Matrix Isolation Method

2020/5/18

M2 Yuki Nishioka

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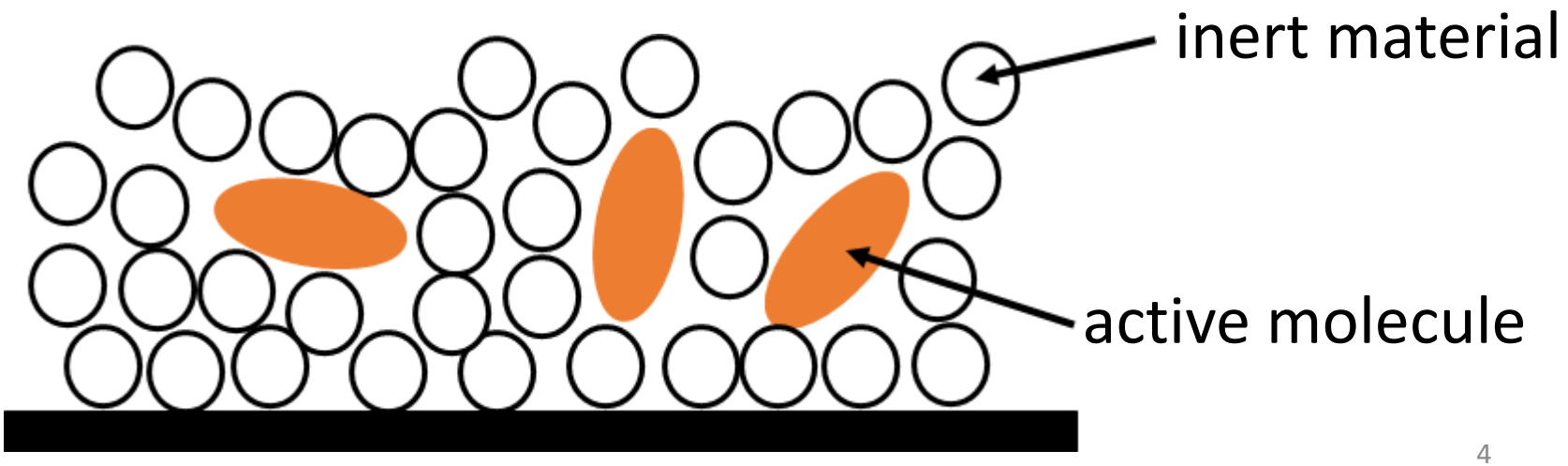
What is Matrix Isolation?

・One of the method of observation unstable materials

・George C. Pimentel developed in 1954.



George C. Pimentel *et al*. *J. Chem. Phys*. 1954, **22**, 1943.

George Claude Pimentel

1943: B.S. from University of California, Los Angeles
1949: Ph.D. from University of California, Berkeley
1949-1989: teaching at University of California, Berkeley

He was the inventor of the chemical laser.

・In low-temperature chemistry; he developed the technique of matrix isolation.

・In theoretical chemistry; he proposed the three-center four-electron bond which is now accepted as the best simple model of hypervalent molecules.

Source: https://www.asl-associates.com/Images/pimentel-george.pdf

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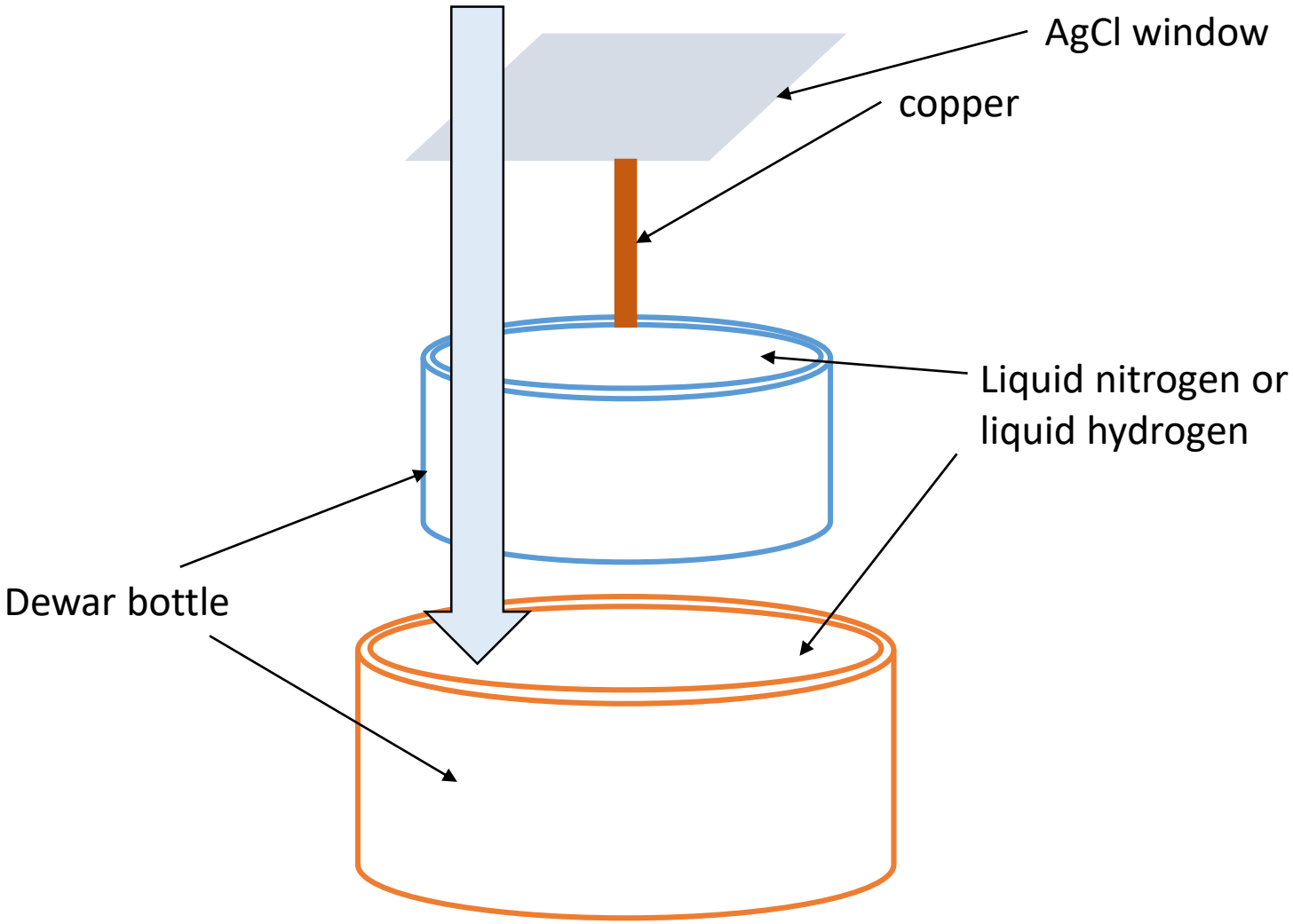
Experimental Method



George C. Pimentel *et al*. *J. Chem. Phys*. 1956, **25**, 224.

Desirable Properties of Matrix

1. Inertness

2. Rigidity

3. Transparency

4. Volatility

George C. Pimentel *et al*. *J. Chem. Phys*. 1956, **25**, 224.

Desirable Properties of Matrix

1. Inertness……A rare gas is ideal. In N_2 and a hydrocarbon cases, it depends on active molecules.

2. Rigidity……The matrix must be sufficiently rigid to prevent diffusion of the active species.

George C. Pimentel *et al*. *J. Chem. Phys*. 1956, **25**, 224.

Desirable Properties of Matrix

3. Transparency…. The matrix must have no absorption in the spectral region of interest. Also, glassy rather than a crystalline matrix is desirable.

4. Volatility…… The matrix must have a sufficiently high vapor pressure at room temperature to permit convenient handling of the gas in a vacuum line but a sufficiently low pressure at the temperature of the refrigerant.

George C. Pimentel *et al*. *J. Chem. Phys*. 1956, **25**, 224.

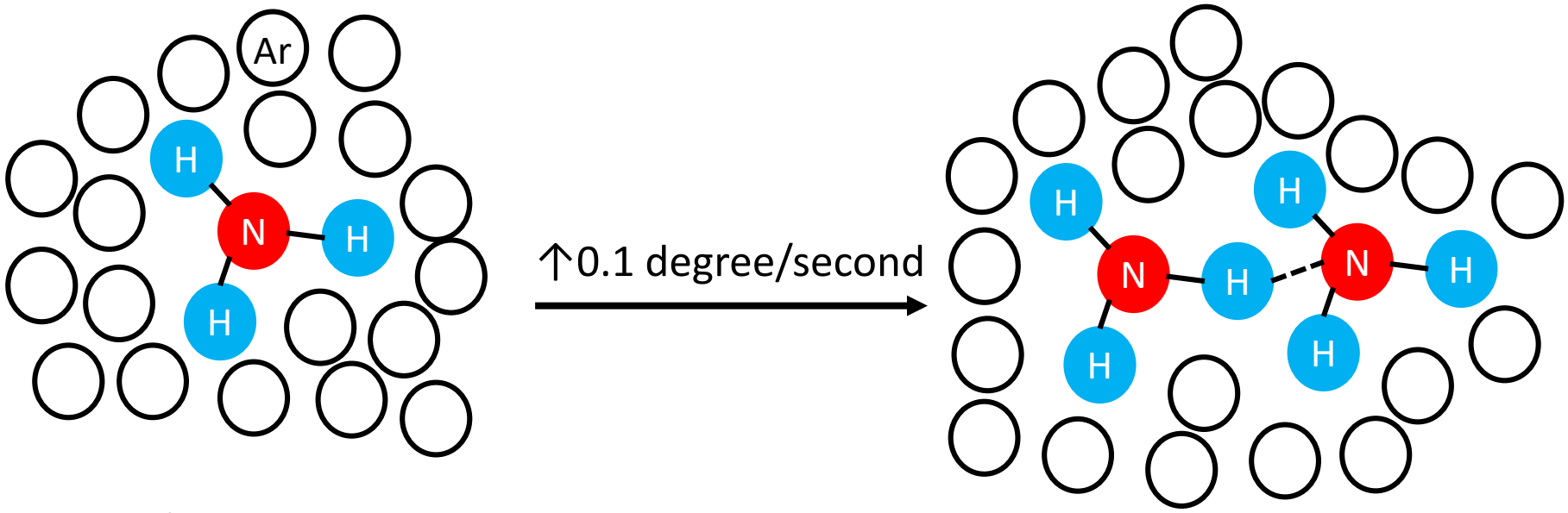
Application to Reaction Kinetics Analysis

- Matrix Isolation Method can also be used for reaction kinetics analysis.

- It can be effectively used for a reaction having a heat of activation of 2 kcal or less.(e.g. isomerization, bond rupture and bond formation)

George C. Pimentel *J. Am. Chem. Soc*. 1958, **80**, 62.

Bring Together the Active Molecules



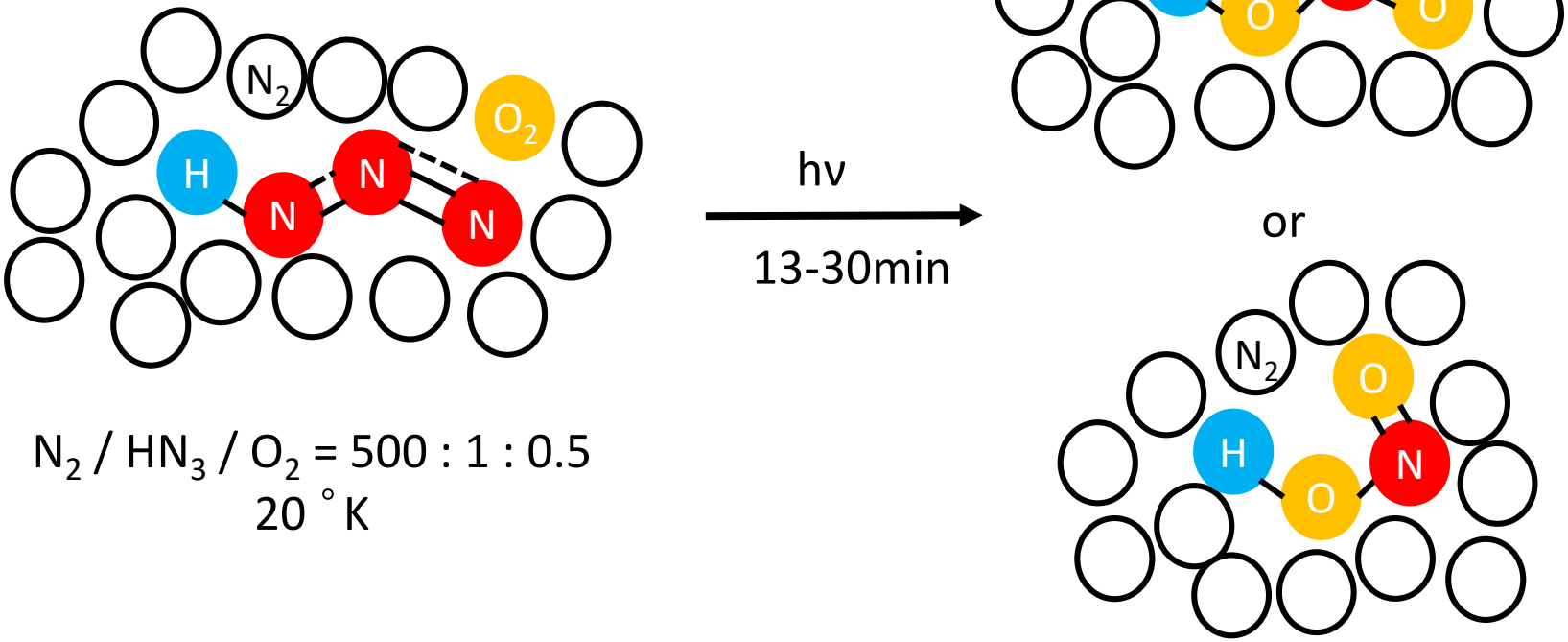
Ar / NH_3 = 195
40 ° K

47.5 ° K

After 75 seconds, spectra revealed the disappearance of about 88 ± 6% of the monomer.

George C. Pimentel *J. Am. Chem. Soc*. 1958, **80**, 62.

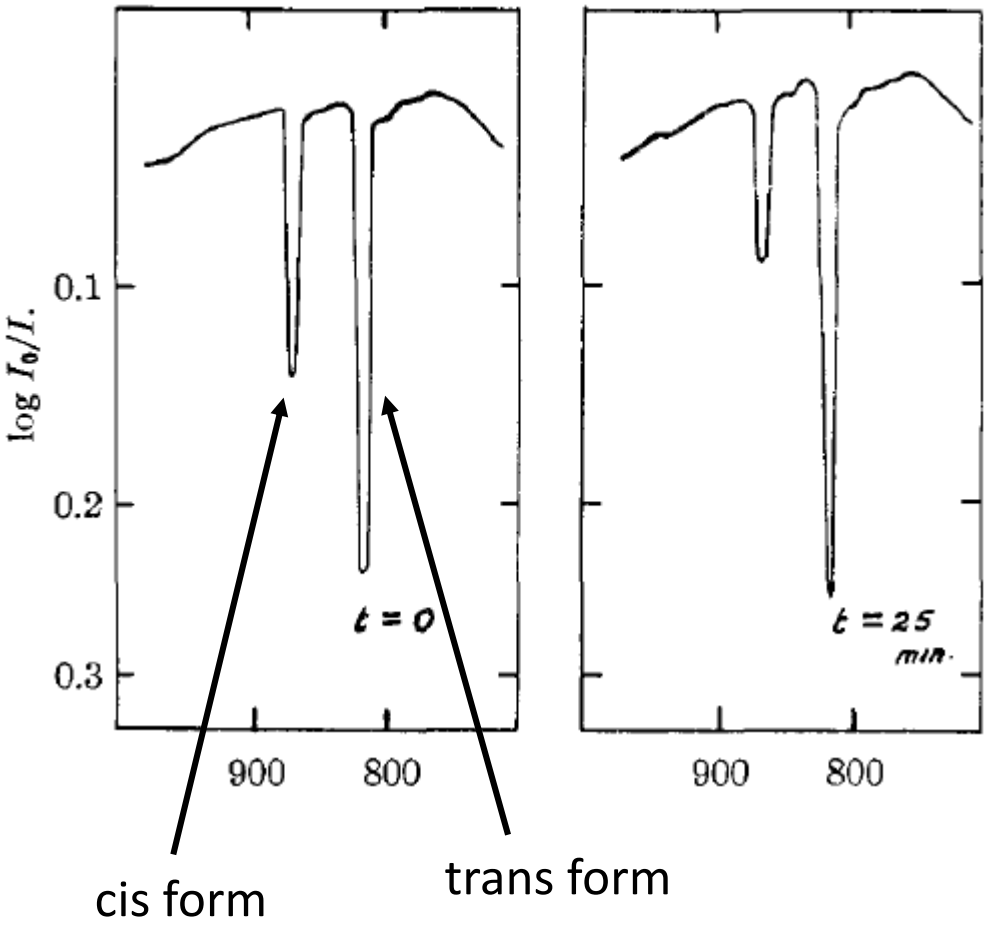
Reaction Kinetics of Isomerization



N_2 / HN_3 / O_2 = 500 : 1 : 0.5
20 ° K

George C. Pimentel *J. Am. Chem. Soc*. 1958, **80**, 62.

Change in Absorbance



Cis form decreased and trans form increased.

George C. Pimentel *J. Am. Chem. Soc*. 1958, **80**, 62.

Calculating the Heat of Activation

$$k_{1,2} = \frac{\boldsymbol{k}T}{h} e^{\Delta S^{0\ddagger}/R} \cdot e^{-\Delta H^{0\ddagger}/RT} \qquad (1)$$

If equation 1 is applicable and $\Delta S^{\ddagger} = 0$, the disappearance of the band at 865 cm^{-1} is governed by a process with a heat of activation of 1500 ± 130 cal.

George C. Pimentel *J. Am. Chem. Soc*. 1958, **80**, 62.

Short Summary

- Desirable properties of matrix

1. Inertness
2. Rigidity
3. Transparency
4. Volatility

- Application to Reaction kinetics analysis

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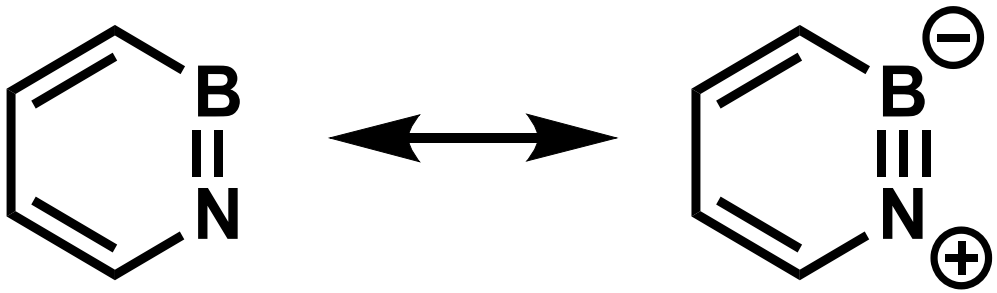
The Reactivity of 1,2-Azaborine



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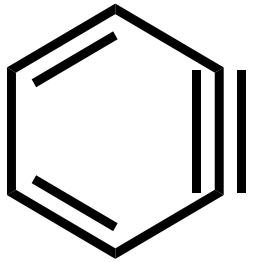

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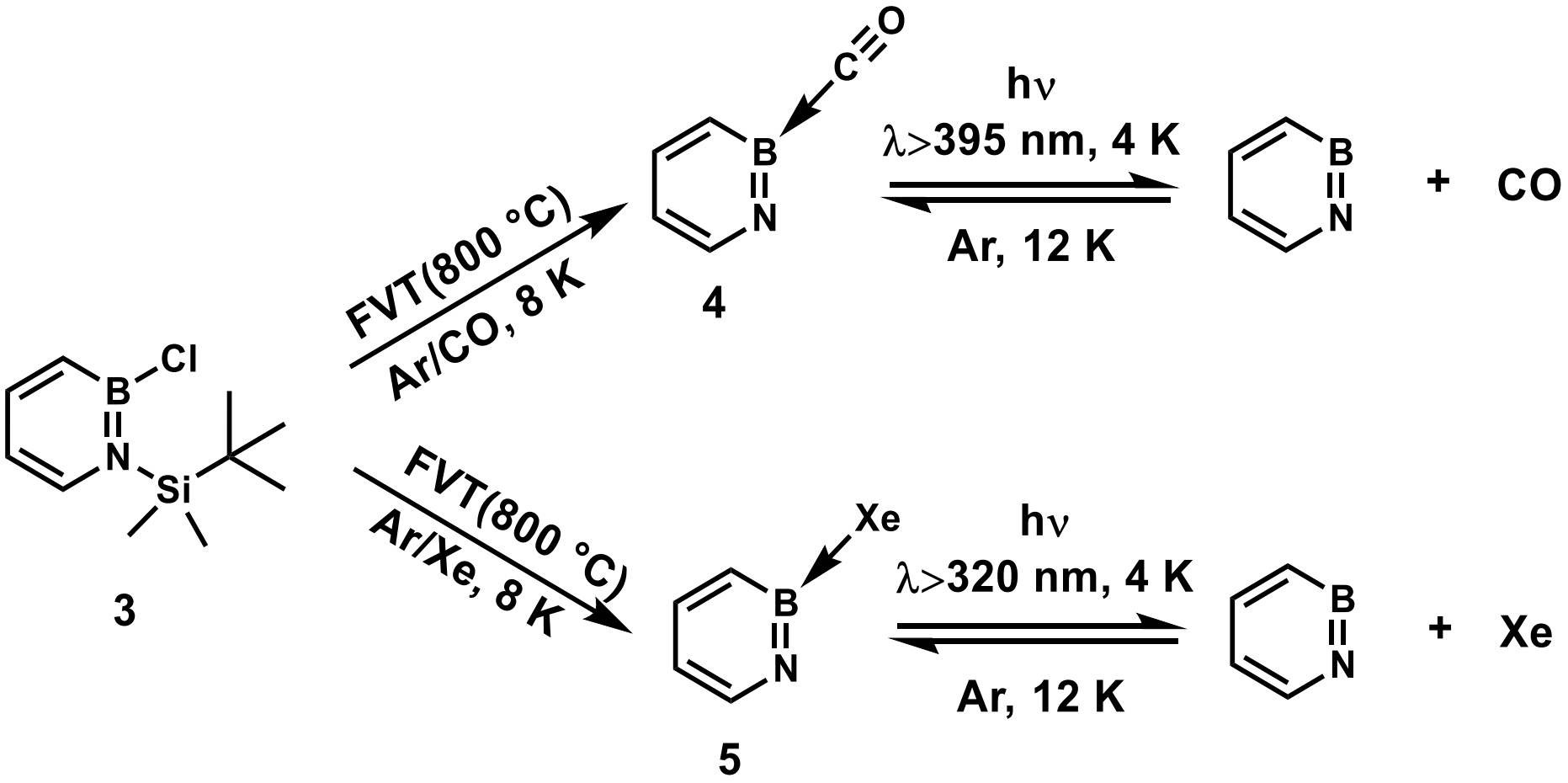
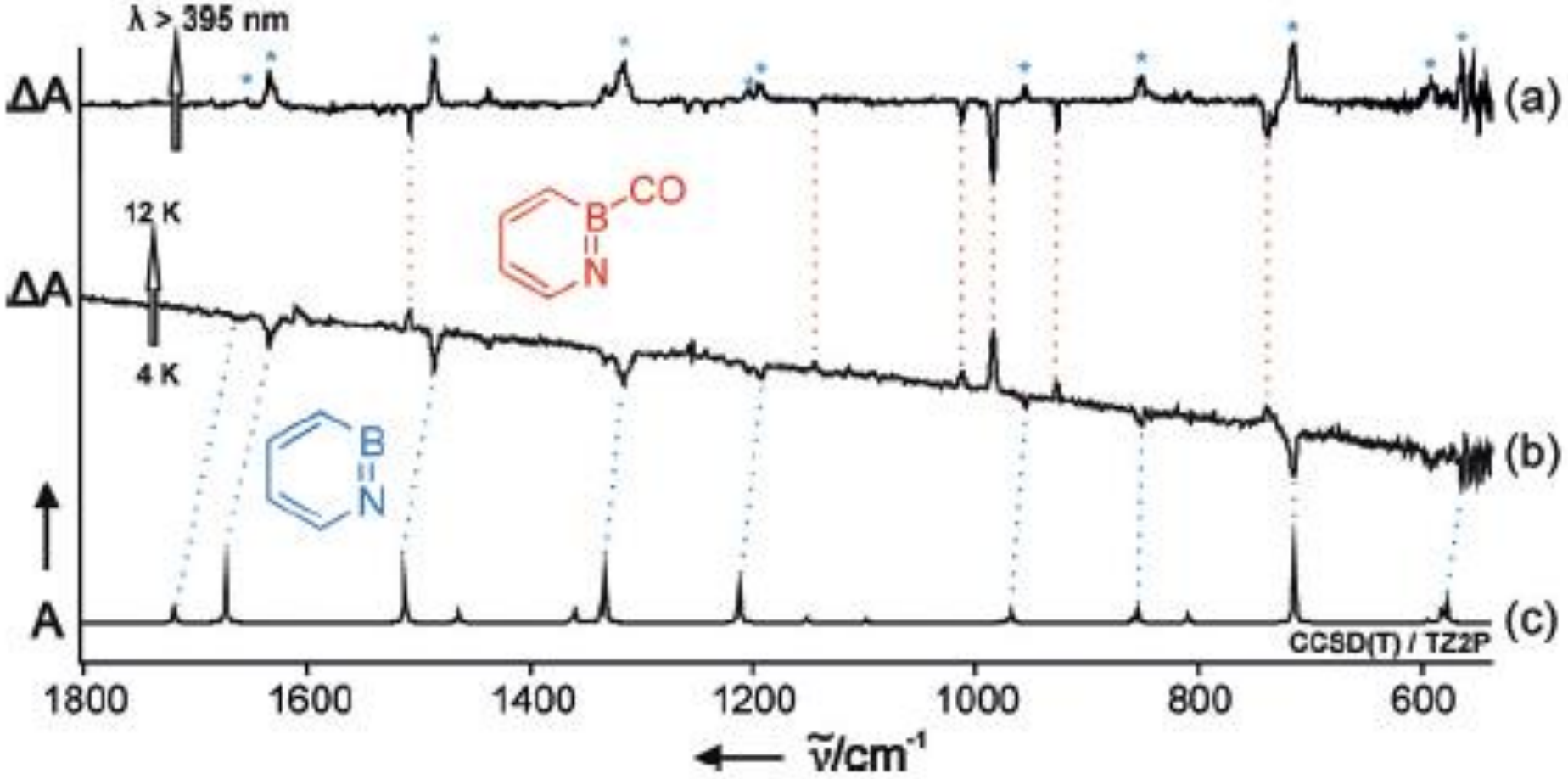
Experimental Method



FVT...Flash Vacuum Thermolysis

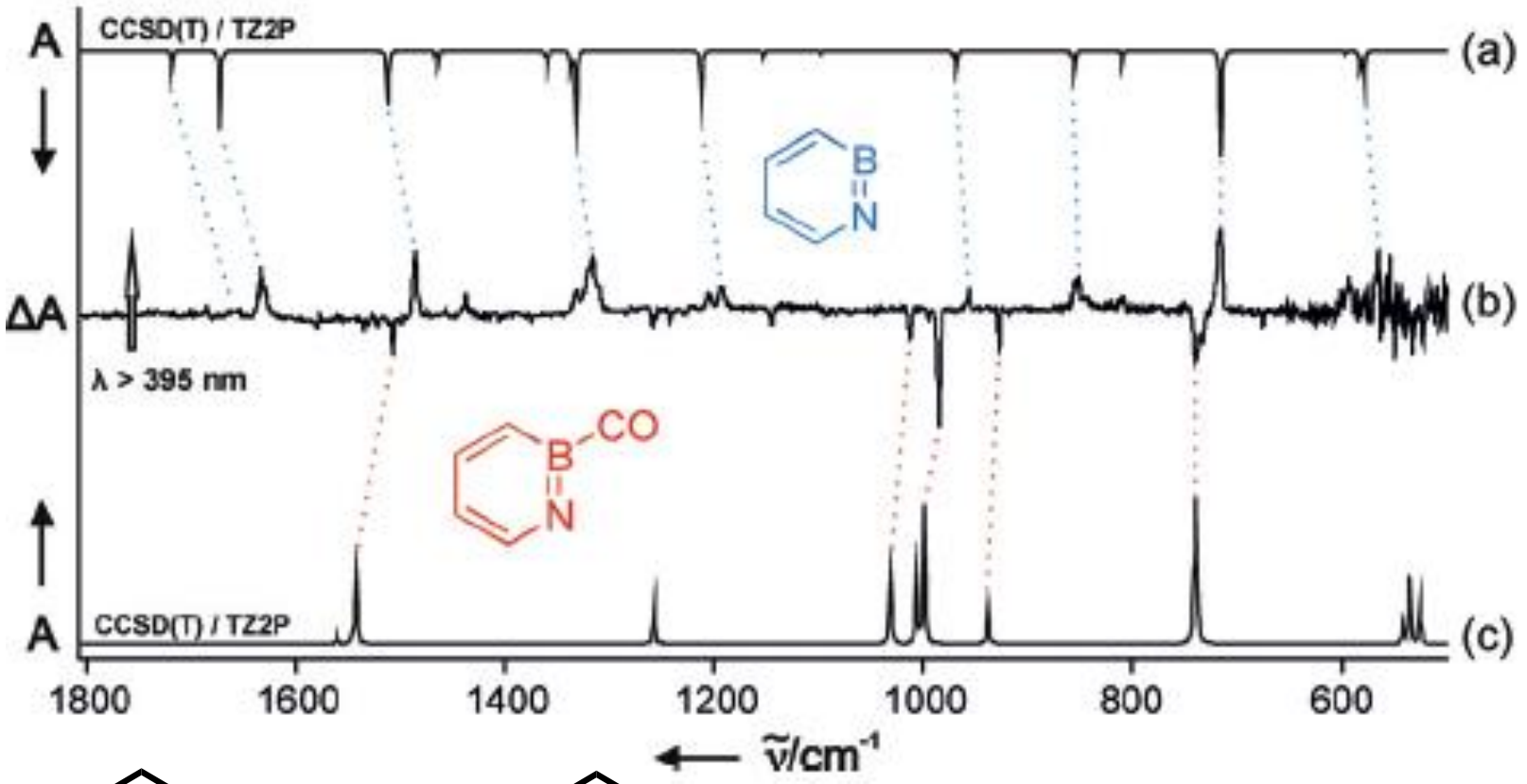
Klara Edel *et al. Angew. Chem. Int. Ed.* 2019, **58**, 4061.

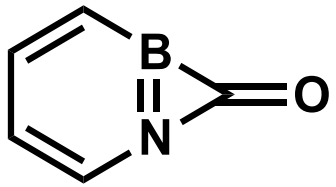
Suggested Binding with CO



Klara Edel *et al.* *Angew. Chem. Int. Ed.* 2019, **58**, 4061.

The Computed Vibrational Spectrum





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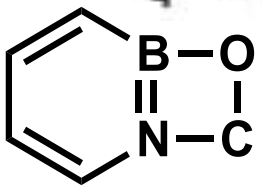

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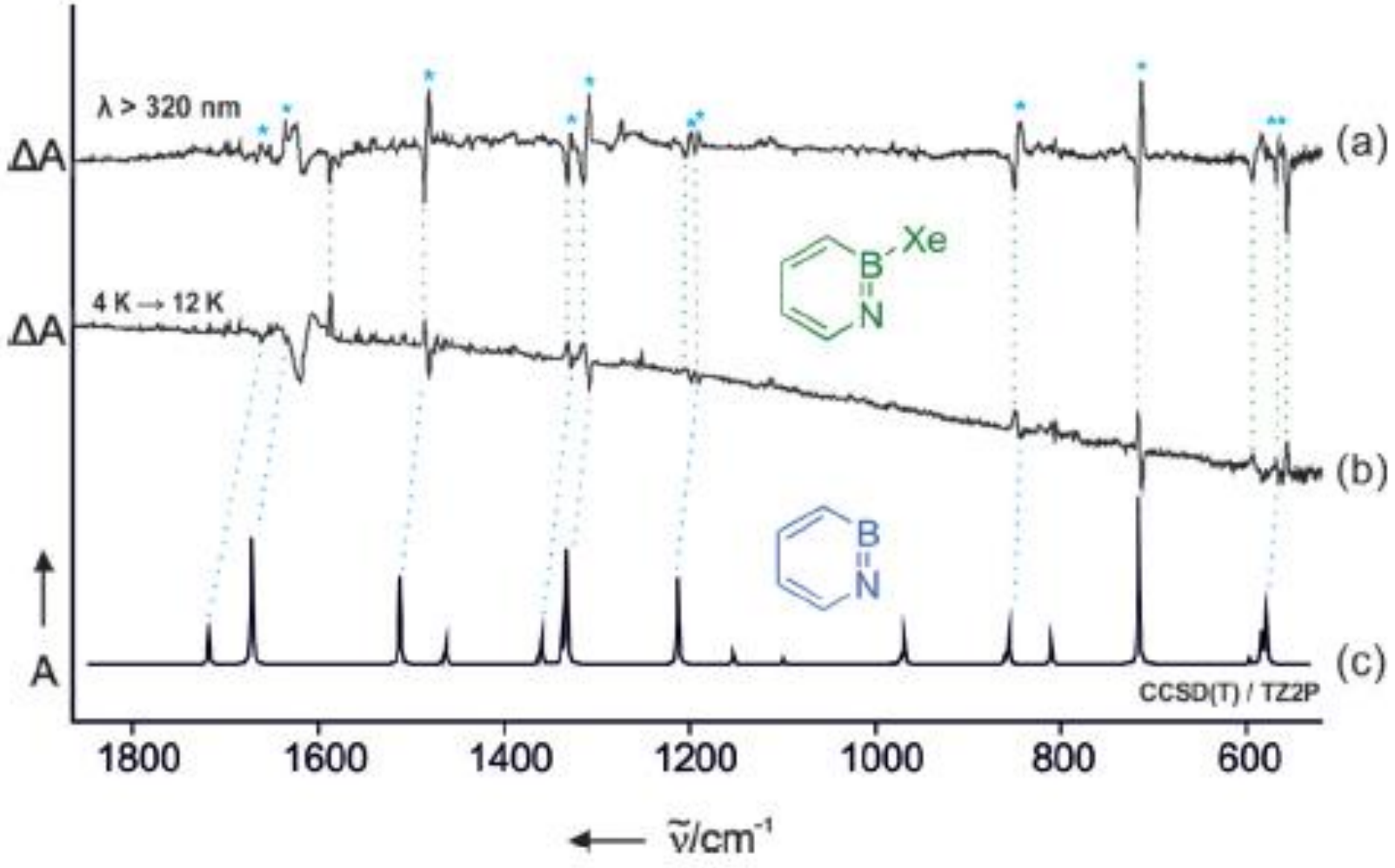
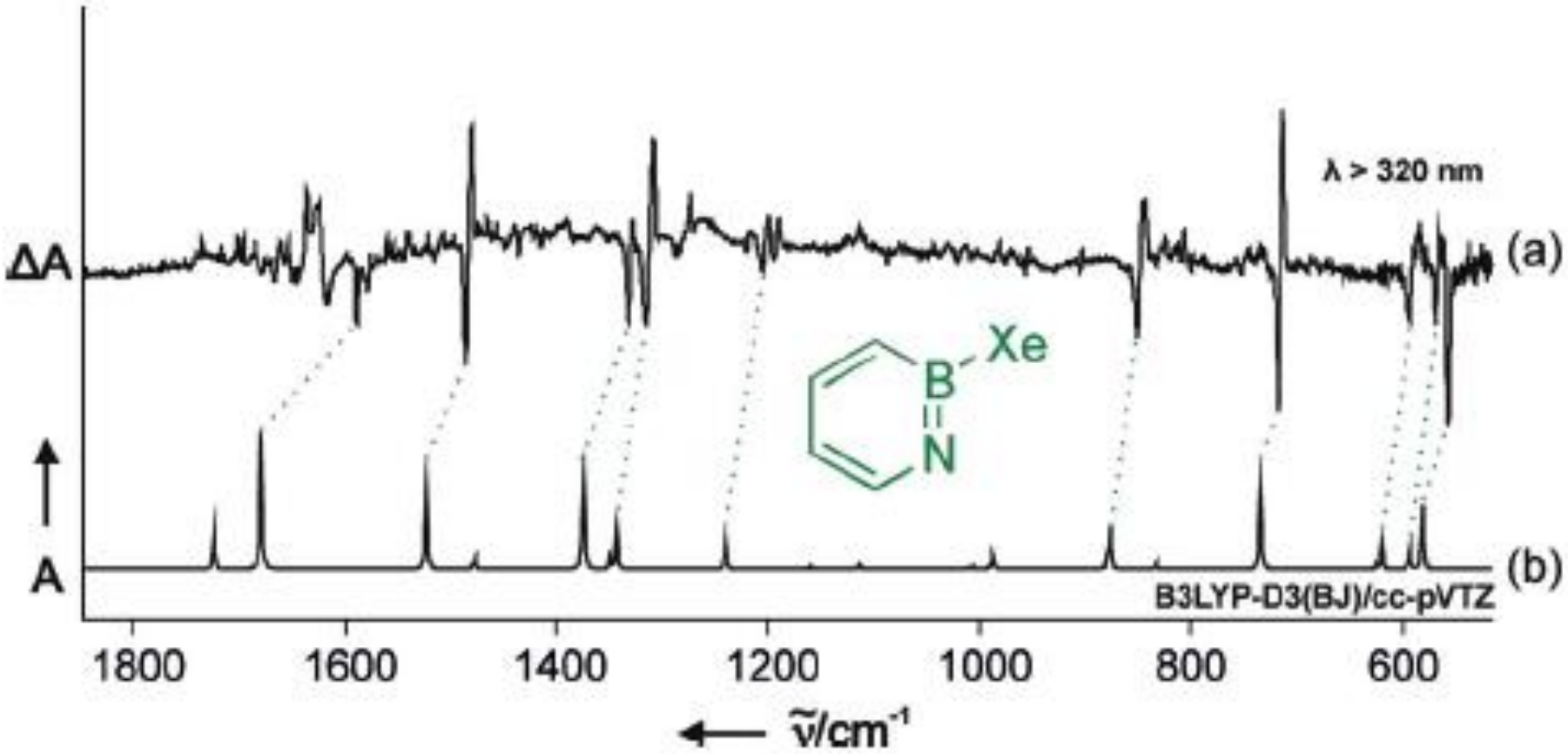
Klara Edel *et al.* *Angew. Chem. Int. Ed.* 2019, **58**, 4061.

Suggested Binding with Xe



Klara Edel *et al.* *Angew. Chem. Int. Ed.* 2019, **58**, 4061.

The Computed Vibrational Spectrum

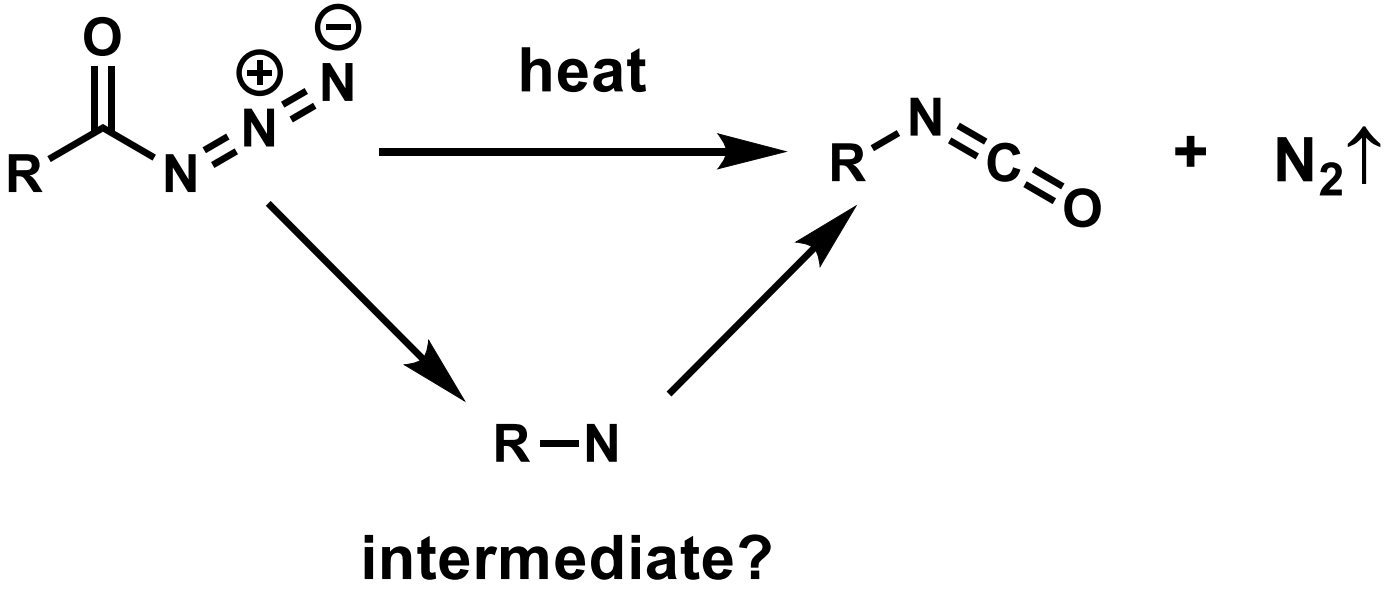


Klara Edel *et al.* *Angew. Chem. Int. Ed.* 2019, **58**, 4061.

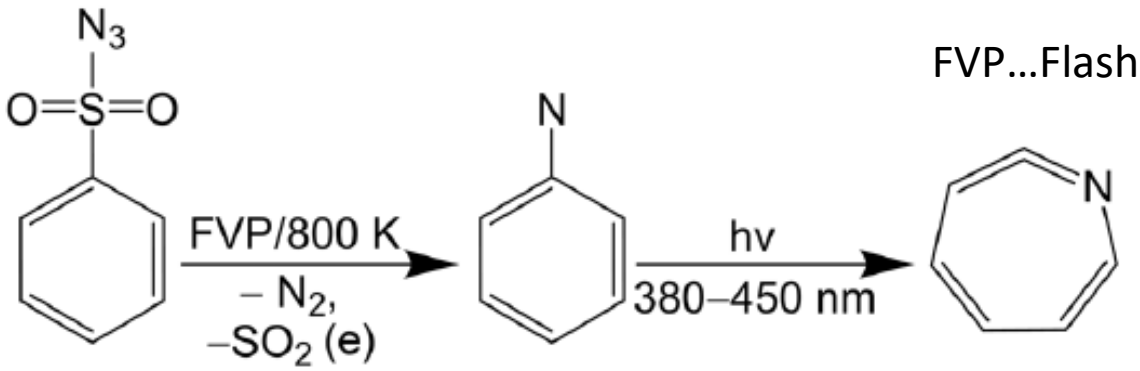
Short Summary

In line with the character of the lowest unoccupied molecular orbital of 1,2-azaborine, which is boron centered and lies in the molecular plane, the boron center preferentially acts as a Lewis acid towards Lewis bases of variable strength (Xe, CO).

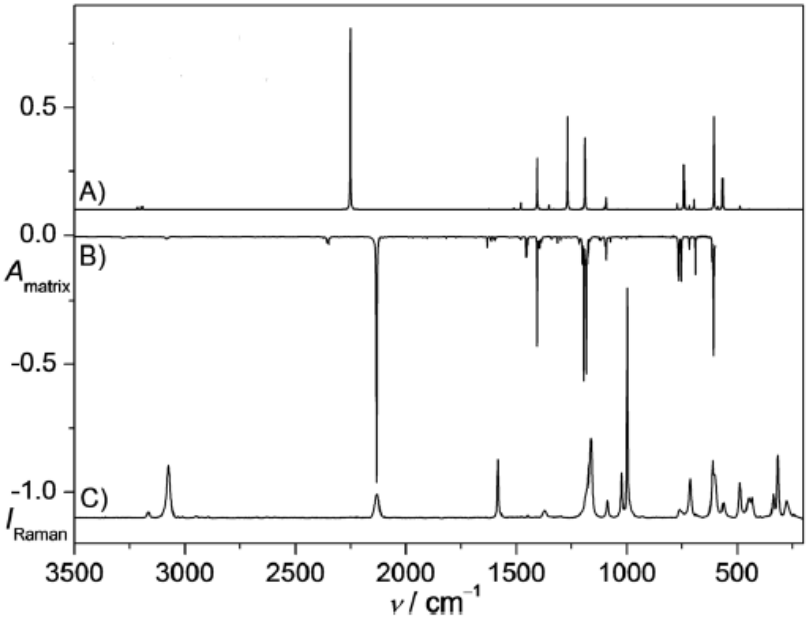
Curtius Rearrangement



Pseudo-Curtius Rearrangement



FVP…Flash Vacuum Pyrolysis



A; Calculated IR spectrum of $PhS(O)_2N_3$ at the B3LYP/6-311++G(3df,3pd) level

B; The observed IR spectrum of $PhS(O)_2N_3$ in the solid Ne matrix at 2.8 K (absorbance A, resolution 0.5 cm^{-1})

C; Raman spectrum of liquid $PhS(O)_2N_3$ at 298 K (Raman intensity I, resolution 2 cm^{-1}).

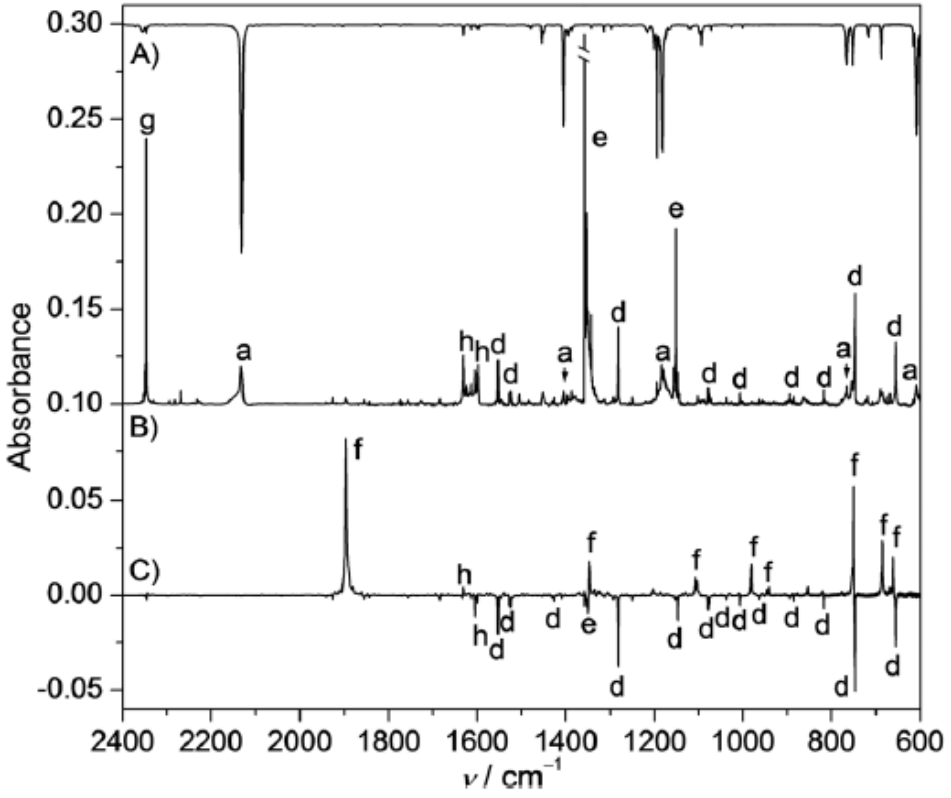
Guohai Deng *et al.* *Phys. Chem. Chem. Phys.* 2017, **19**, 3792.

Analysis of Spectral Data

Observed[b]				Calculated[c]		
IR (Ne matrix)	IR (Ar matrix)	IR (liquid)[e]	Raman (liquid)	B3LYP	M06-2X	Approximate assignment[d]
3281.9 vw	3280.5 vw	3276 w		3215 (5)	3209 (6)	ν(CH)
			3166 w	3214 (<1)	3205 (<1)	ν(CH)
3084.9 vw	3080.6 vw	3069 w	3075 m	3199 (6)	3198 (<1)	ν(CH)
				3190 (7)	3192 (4)	ν(CH)
				3178 (<1)	3181 (<1)	ν(CH)
2131.7 vs	2129.0 vs	2129 s	2131 m	2251 (554)	2348 (515)	$\nu_{as}(N_3)$
1591.8 w	1589.7 w	1584 w	1588 m	1622 (2)	1661 (2)	ν(CC)
				1621 (<1)	1658 (<1)	ρ(CH)
1479.2 w	1478.0 w	1477 w		1511 (4)	1519 (3)	ρ(CH)
1454.9 w	1452.7 w	1450 m	1449 vw	1479 (21)	1488 (29)	ρ(CH)
1405.2 s	1397.2 s	1372 s	1371 w	1404 (152)	1450 (164)	$\nu_{as}(SO_2)$
1341.9 vw	1341.2 vw			1351 (12)	1342 (9)	ρ(CH)
1314.4 vw	1312.5 vw	1313 w		1330 (2)	1326 (<1)	ρ(CH)
1298.6 w	1297.8 w	1298 w		1269 (244)	1279 (267)	$\nu_s(N_3)$
1194.5 s	1194.1 s		1185 w, sh	1204 (4)	1231 (268)	ρ(CH)
1182.3 s	1180.5 s	1170 s	1162 s	1189 (143)	1200 (7)	$\nu_s(SO_2)$
				1188 (<1)	1177 (<1)	ρ(CH)
1118.3 vw	1119.4 vw			1104 (5)	1124 (36)	ρ(CH)
1093.4 w	1091.9 w	1088 m	1087 w	1094 (31)	1110 (5)	ν(SC) + ρ(CH)
1025.5 vw	1024.6 vw	1023 w	1023 m	1041 (1)	1056 (1)	Ring distortion
				1024 (<1)	1038 (<1)	Ring distortion
				1006 (<1)	1016 (<1)	ω(CH)
1002.4 vw	1000.9 vw	1000 w	998 vs	1000 (2)	1005 (1)	Ring breathing
				958 (<1)	967 (<1)	ω(CH)
				865 (<1)	874 (<1)	ω(CH)
765.2 vw	764.0 vw		761 w	773 (15)	803 (121)	ν(SN)
753.4 s	751.4 s	751 m		742 (122)	778 (25)	ν(SC)
716.9 vw	715.1 vw		713 m	717 (11)	735 (44)	δ(CH)
688.1 w	686.5 w	685 m		695 (32)	703 (39)	δ(CH)
			612 m	627 (<1)	635 (183)	δ(CH)
607.9 s	603.9 s	601 s		606 (259)	624 (36)	ν(SN) + $\delta(SO_2)$
		564 s	563 w	586 (8)	623 (7)	$\delta_{o.o.p}(N_3)$
				566 (86)	581 (93)	ν(SN) + $\delta(SO_2)$

Guohai Deng *et al.* *Phys. Chem. Chem. Phys.* 2017, **19**, 3792.

Pyrolysis of Arylsulfonylazides



A; IR spectrum of $PhS(O)_2N_3$ in the solid Ne matrix at 2.8 K.

B; IR spectrum of the flash vacuum pyrolysis of $PhS(O)_2N_3$ in the solid Ne matrix at 2.8 K.

C; IR difference spectrum showing the change of the matrix containing flash vacuum pyrolysis products of $PhS(O)_2N_3$ upon visible light (λ = 380–450 nm, 20 W, 5 min) irradiation.

d; PhN
e; SO_2

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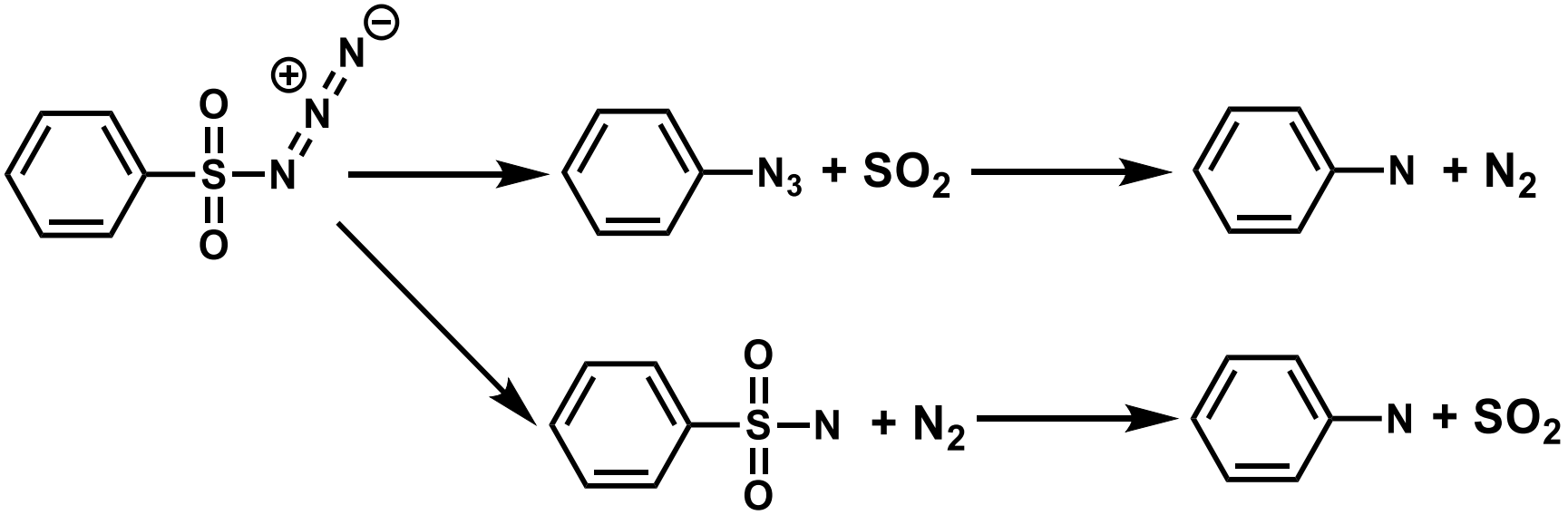
Consideration of Reaction Pathway



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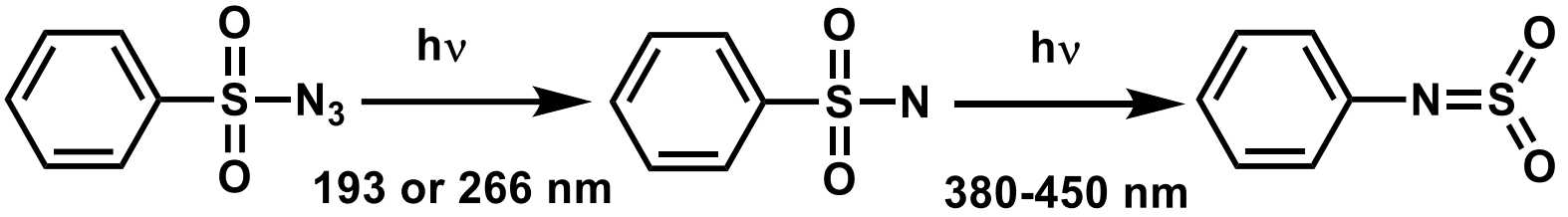
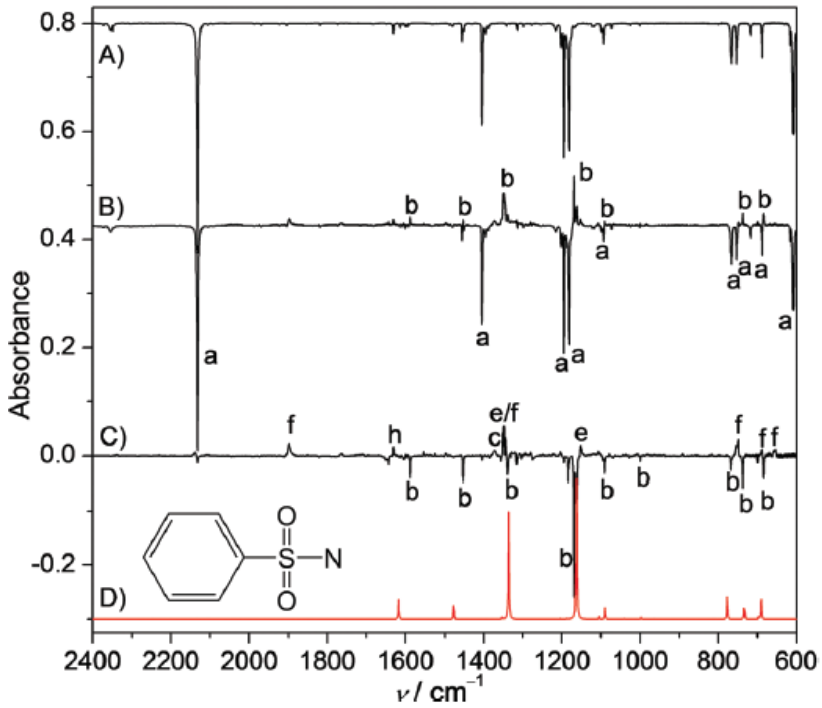
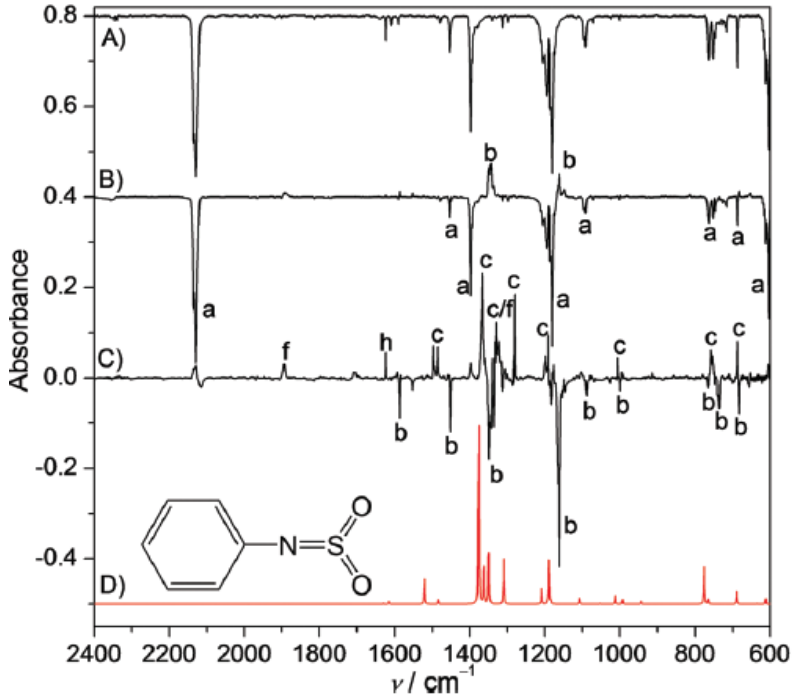
Photolysis of Arylsulfonylazides







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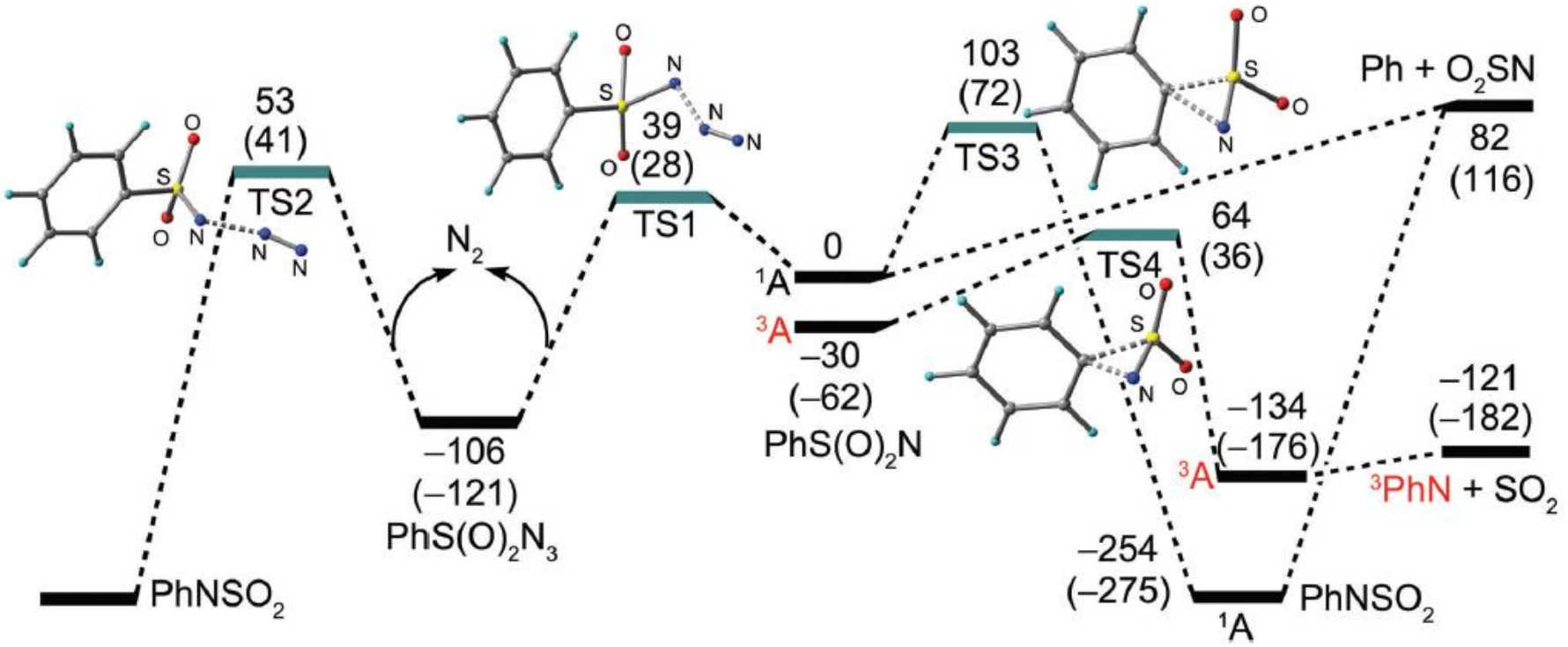
Quantum Chemical Calculation



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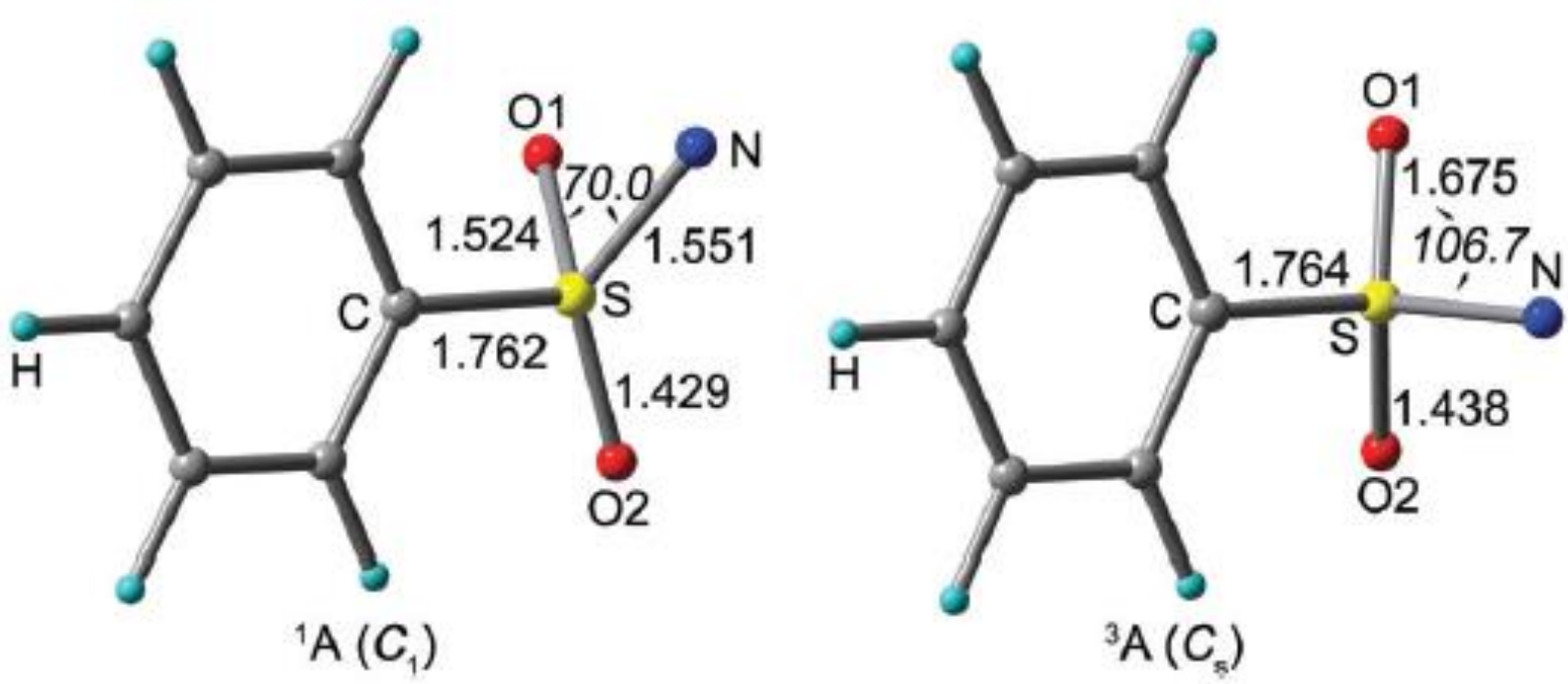
Structure of Nitrene Intermediates



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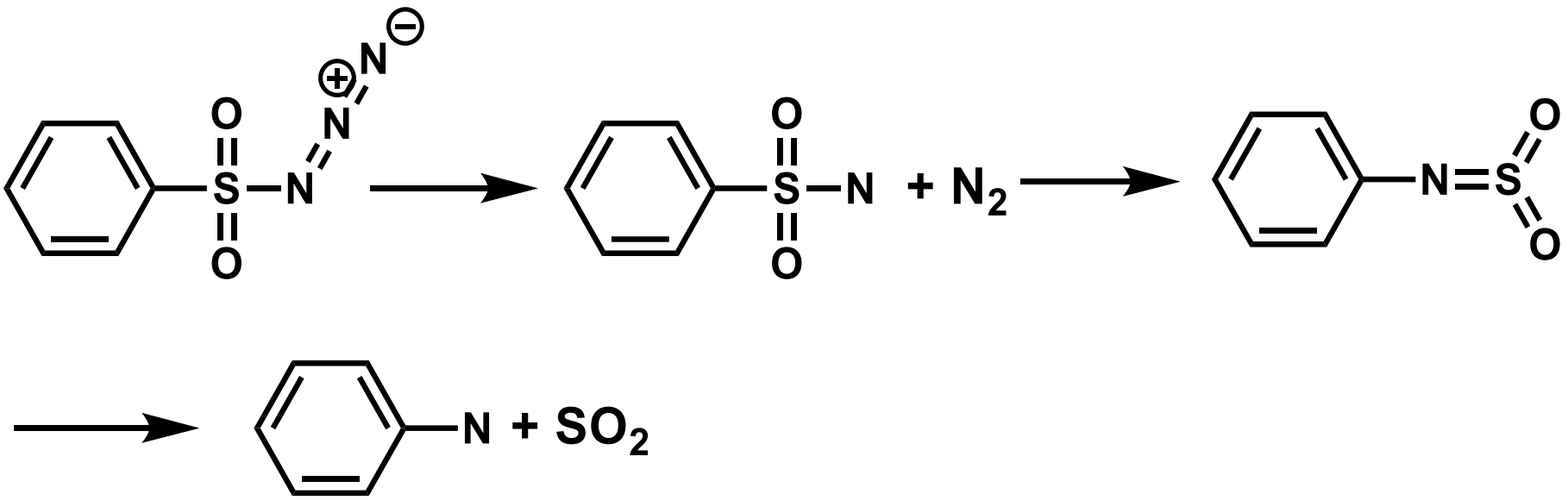
Short Summary



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Summary

・One of the method of observation unstable materials

・There are a lot of conditions that go into the choice of the matrix.

・Matrix isolation method can also be applied to reaction kinetics analysis.

・In combination with quantum chemical calculation, the detailed reaction pathways can be revealed.