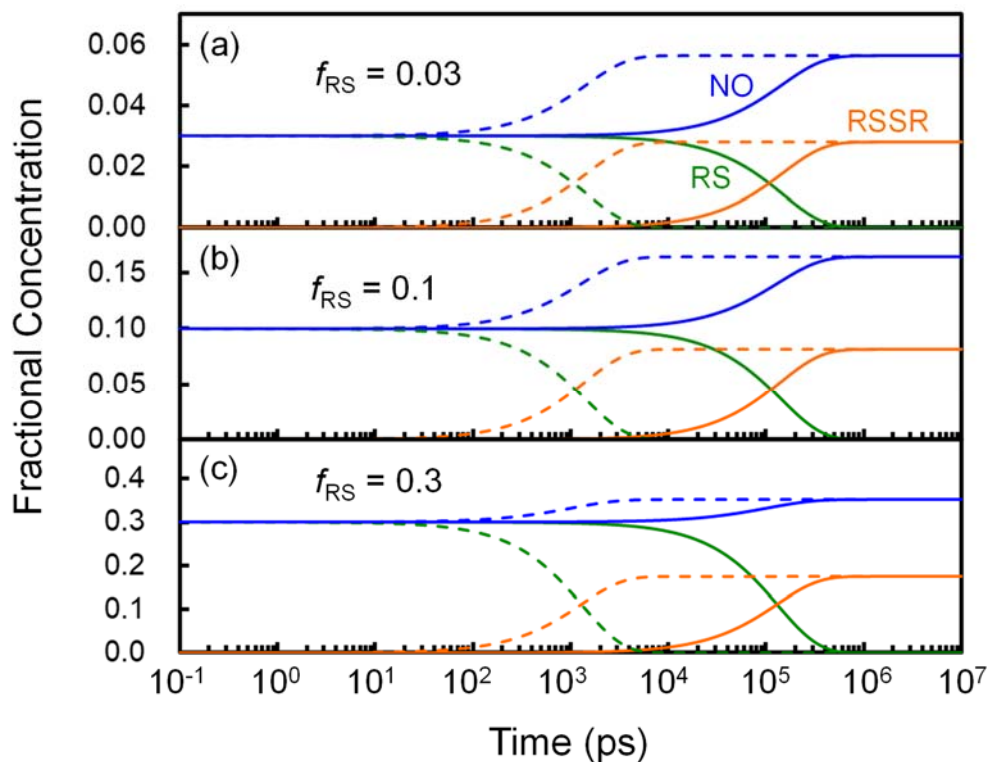


**Figure S4.** (a) Basis absorption spectra used to fit the TRIR spectra of NapSNO with optimised molecular structures and the calculated frequencies shown as sticks. The spectra of NapSNO and NapSSNap are equilibrium IR spectra and that of NapS obtained by the global fitting of the TRIR spectra of NapSNO. The equilibrium IR spectrum of NapSNO (thick grey line) fitted with four bands (dashed black lines) and that of NapSSNap (thick light orange line) fitted with three bands (dashed orange lines). In the ball-and-stick molecular model, white, grey, blue, red, and yellow spheres depict hydrogen, carbon, nitrogen, oxygen, and sulfur atoms, respectively. (b) The time-dependent amplitude changes of the basis spectra for NapSNO (black circles),

NapS (green circles), and NapSSNap (orange circles). The value represents the magnitude of the sum of the integrated areas of new absorptions for NapS, and NapSSNap; it represents that of the bleach (negative-going feature) for NapSNO. Time constants for the exponential decay or grow were shown in the figure with colour coding. The time-dependent amplitude changes were well reproduced by Scheme 1 (solid lines) and omitting the path to RSNO\* (see text)



**Figure S5.** Basis spectra of the intermediate state with the  $1830\text{ cm}^{-1}$  band obtained from the global fitting of TRIR spectra for TgSNO (top), CySNO (middle), and NacSNO (bottom) overlapped with the calculated spectra (sticks) of the corresponding RSONs. Note that the spectral window is expanded from  $1850\text{--}1350$  ( $1450$ )  $\text{cm}^{-1}$  to  $1900\text{--}1300\text{ cm}^{-1}$  to include the calculated values. Even after the expansion, the symmetric CO stretching mode of the acetate in TgSNO cannot be shown because it is  $1274\text{ cm}^{-1}$ , which is outside the spectral window shown in this figure.



**Figure S6.** Simulated fractional concentration changes of RS (green), NO (blue), and RSSR (red) when the fractional concentration of RSNO remaining dissociated in RS and NO after geminate rebinding subsequent to the photodissociation of RSNO ( $f_{RS}$ ) is (a) 0.03, (b) 0.1, and (c) 0.3 while the sample concentration is 1 mM (solid lines) and 100 mM (dashed lines). The RS is assumed to react with NO and RSNO at the diffusion-limited rate constants of  $9.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  and  $6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , respectively;  $\text{RS} + \text{NO} \rightarrow \text{RSNO}$  ( $k_{\text{NO}} = 9.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ),  $\text{RS} + \text{RSNO} \rightarrow \text{NO} + \text{RSSR}$  ( $k_{\text{RSSR}} = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ). Note that the fractional concentration of RSNO ( $f_{\text{RSNO}}$ ) is related to that of NO ( $f_{\text{NO}}$ ),  $f_{\text{RSNO}} = 1 - f_{\text{NO}}$ .