Mechanistic Insight into Carbene-mediated CO_2-Activiation

Seminar talk presented by

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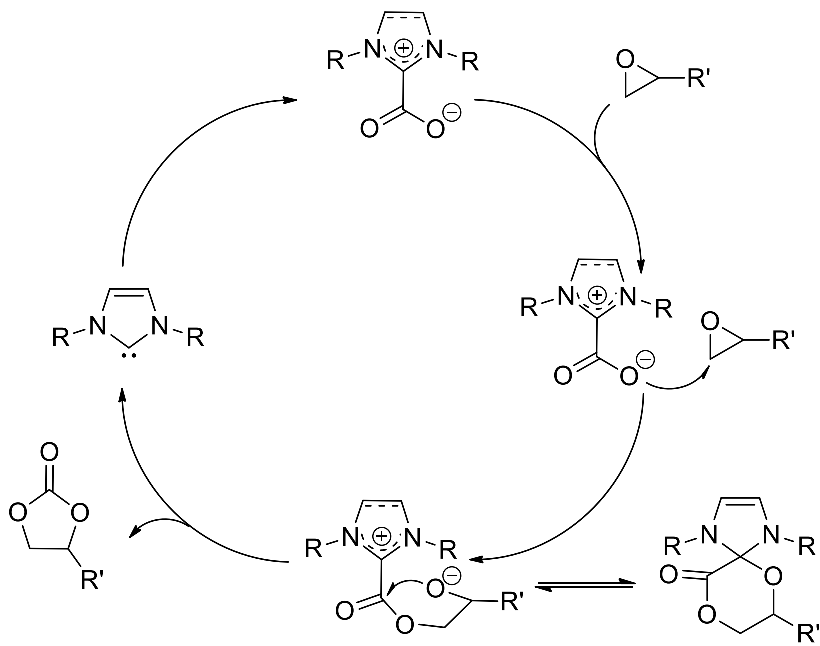
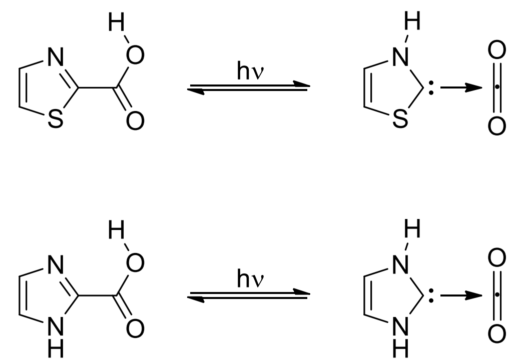
- CO_2 Activation: FLPs, Ils, Superbases, Polyoxometallates, Phosphorus Ylides, and NHCs

- Carboxylates in Synthesis e.g. Oxidation of Aldehydes, Epoxides to Cyclic Carbonate Esters



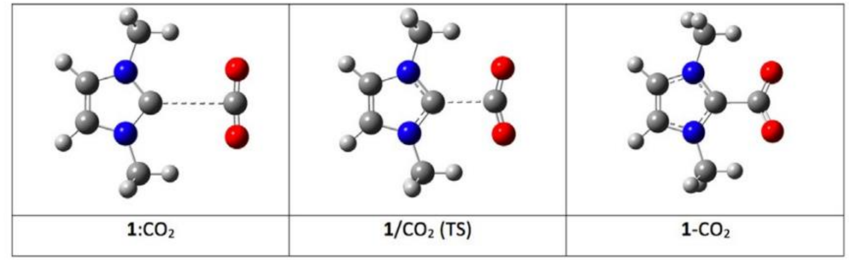
- Carbene CO_2 complexes under Matrix Isolation Conditions:



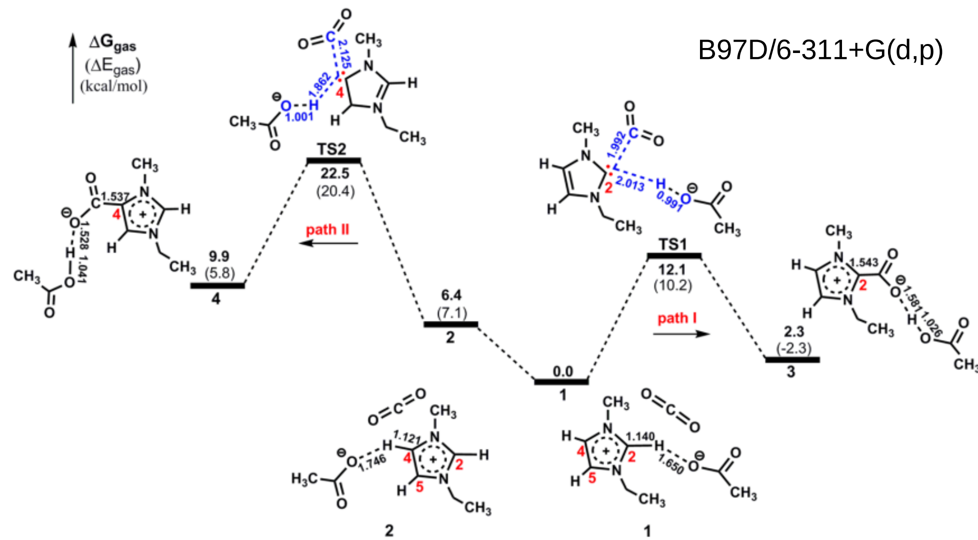
H. Zhou, W.-Z. Zhang, C.-H. Liu, J.-P. Qu, X.-B. Lu, *J. Org. Chem.* **2008**, *73*, 8039 – 8044. **Carbene-CO_2 Complexes:** G. Maier, J. Endres, *Eur. J. Org. Chem.* **1998**, *1998*, 1517-1520; G. Maier, J. Endres, H. P. Reisenauer, *Angew. Chem. Int. Ed.* **1997**, *36*, 1709-1712; **CO_2 Activation/Fixation Review:** L. Yang, H. Wang, *ChemSusChem* **2014**, *7*, 962-998.

Carbene-CO_2-Complexes

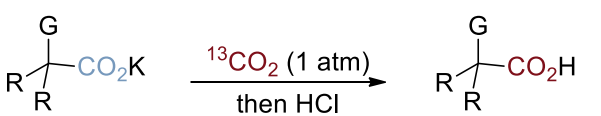
- Number of N-atoms in the NHC correlated with more stable complexes compared to their covalent carboxylates



- NHC-based ILs react with CO_2 to give the corresponding carboxylates



- Anionic Mechanism was proposed
- No reaction with TEMPO, BHT

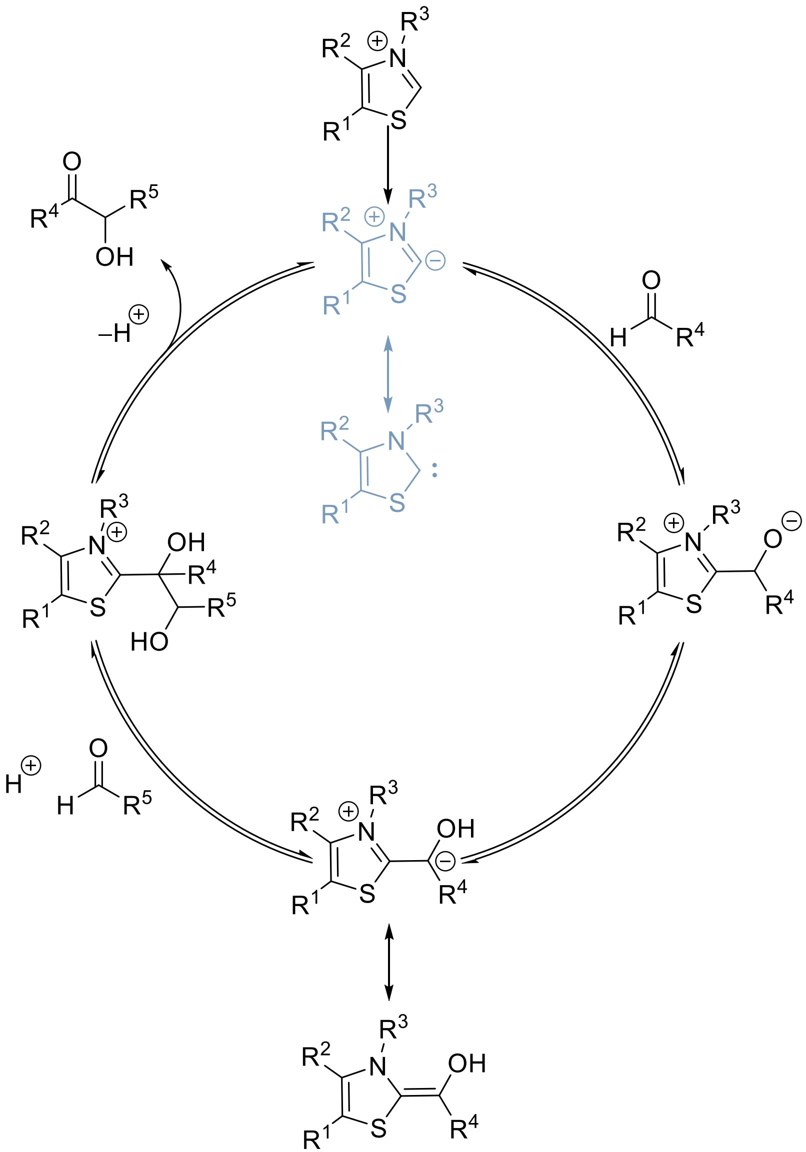


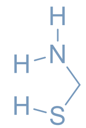
G = (hetero)aryl, ester, ketone, amide, sulforyl, nitrile
R = aryl, alkyl, H

^{13}C incorporation up to 95%

I. Alkorta, M. M. Montero-Campillo, J. Elguero, *Chem. Eur. J.* **2017**, *23*, 10604-10609; M. Dong, J. Gao, C. Liu, D. Zhang, *J. Phys. Chem. B* **2017**, *212*, 10276-10284; P. J. M. D. Kong, E. K. J. Lui, O. Bsharat, R. J. Lundgren, *Science* **2020**, *369*(6503), 557-561.

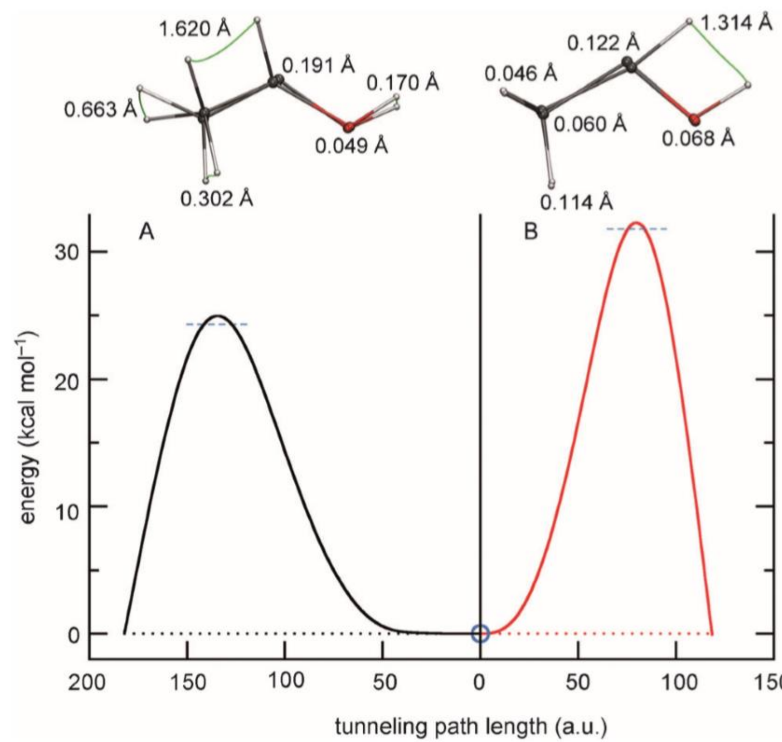
Mercapto Carbenes





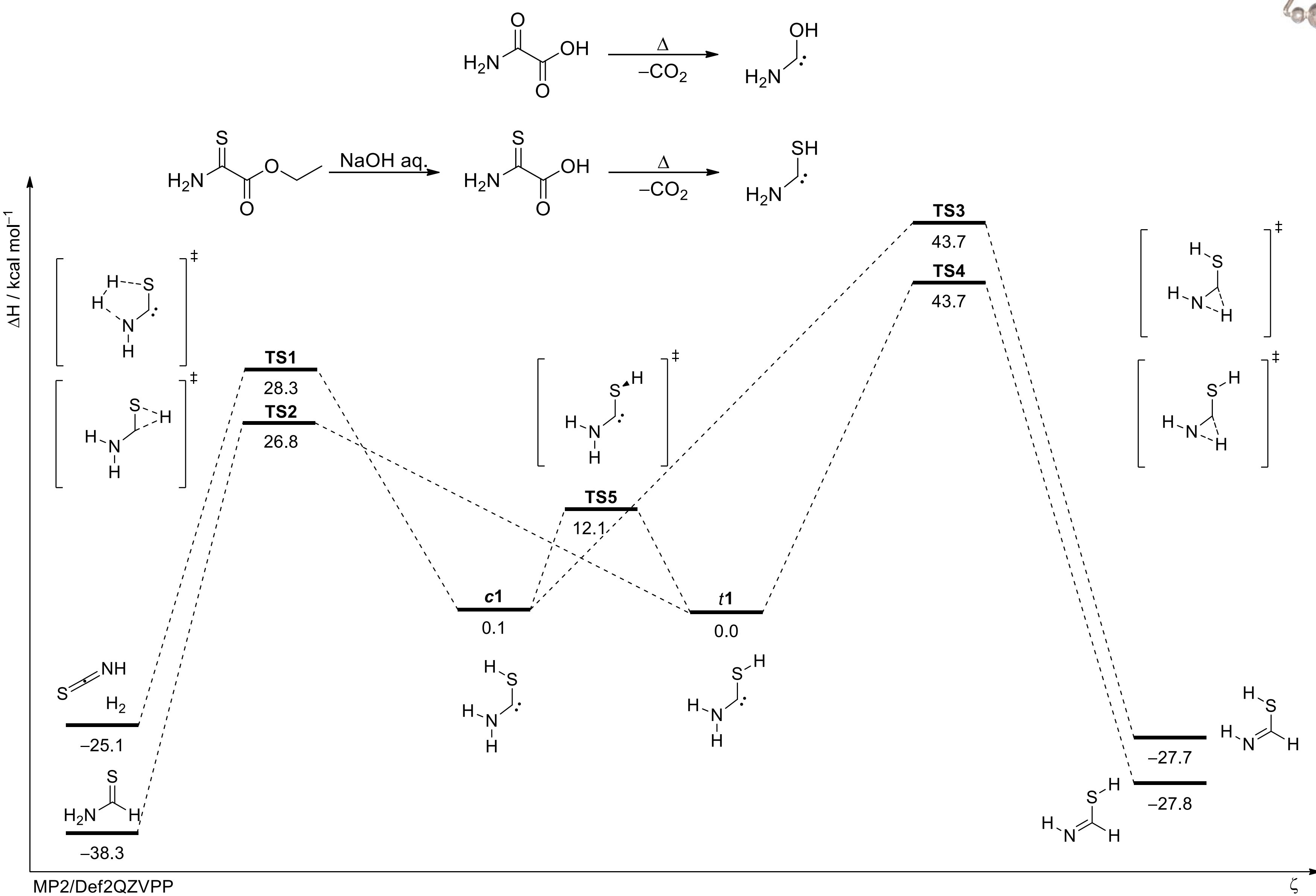
- Amino mercapto methylene as the centerpiece of thiazolylidene (and NHCs in general)

- Mercapto carbenes are yet unknown species



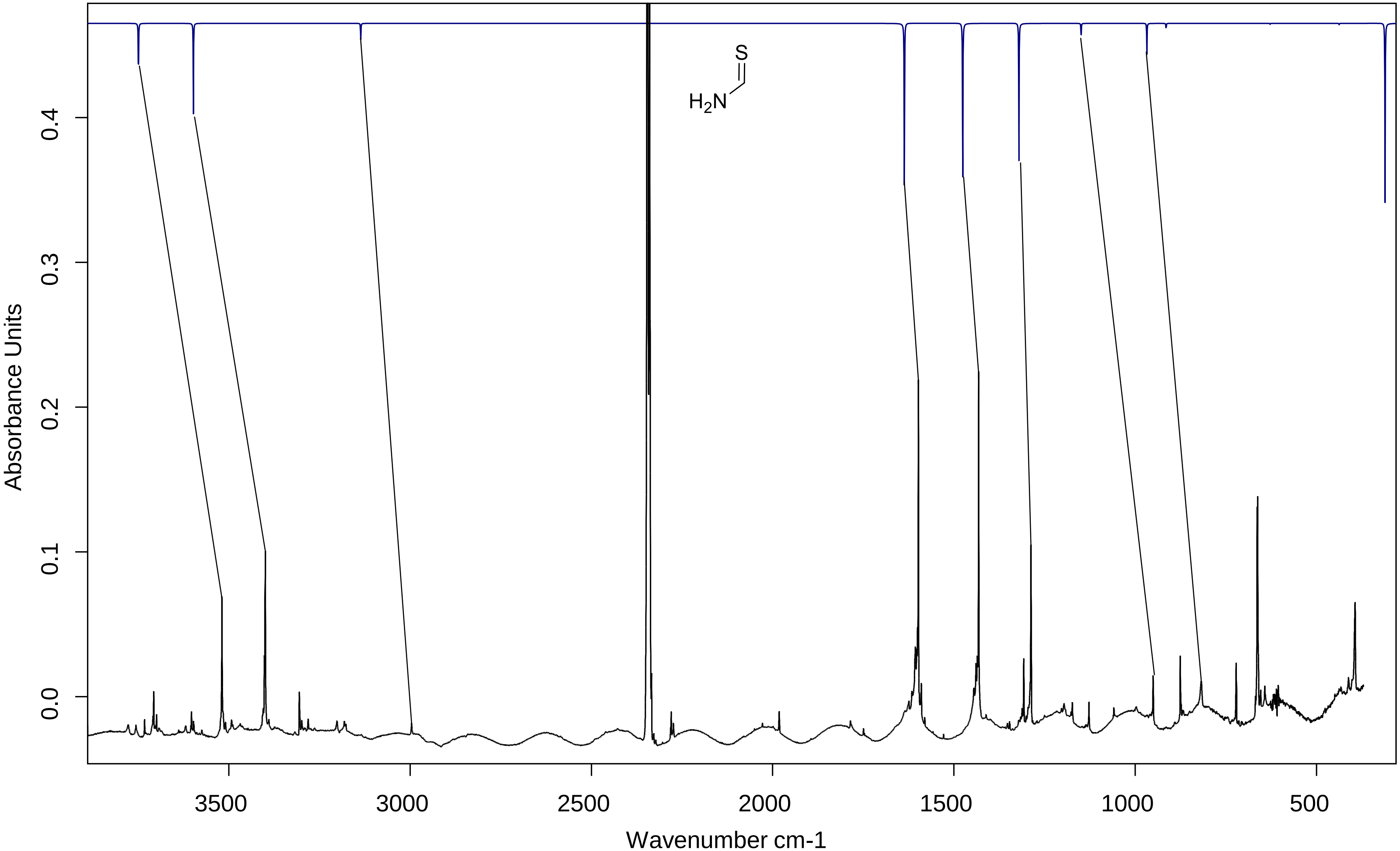
C. Emmeluth, M. A. Suhm, *Phys. Chem. Chem. Phys.* **2003**, *5*, 3094-3099; A. Mardyukov, P. R. E. Sánchez-Garcia, N. L. Doltsinis, W. Sander, *J. Phys. Chem. A* **2007**, *111*, 10552-10561; P. R. Schreiner, H. P. Reisenauer, D. Ley, D. Gerbig, C.-H. Wu, W. D. Allen, *Science* **2011**, *332*(6035), 1300-1303; J. Kästner, *Chem. Eur. J.* **2013**, *19*, 8207-8212.

Amino Mercapto Methylene

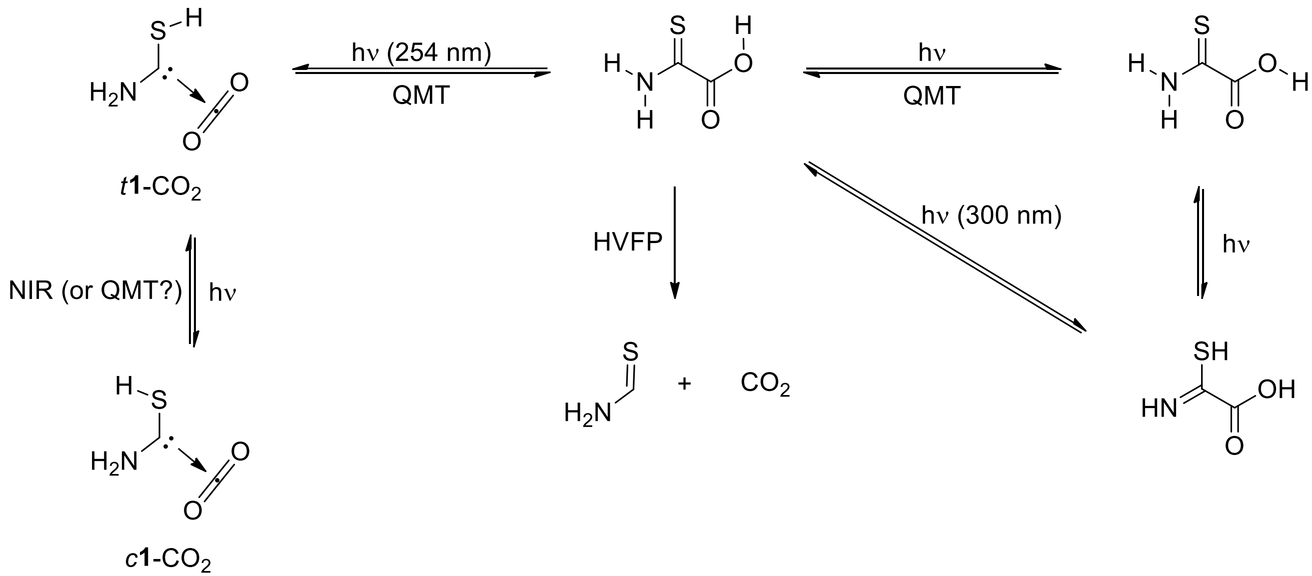


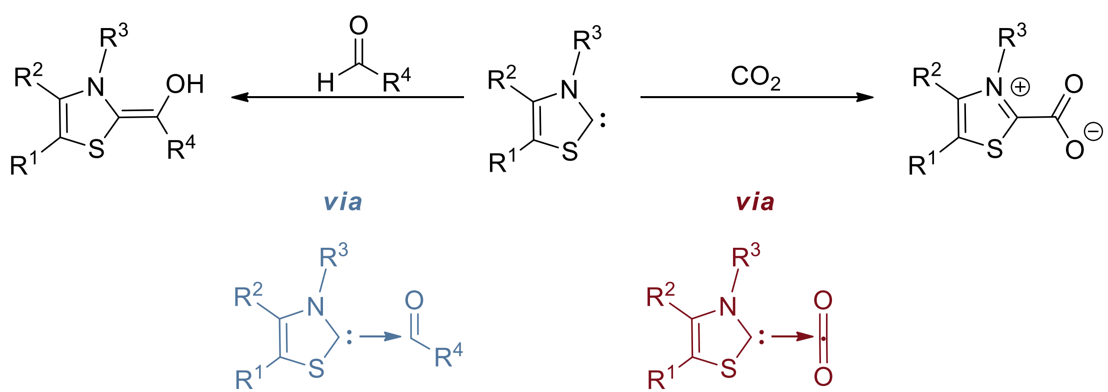
H. P. Reisenauer, unpublished results.

MP2/Def2QZVPP

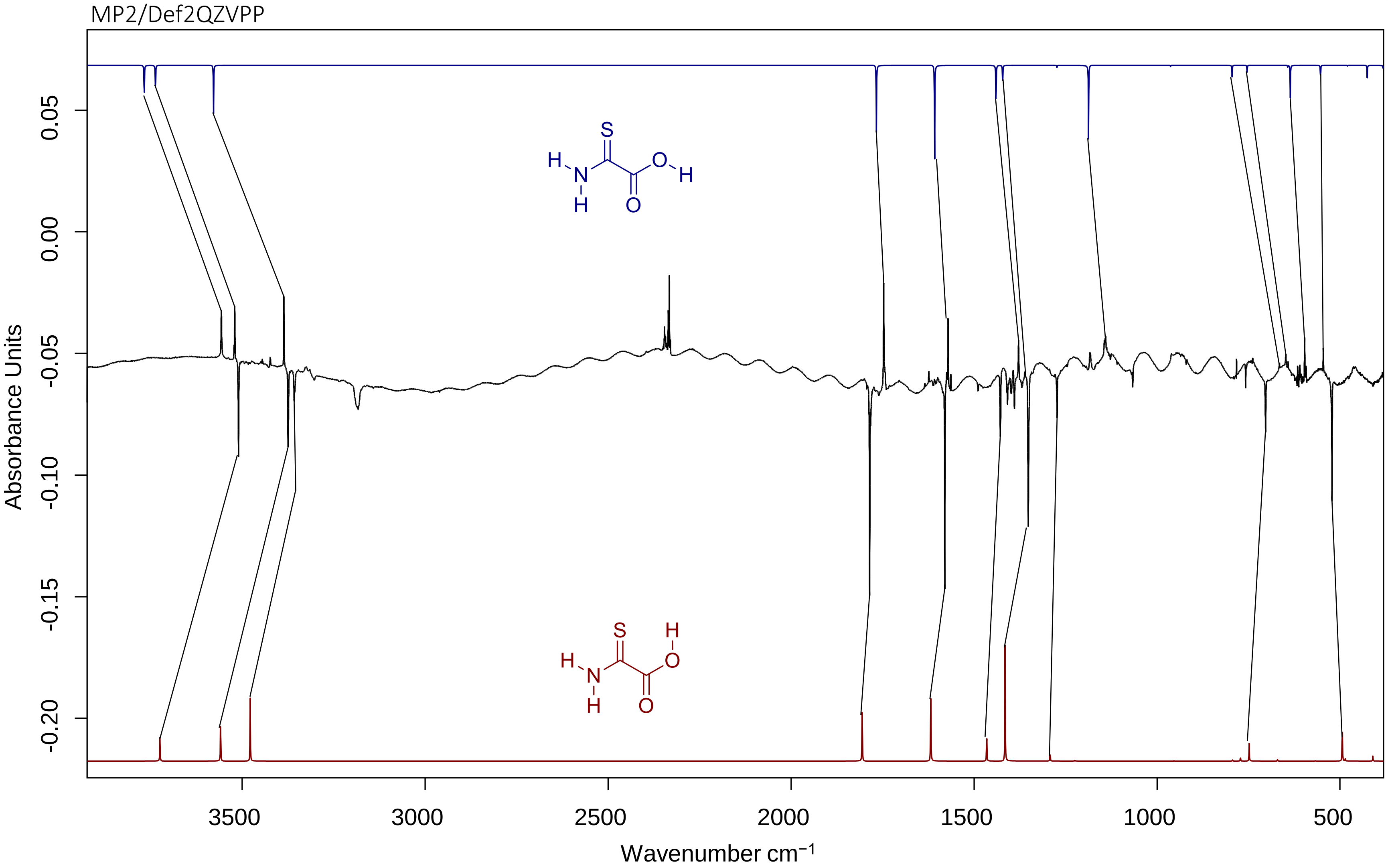


Amino Mercapto Methylene – Reaction Network



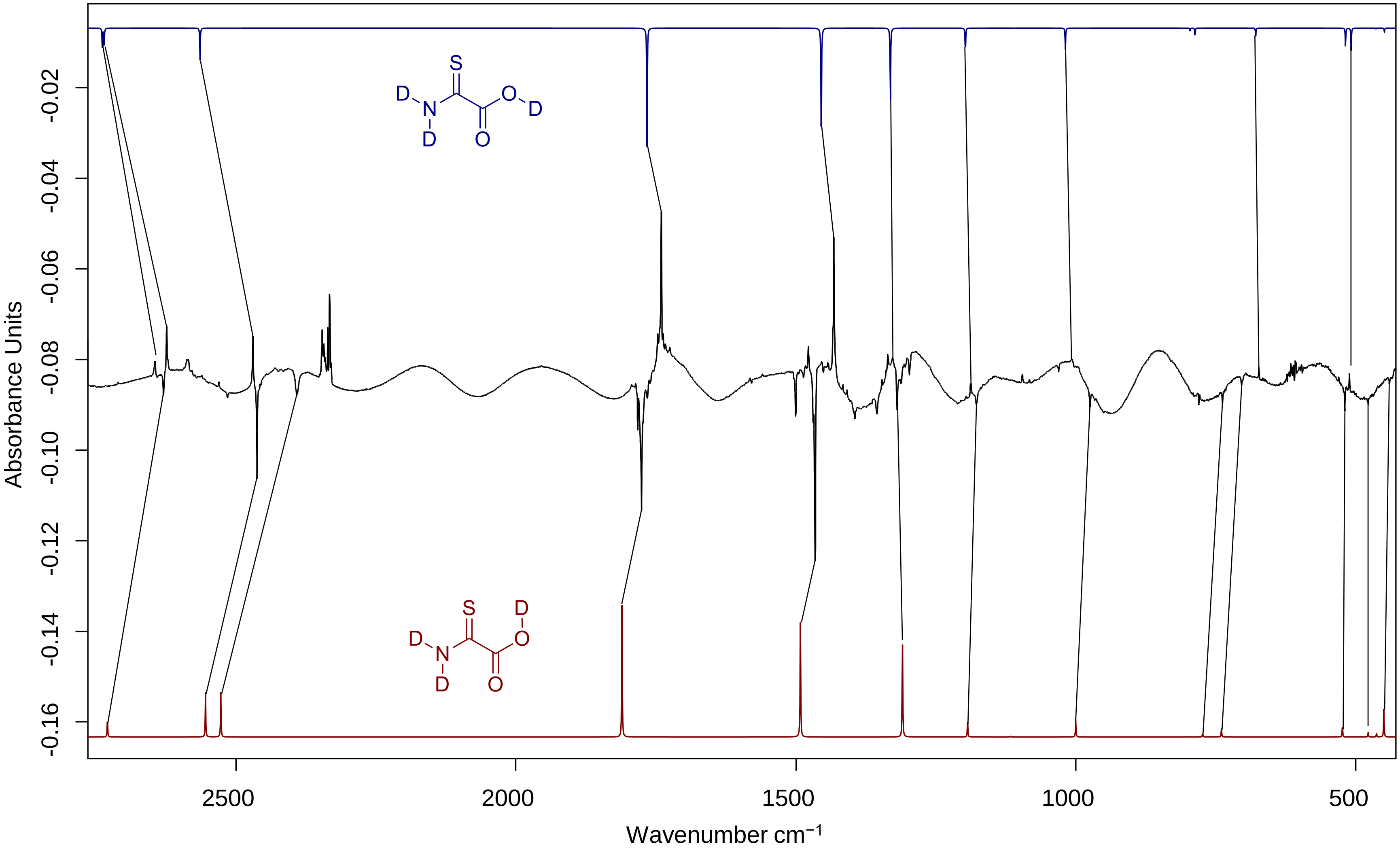


S. Gobi, I. Reva, I. P. Csonka, M. N. C, G. Tarczay, R. Fausto, *Phys. Chem. Chem. Phys.* **2019**, *21*, 24935-24949; H. Rostkowska, L. Lapinski, M. J. Nowak, *Phys. Chem. Chem. Phys.* **2018**, *20*, 13994-14002; S. Gobi, C. M. Nunes, I. Reva, G. Tarczay, R. Fausto, *Phys. Chem. Chem. Phys.* **2019**, *21*, 17063-17071.

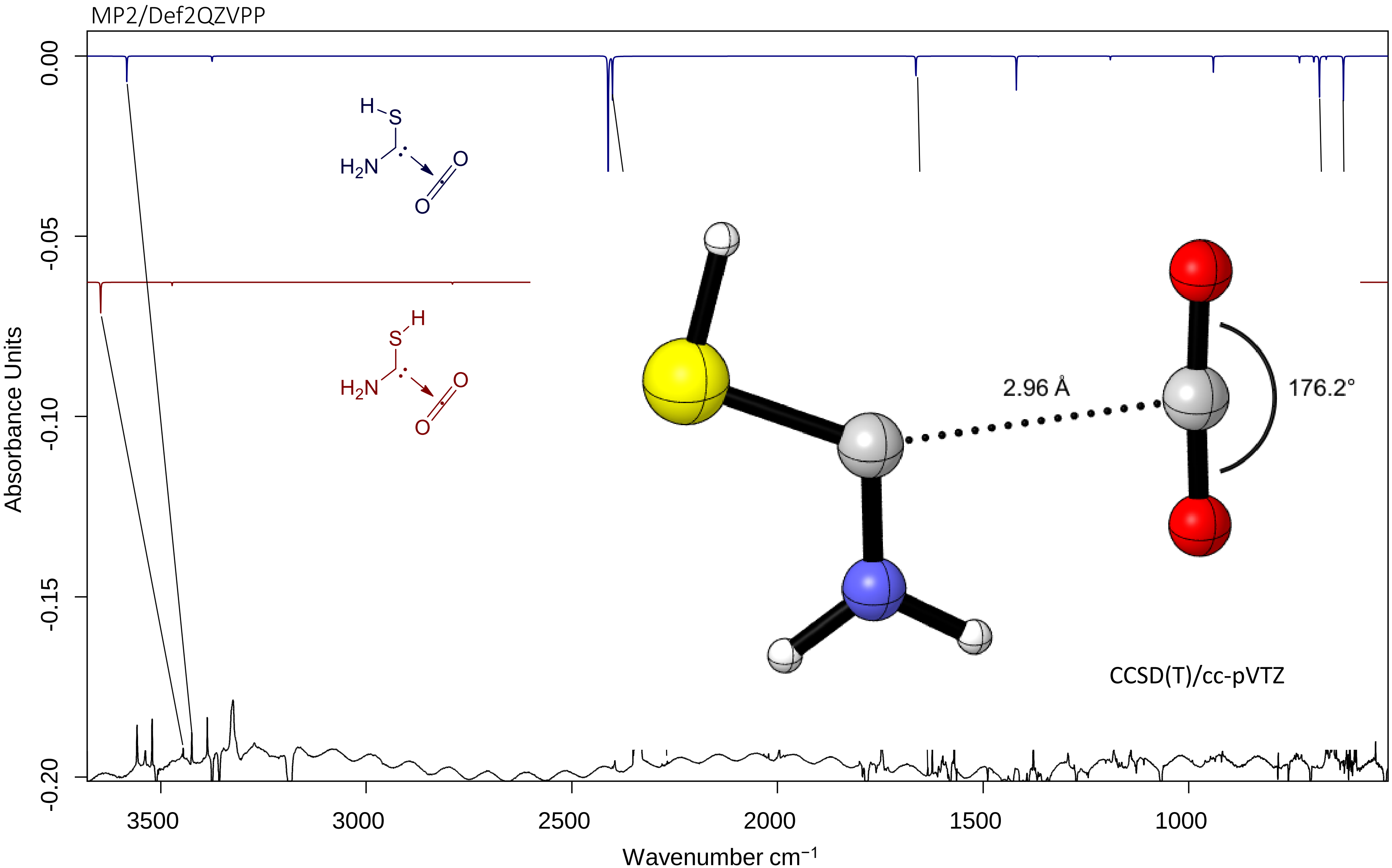

MP2/Def2QZVPP
0.05
0.00
-0.05
-0.10
-0.15
-0.20
Absorbance Units
3500
3000
2500
2000
1500
1000
500
Wavenumber cm⁻¹
S
H
N
H
O
H
O
S
H
H
N
H
O
O

cis/*trans*-conformers

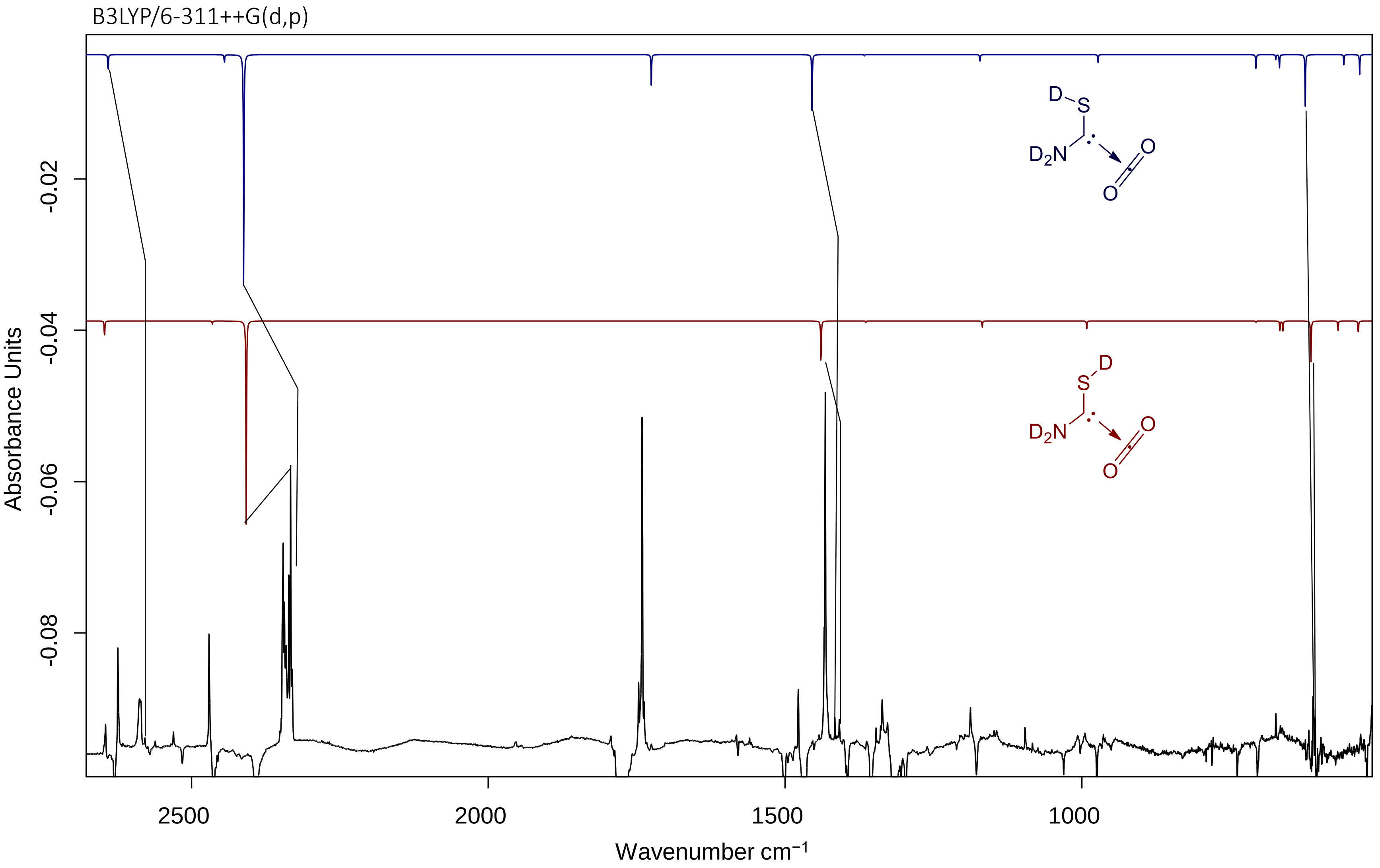
B3LYP/6-311++G(d,p)

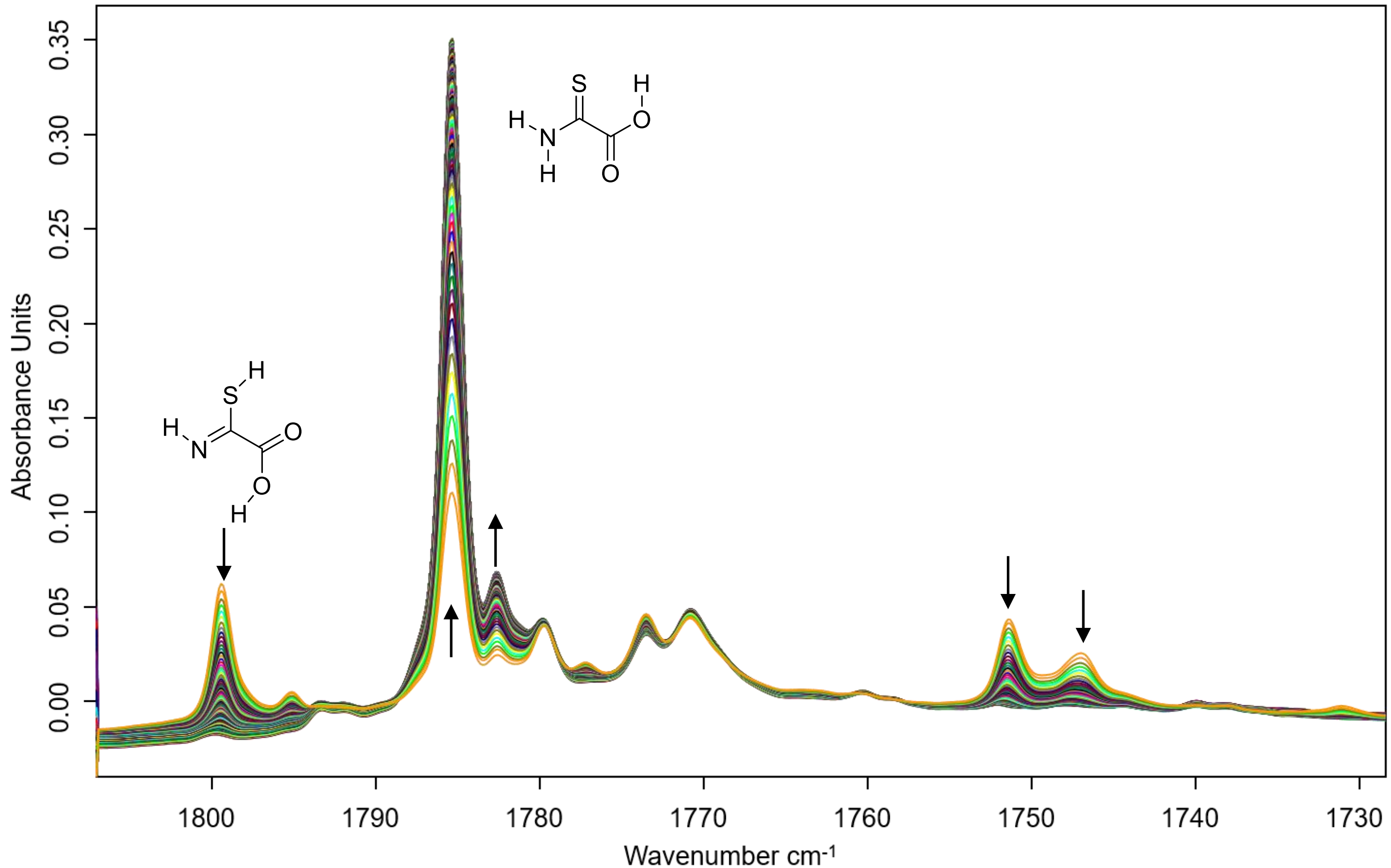


cis/*trans*-carbene-CO_2 complex

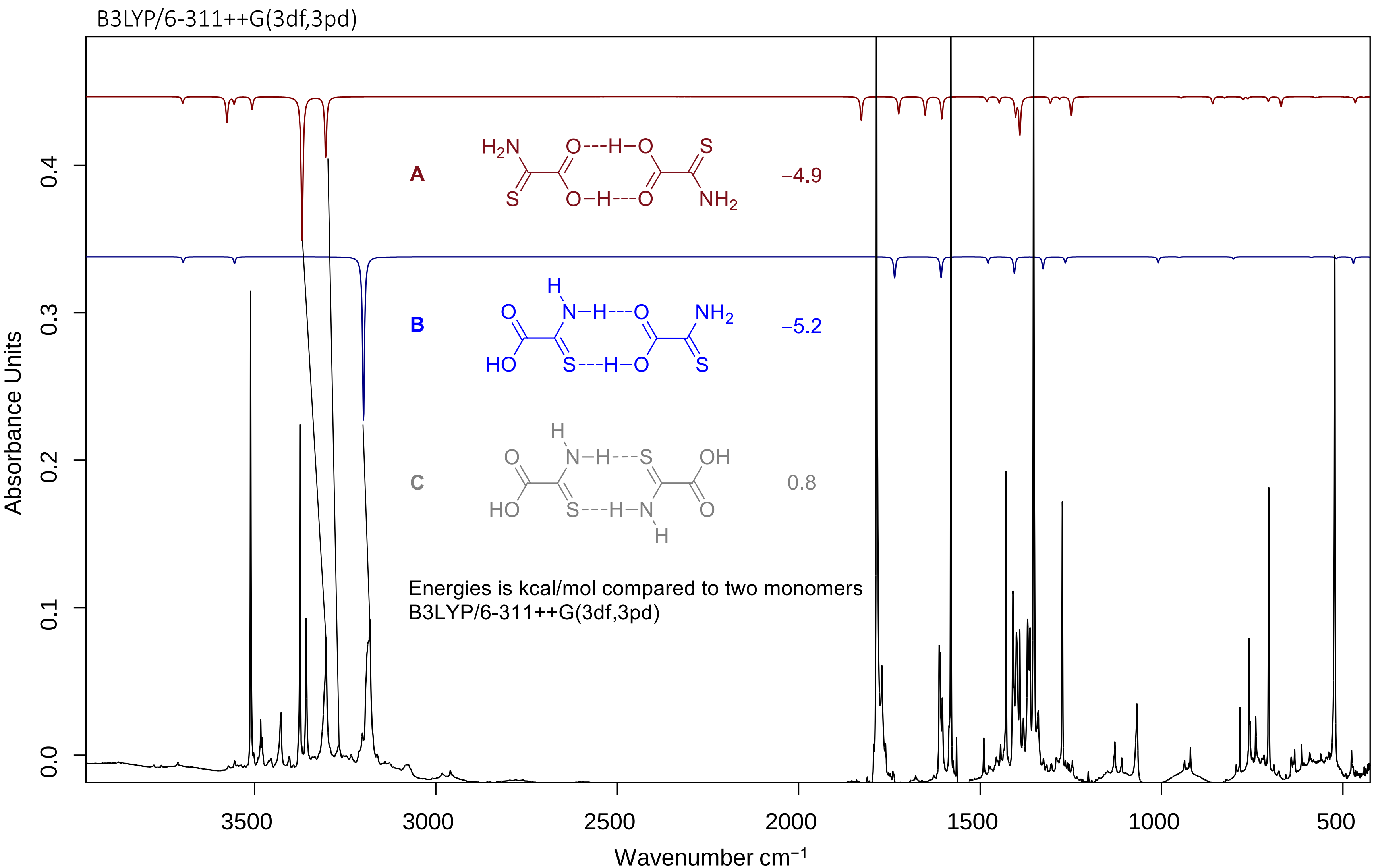


Deuterated *cis*/*trans*-carbene-CO_2 complex



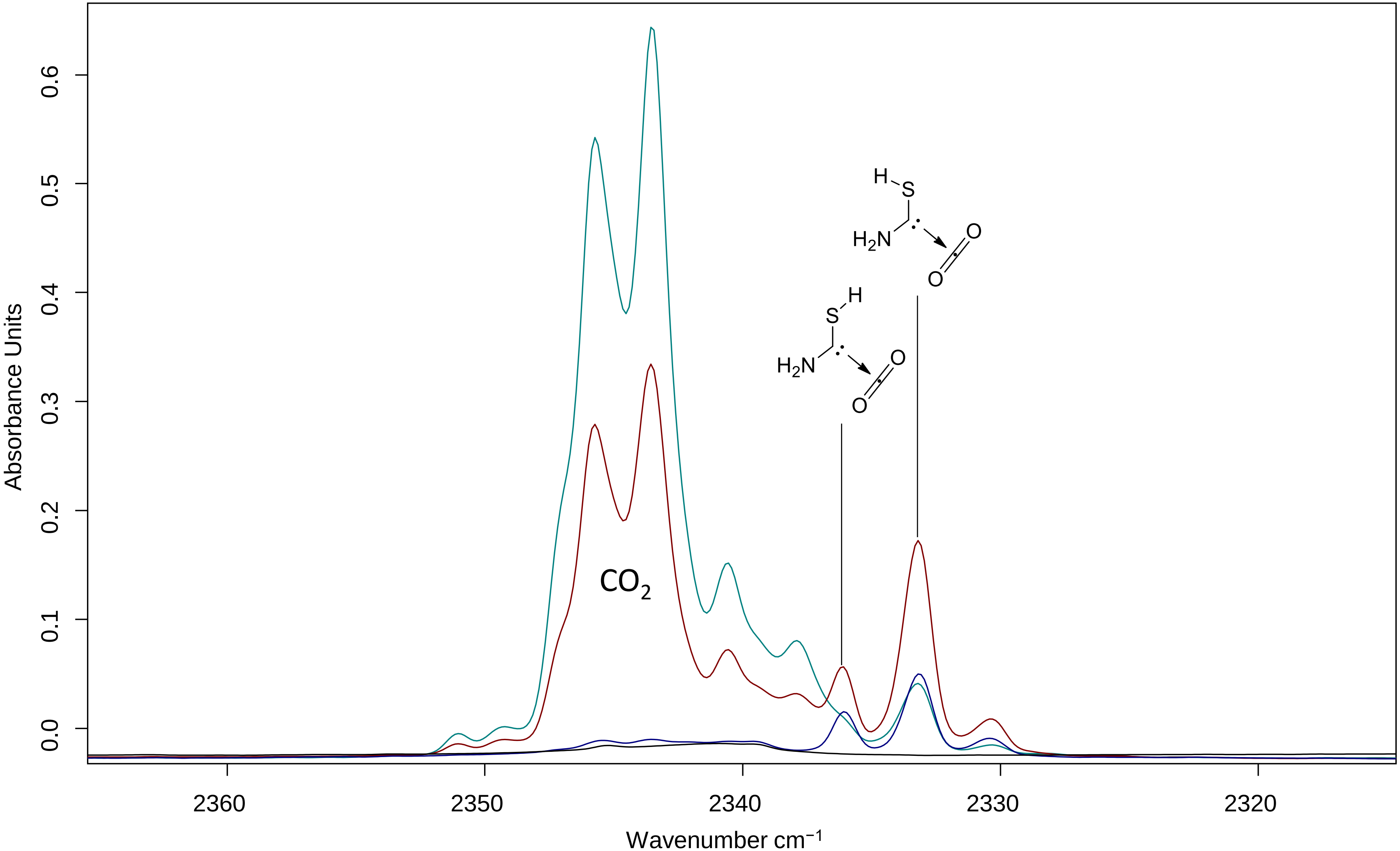

Absorbance Units
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
1800
1790
1780
1770
1760
1750
1740
1730
Wavenumber cm-1

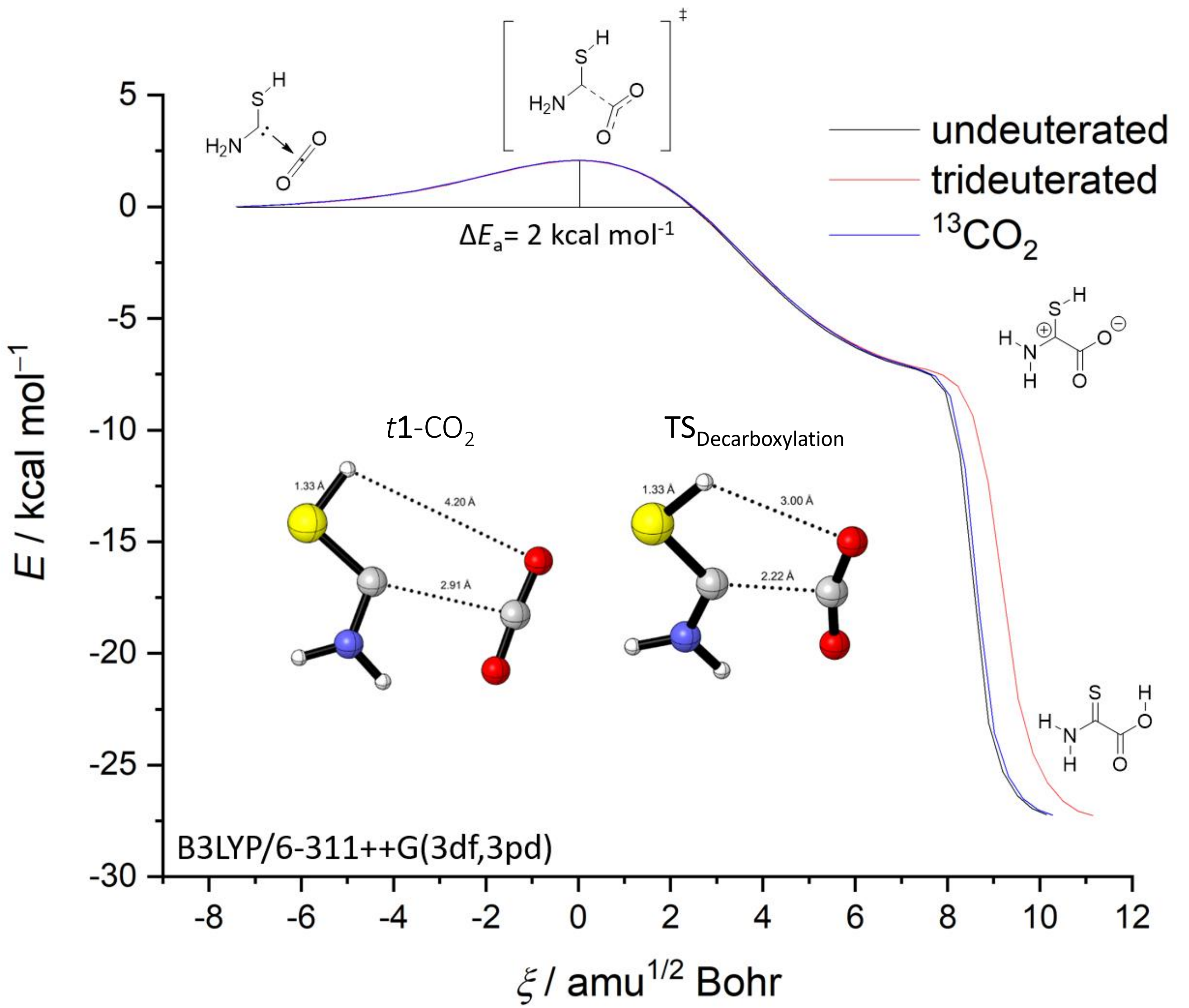
Dimers



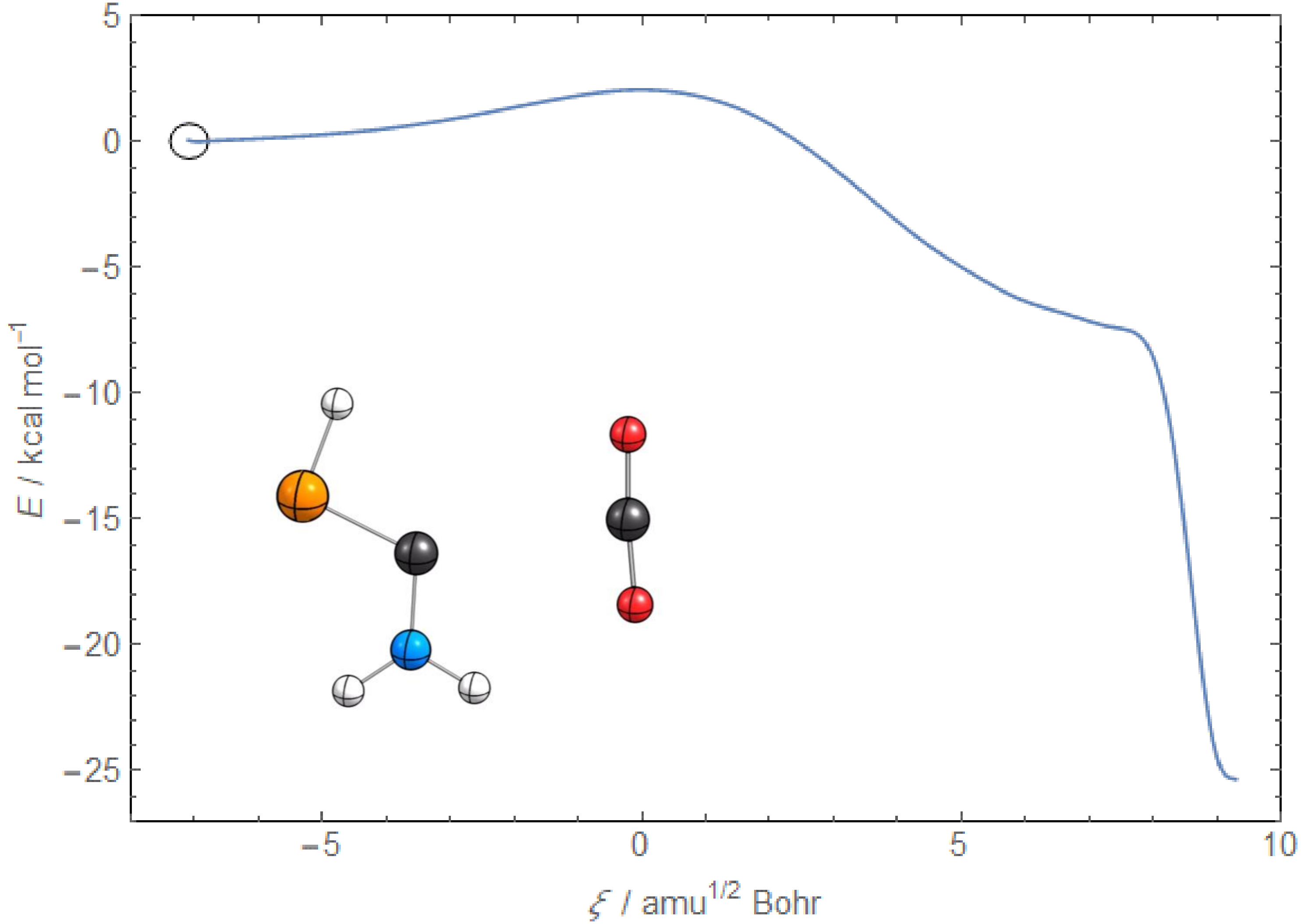
C. Emmeluth, M. A. Suhm, *Phys. Chem. Chem. Phys.* **2003**, *5*, 3094-3099; A. Mardyukov, P. R. E. Sánchez-Garcia, N. L. Doltsinis, W. Sander, *J.Phys. Chem. A* **2007**, *111*, 10552-10561.

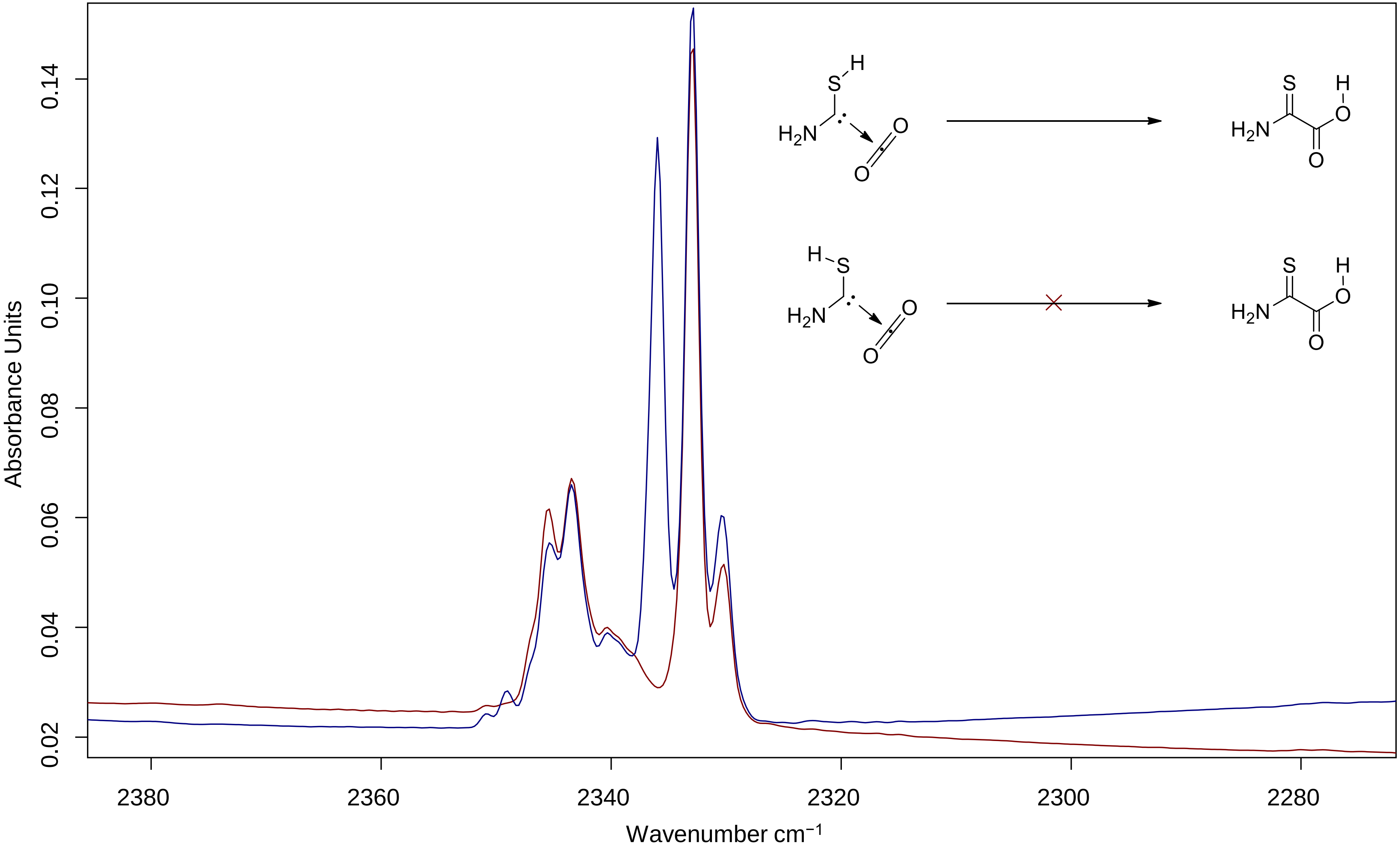
Further irradiation

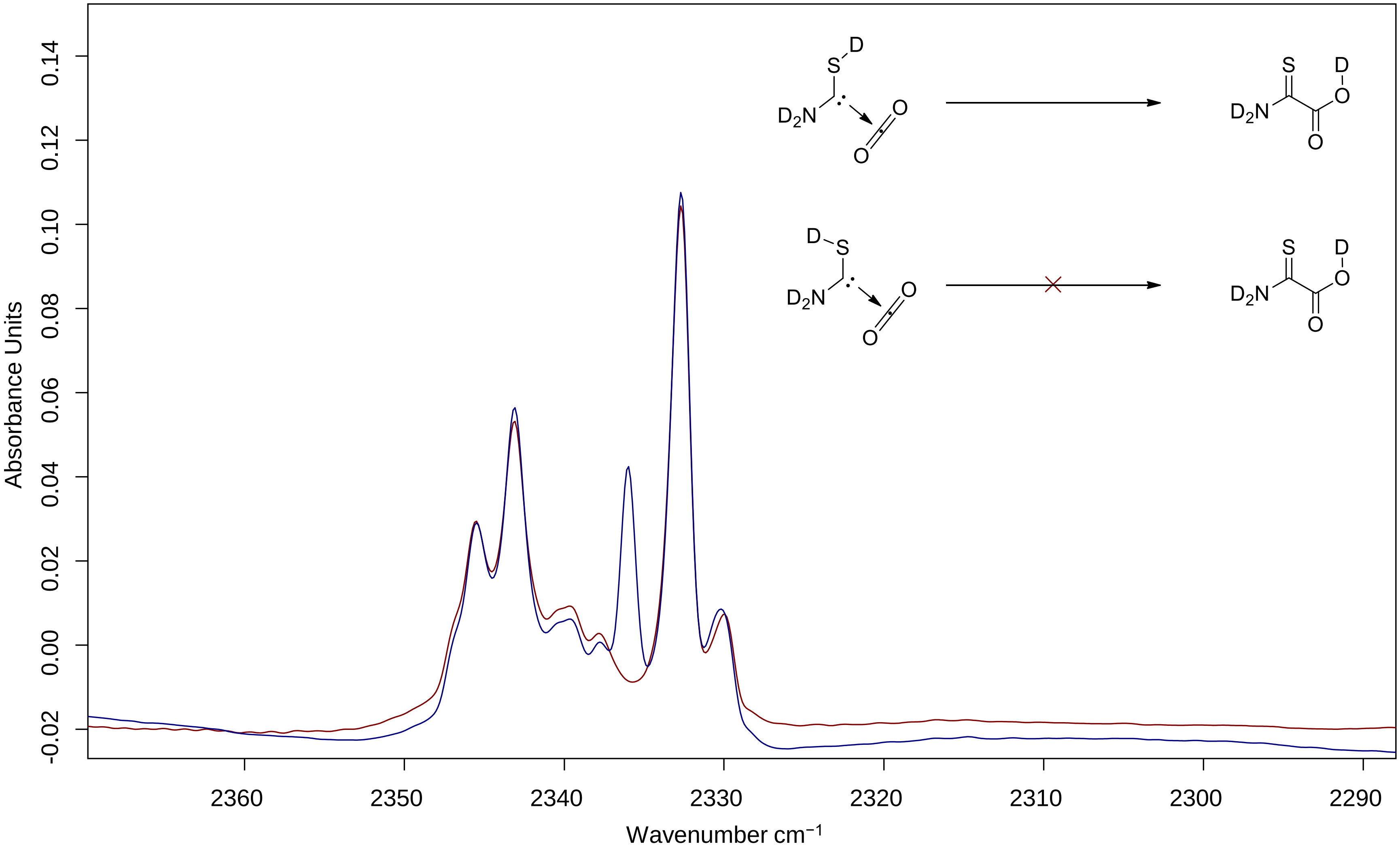




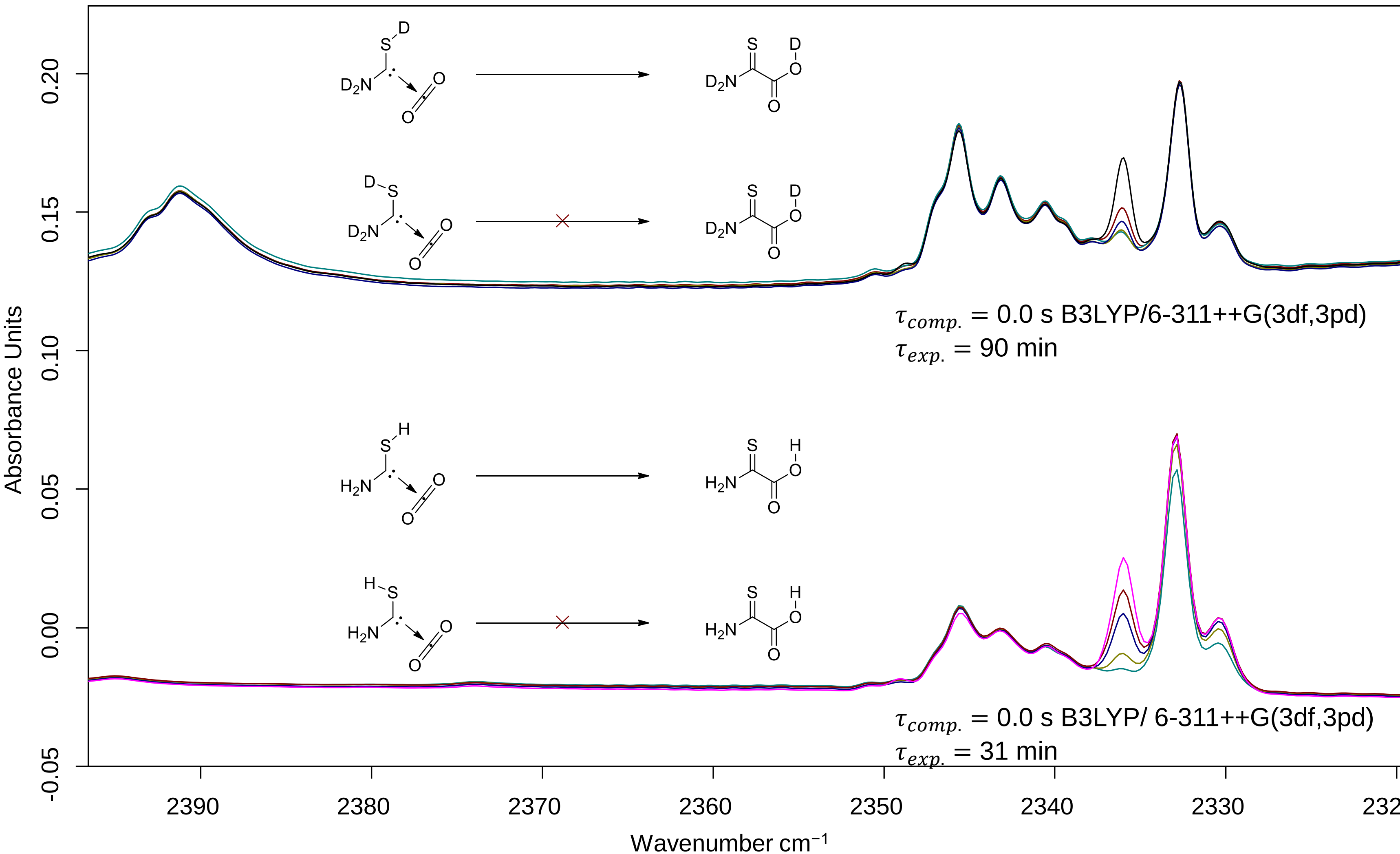
undeuterated
trideuterated
$^{13}CO_2$
ΔE_a= 2 kcal mol^{-1}
t**1**-CO_2
$TS_{Decarboxylation}$
1.33 Å
4.20 Å
2.91 Å
3.00 Å
2.22 Å
B3LYP/6-311++G(3df,3pd)
E / kcal mol^{-1}
ξ / amu$^{1/2}$ Bohr


5
0
−5
−10
−15
−20
−25
−5
0
5
10
E / kcal mol^{-1}
ξ / amu$^{1/2}$ Bohr


Absorbance Units
0.02
0.04
0.06
0.08
0.10
0.12
0.14
2380
2360
2340
2320
2300
2280
Wavenumber cm^{-1}
H
S
H_2N
O
O
S
H
O
H_2N
O
H
S
H_2N
O
O
S
H
O
H_2N
O

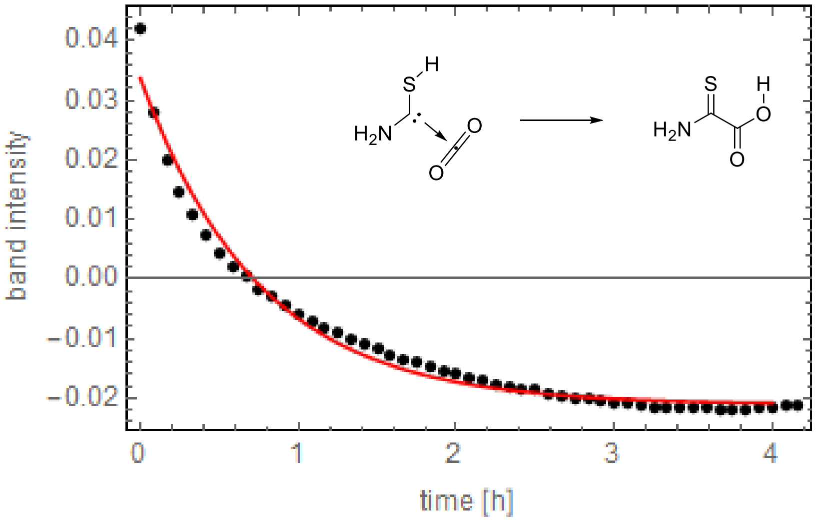

D
S
D2N
O
O
S
D
O
D2N
O
D
S
D2N
O
O
S
D
O
D2N
O
Absorbance Units
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
2360
2350
2340
2330
2320
2310
2300
2290
Wavenumber cm−1

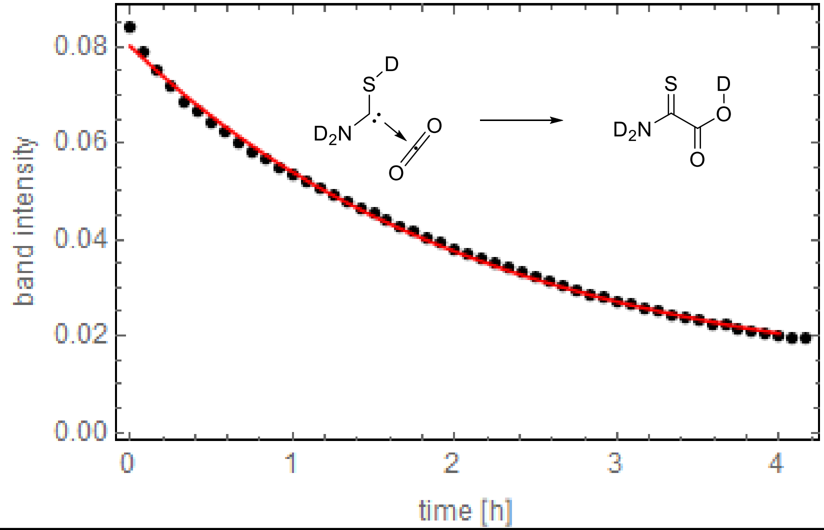
Kinetics

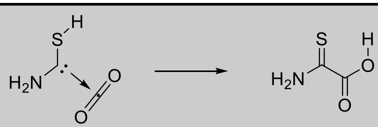
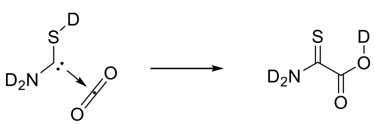
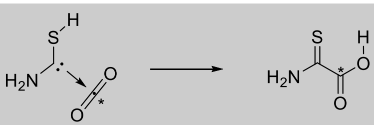


$\tau_{comp.}$ = 0.0 s B3LYP/6-311++G(3df,3pd)
$\tau_{exp.}$ = 90 min
$\tau_{comp.}$ = 0.0 s B3LYP/ 6-311++G(3df,3pd)
$\tau_{exp.}$ = 31 min
Absorbance Units
Wavenumber cm^{-1}

Kinetics

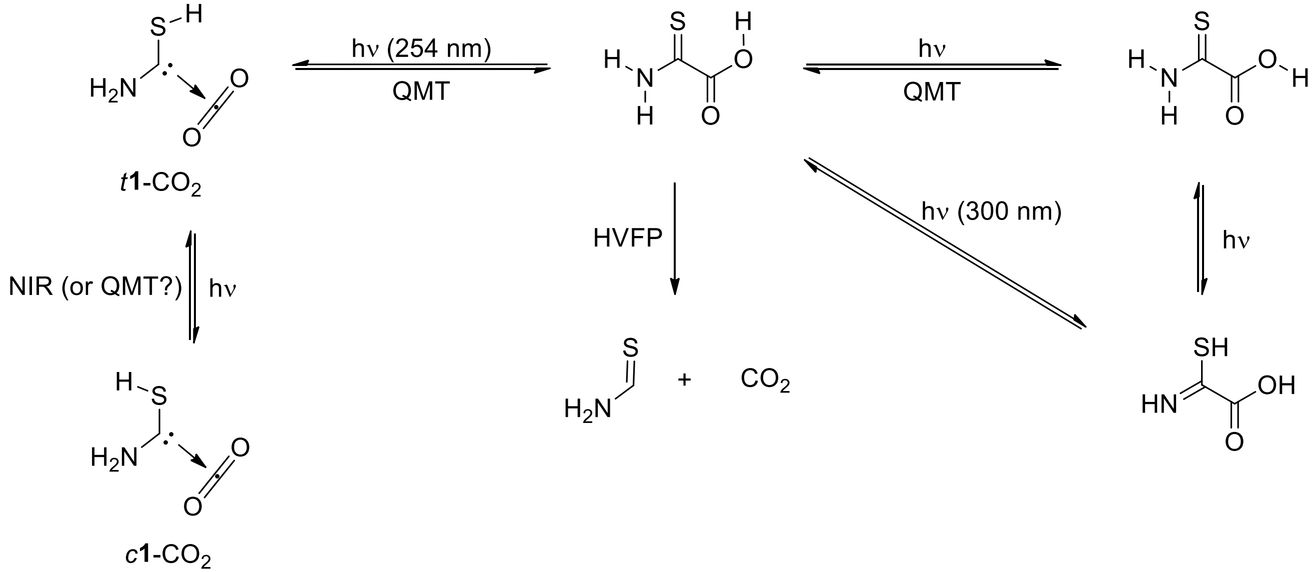




Entry	τ Experiment	τ Polyrate (B3LYP/6-311++G(3df,3pd))	τ Tunnex (B3LYP/6-311++G(3df,3pd)), (\ZPVE)
	31 min	0.00 s	103 d
	90 min	0.01 s	154 d
	?	0.00 s	134 d
cc-**HOCOH** → *ct*-**HOCOH**	18 min	6.10 s	1 d

H. Quanz, B. Bernhardt, F. R. Erb, M. A. Bartlett, W. D. Allen. P. R. Schreiner, *J. Am. Chem. Soc.* **2020**.

Kinetics

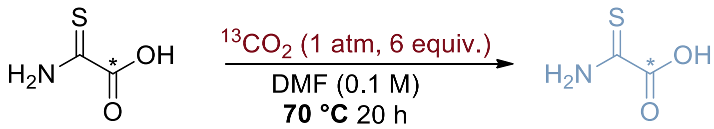


Rotamerization c**1**-CO_2 to t**1**-CO_2 (T = 10 K, Polyrate)

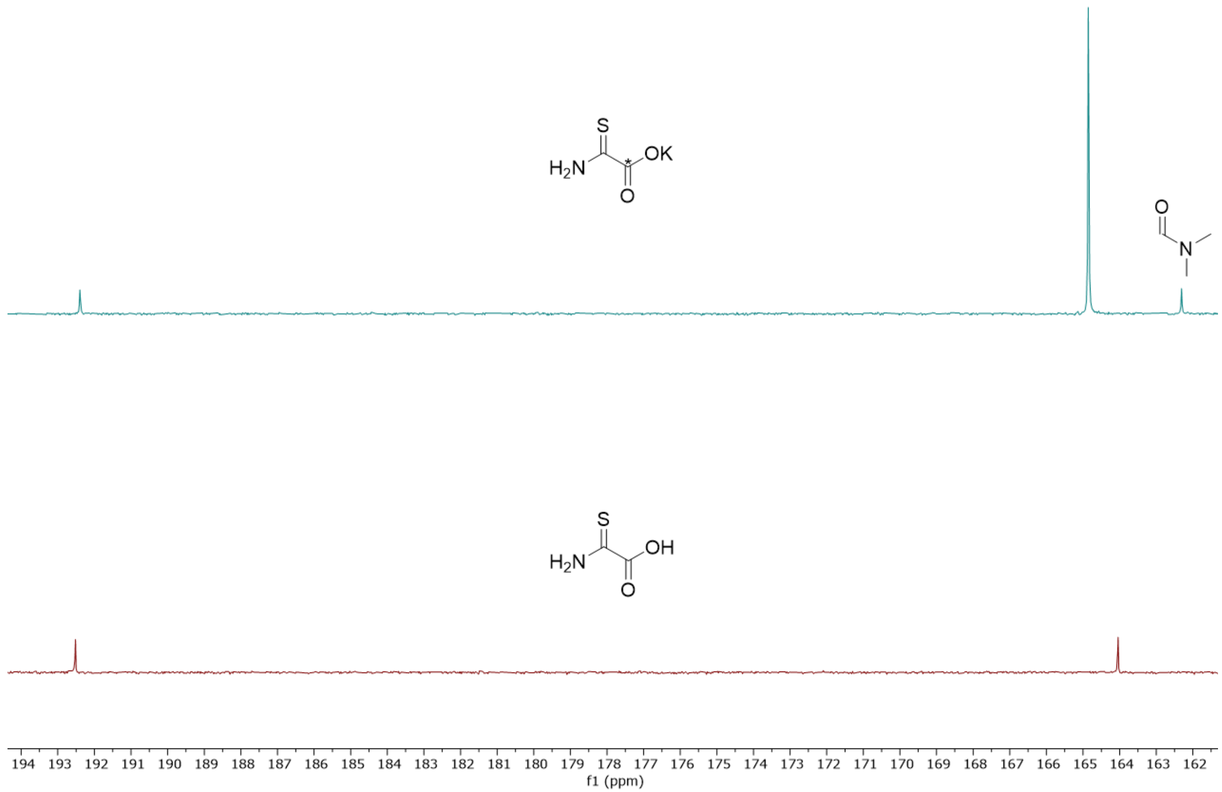
H: $\tau_{comp.}$ = 10^{13} y B3LYP/cc-pVDZ
$\tau_{exp.}$ = 102 d

D: $\tau_{comp.}$ = 10^{22} y B3LYP/cc-pVDZ
$\tau_{exp.}$ = -

- t**1**-CO_2 was not detected at 20 K
- Kinetics dominated by thermal reactivity?

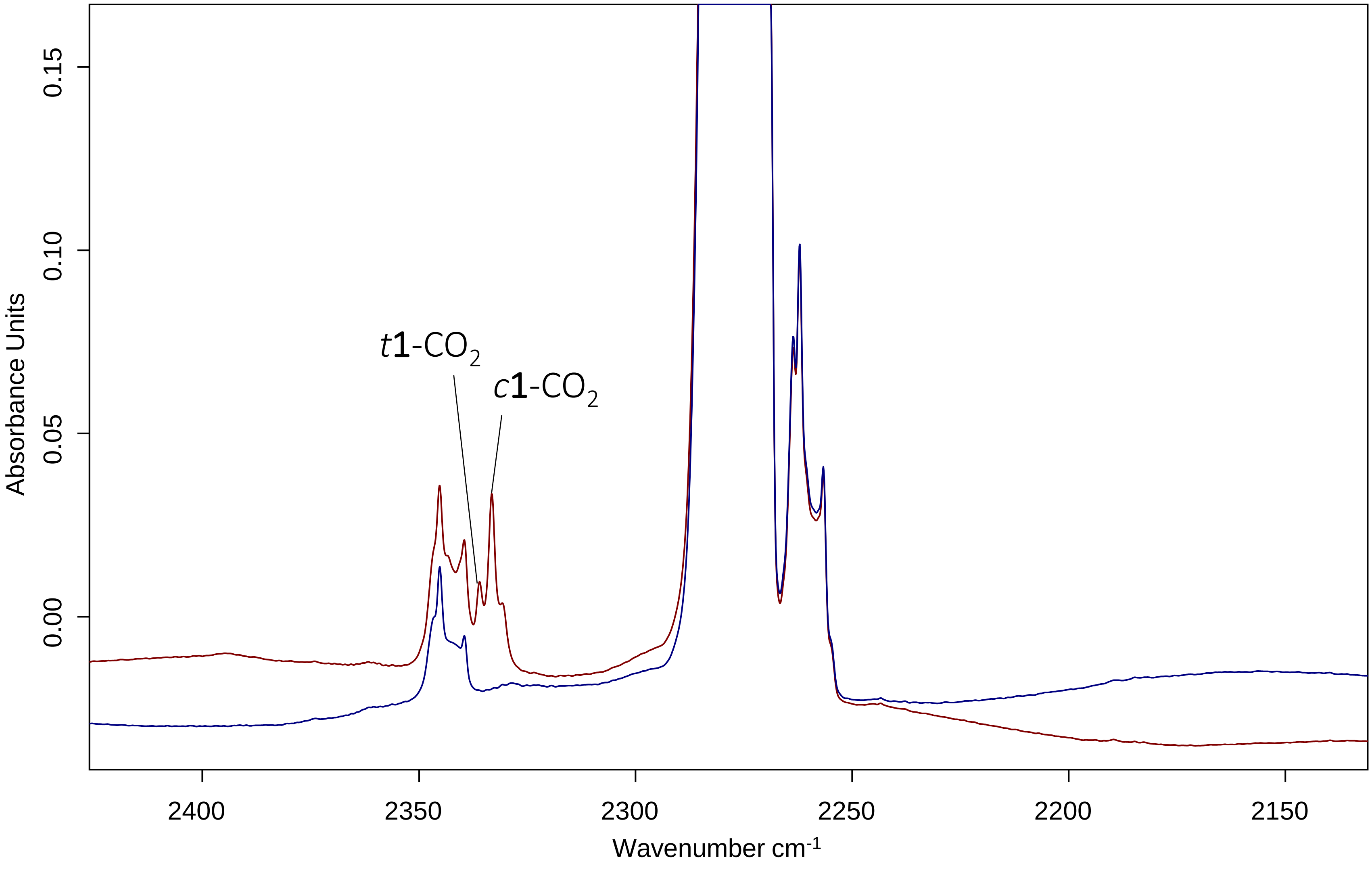


- No reaction with the free acid
- K-salt for better yields
- 13% interconversion (15% under inert conditions)
- No Reaction with Benzaldehyde

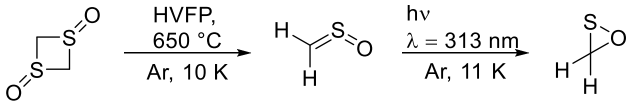


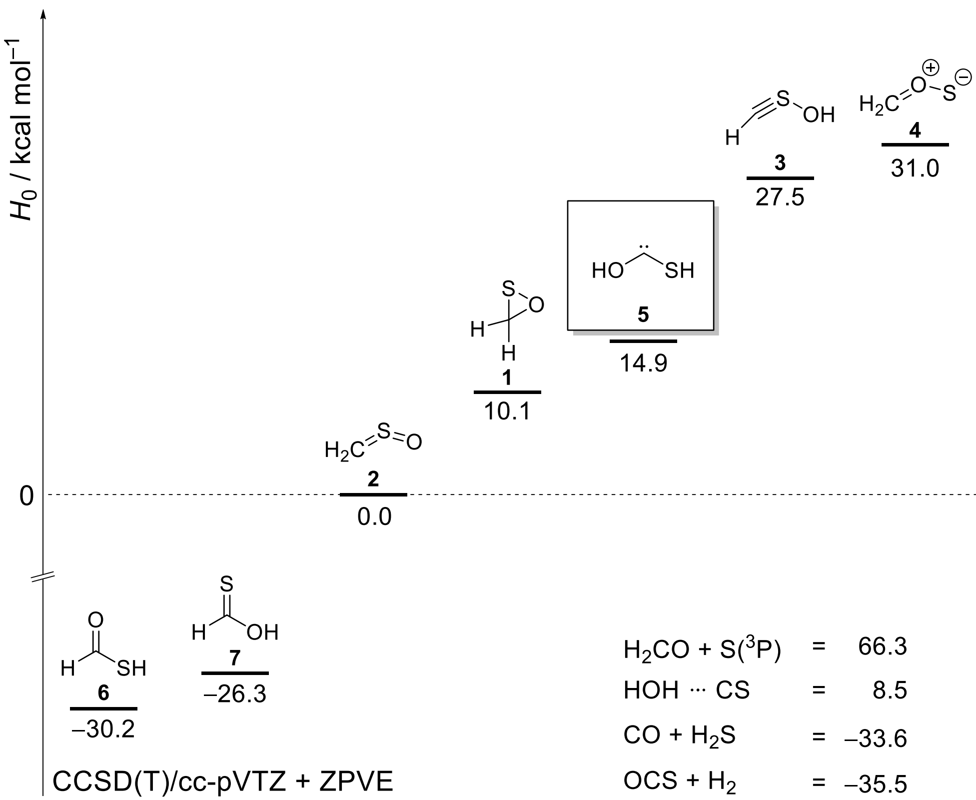
P. J. M. D. Kong, E. K. J. Lui, O. Bsharat, R. J. Lundgren, *Science* **2020**, *369*(6503), 557-561.

$^{13}CO_2$ doped Ar matrix

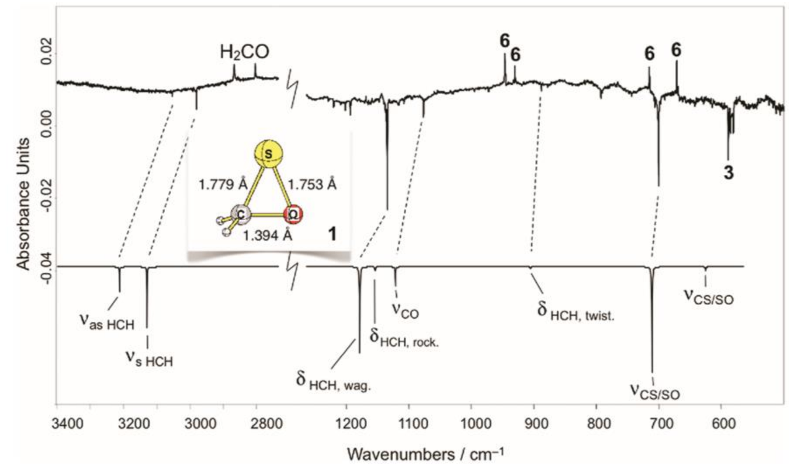


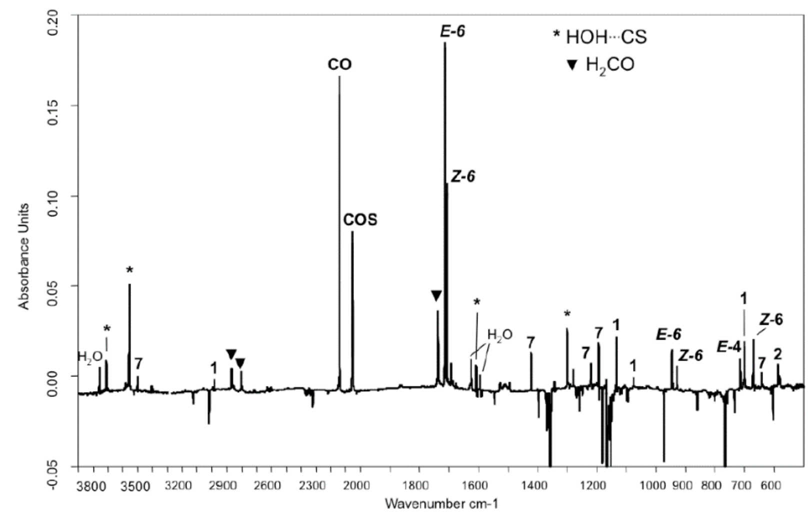
Hydroxy Mercapto Methylene





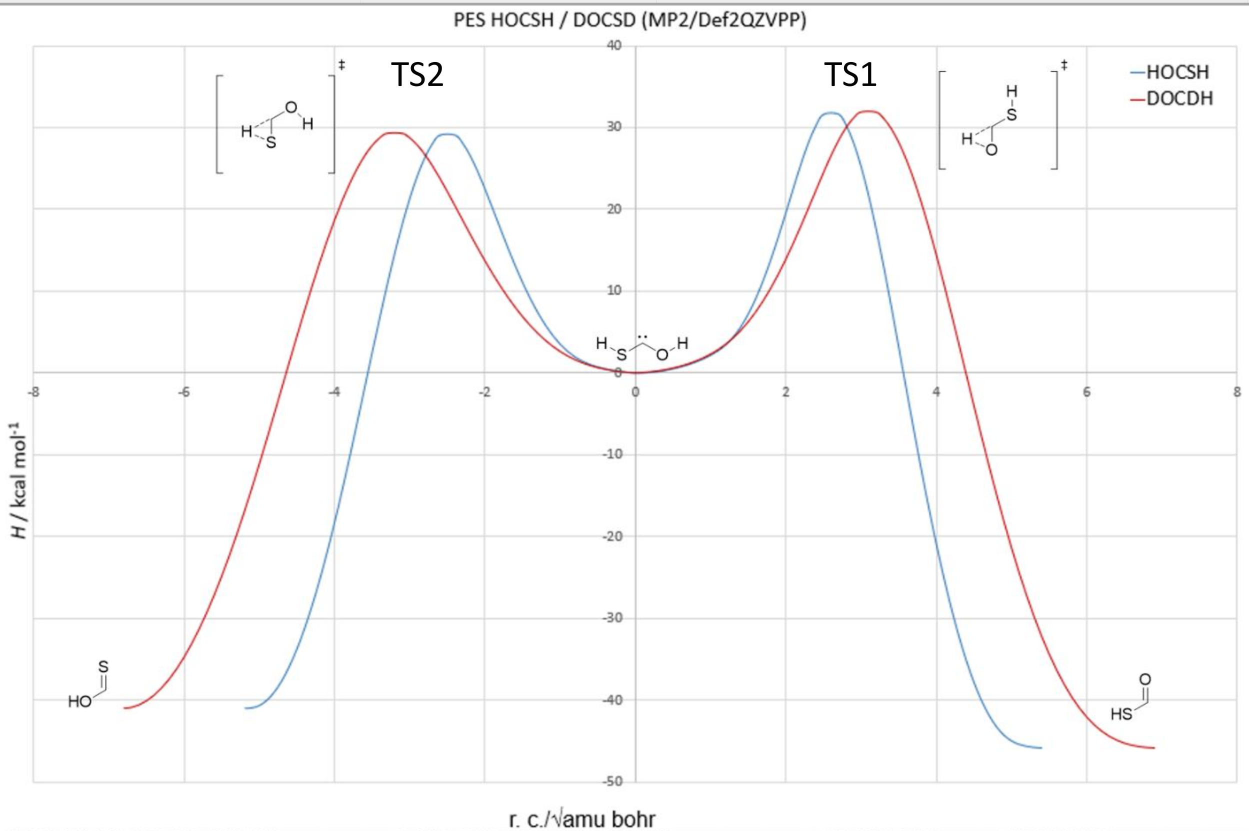
- Conversion of **1** to **6** with λ > 360 nm

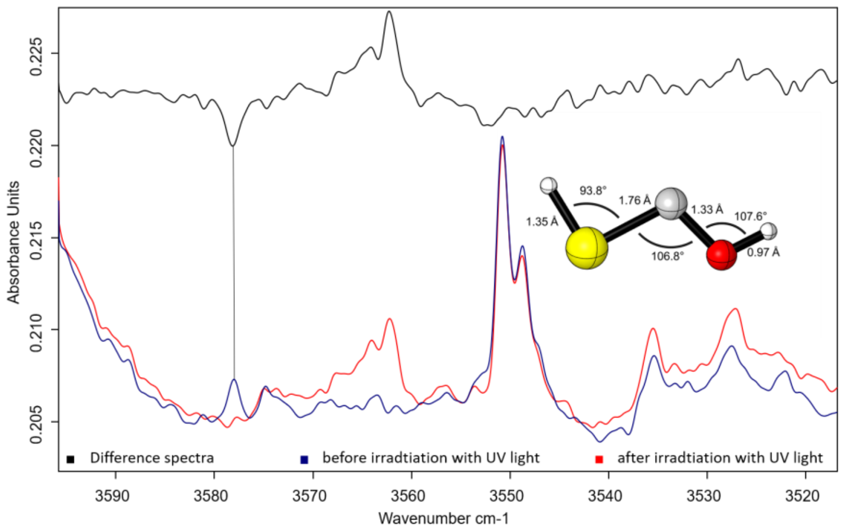




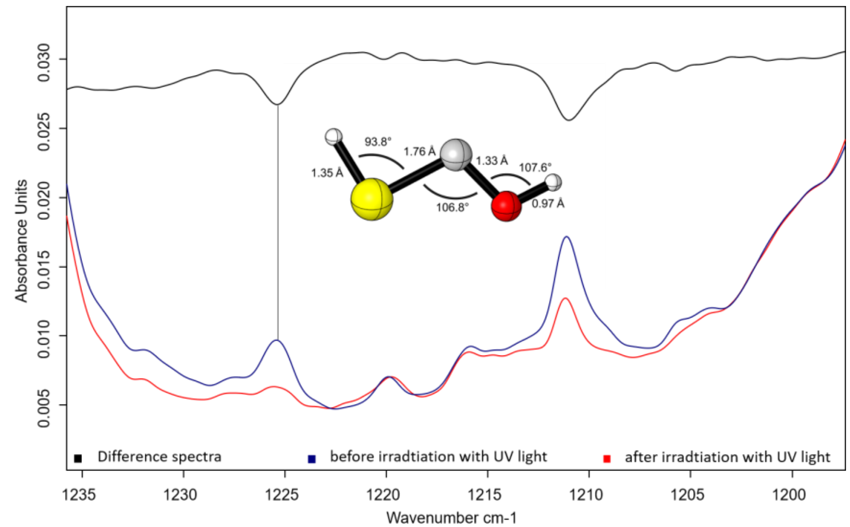
	Route B (*via* TS2)		Route A (*via* TS1)		Polyrate
	electr. Barrier [kcal mol^{-1}] (total barrier)	$\tau_{1/2}$	electr. Barrier [kcal mol^{-1}] (total barrier)	$\tau_{1/2}$	$\tau_{1/2}$
HO-C-SH	29.5 (26.7) 33.4[a]	61 d	32.1 (28.4) 27.0[a]	6 d	76 d (25 K)
DO-C-SD	29.5 (27.5)	1.8 10^{10} d	31.1 (29.3)	1.4 10^{8} d	

[a]CCSD(T)/cc-pVDZ

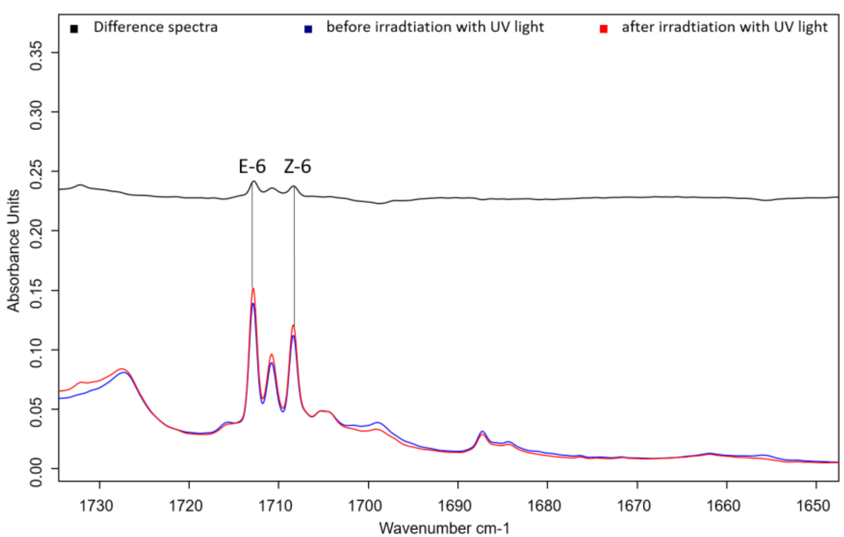


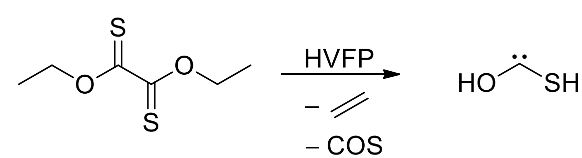


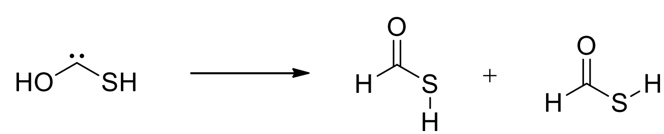
OH str.: 3578.0 cm^{-1} (CCSD(T)/cc-pVTZ: 3821.0 cm^{-1})



CO str.: 1225.4 cm^{-1} (CCSD(T)/cc-pVTZ: 1260.9 cm^{-1})

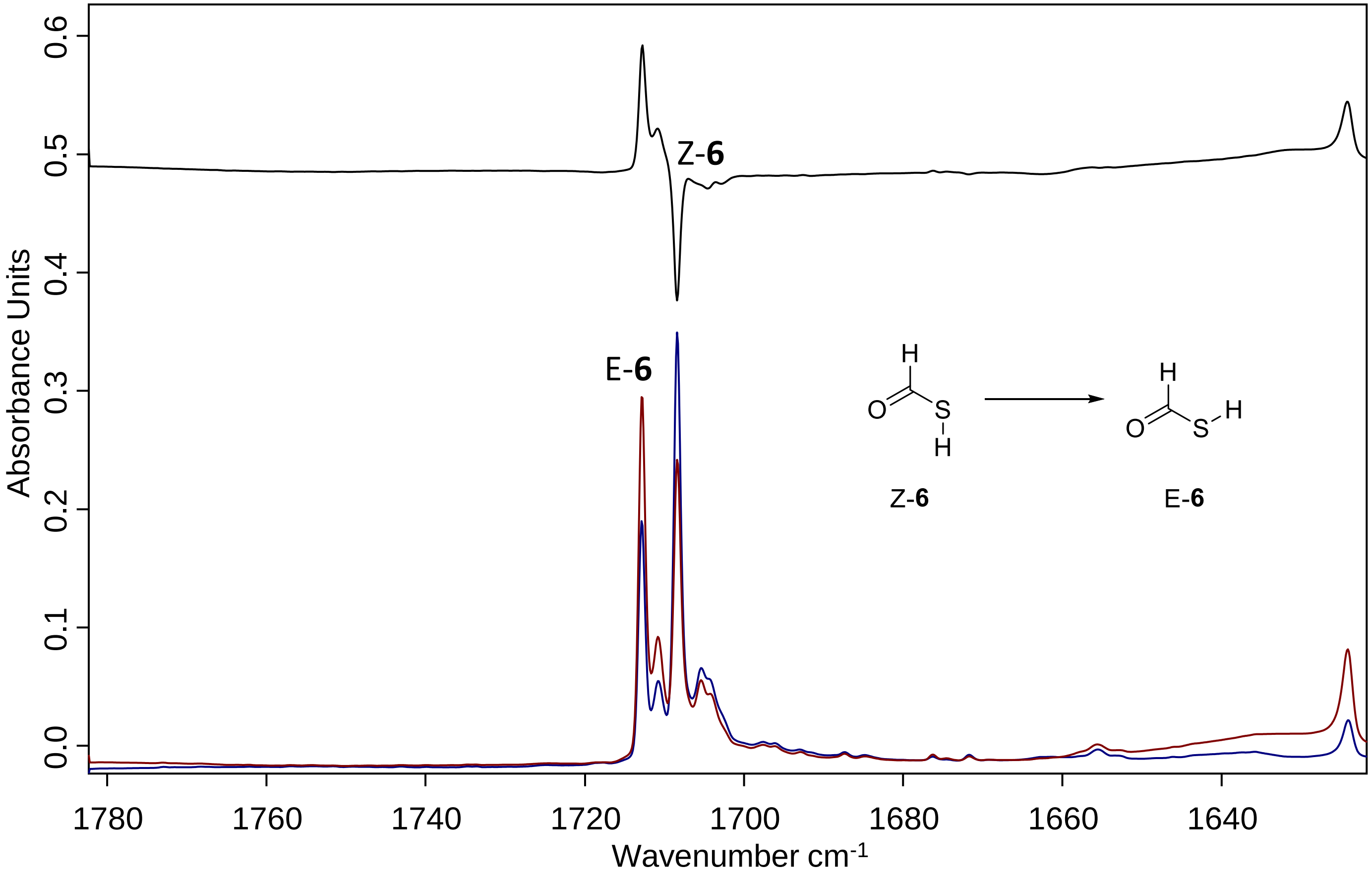






E-6 **Z-6**

66 h in the dark at 3 K



$\Delta_r G$ = 0.6 kcal mol^{-1} (B3LYP/6-311++G(3df,3pd)

ΔE_A = 9.3 kcal mol^{-1} (B3LYP/6-311++G(3df,3pd)

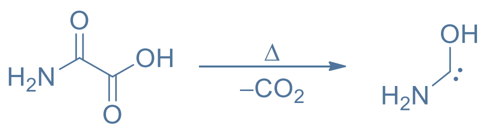
$\Delta_r G$ = 5.4 kcal mol^{-1} (CCSD(T)/cc-pVTZ)

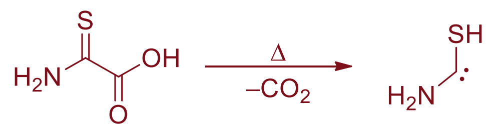
ΔE_A = ? kcal mol^{-1} (CCSD(T)/cc-pVTZ)

P. R. Schreiner, H. Reisenauer, J. Romanski, G. Mloston, *J. Am. Chem. Soc.* **2010**, *132*, 7240-7241.

Conclusion

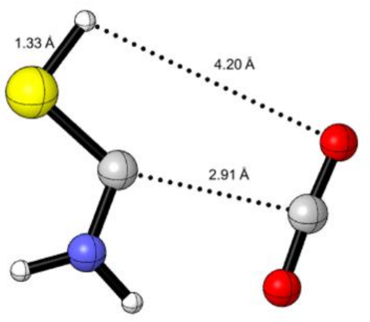
- 2-Amino-2-Thioxoacetic Acid forms the Amino Mercapto Methylene–CO_2
- The free Carbene has not been reported and does not form under HVFP conditions



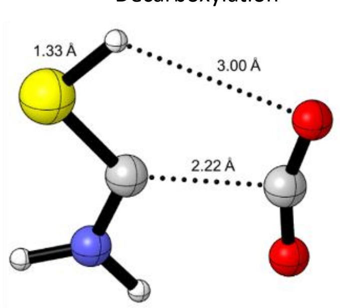


- The *trans*-Complex reacts back to the starting material (heavy atom tunneling and thermal pathway)
- H/D-Atom shows no significant movement when the system reaches the TS (small KIE)
- The *cis*-Complex slowly decays (Rotamerization)

$t\mathbf{1}$-CO_2



$TS_{Decarboxylation}$

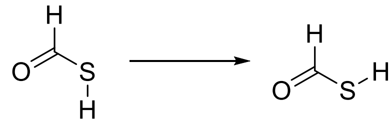


B3LYP/6-311++G(3df,3pd)

- An exchange for $^{13}CO_2$ under matrix isolation conditions was not possible
- This system shows the formation of a carbene-CO_2 complex aswell as CO_2 exchange reactivity in solution: **Complex as intermediate**
- No Umpolung-reactivity or photochemistry was observed in solution (Exchange conditions and under irradiation)

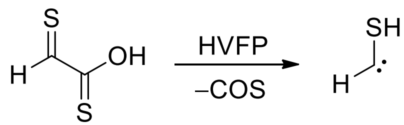
Outlook

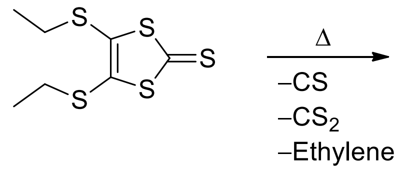
- Reactivity of Z-**6** and E-**6**

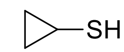


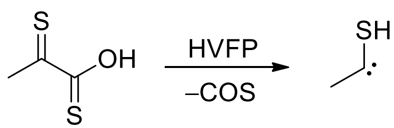
Z-**6** E-**6**

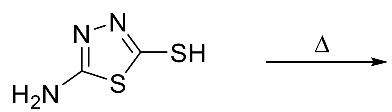
- New suitable precursors for the generation of mercapto carbens

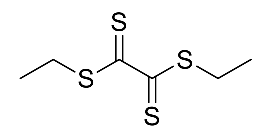


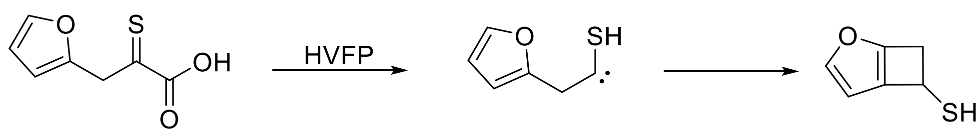


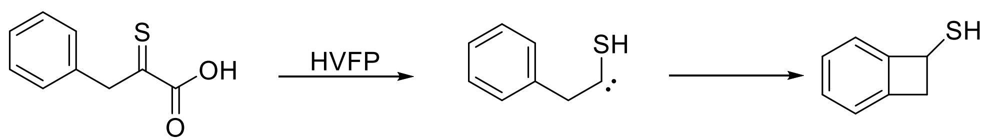












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