Reactions of Atomic Hydrogen with Isotopes of Nitric Oxide in Solid Parahydrogen

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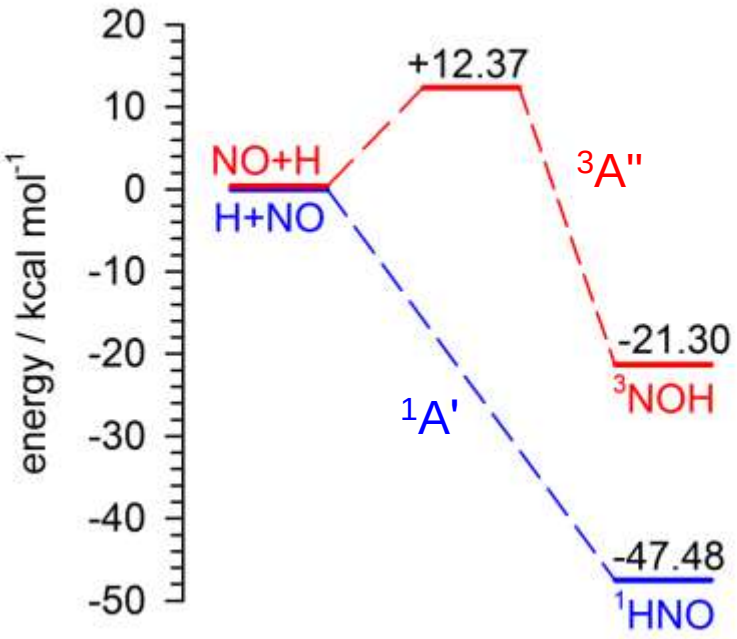
Outline

- The H+NO → HNO/NOH reaction
- Does NO rotate in a hydrogen crystal?
- IR spectroscopic studies of ^{14}NO and ^{15}NO

Reaction of H atoms with NO



RT @ 300 K ≈ 0.6 kcal mol^{-1}

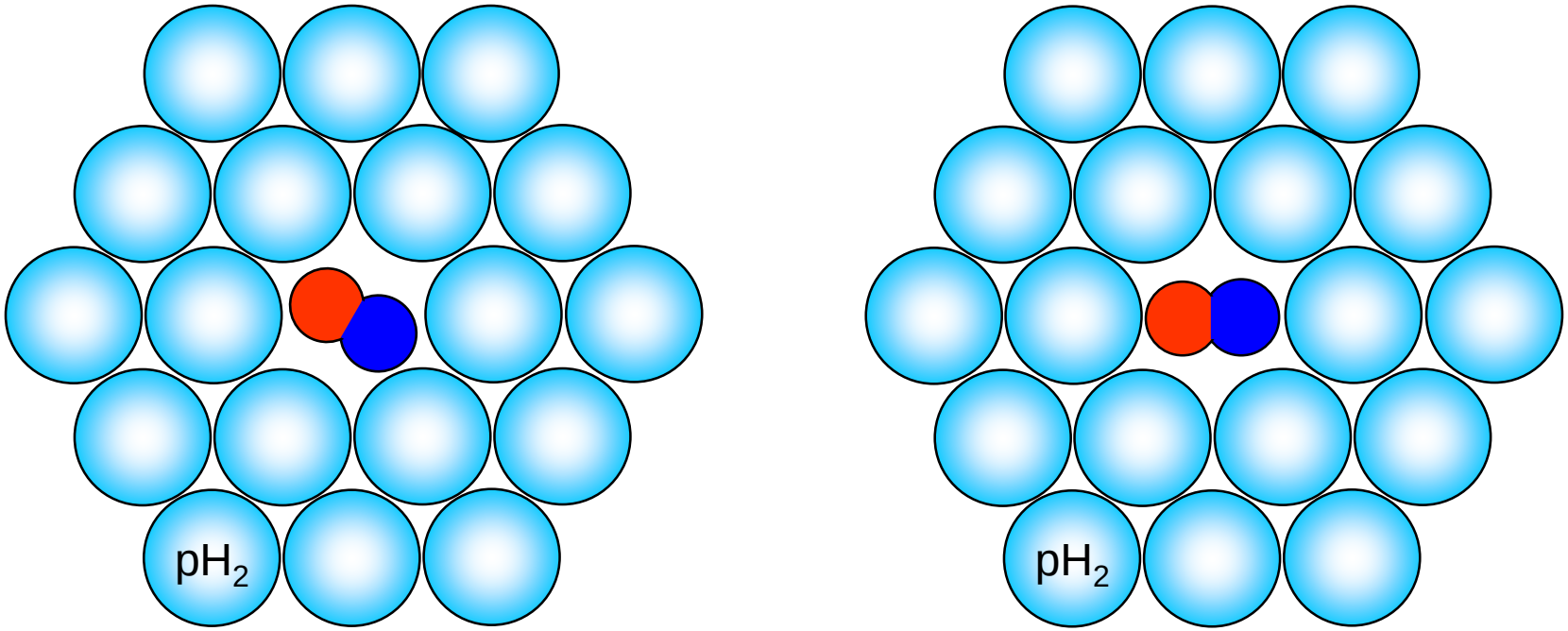
RT @ 4 K ≈ 0.008 kcal mol^{-1}

H+NO → HNO

H+ON → HON

U. Bozkaya et. al., *J. Chem. Phys.* **136**, 164303 (2012).

Does NO rotate in solid para-H_2?



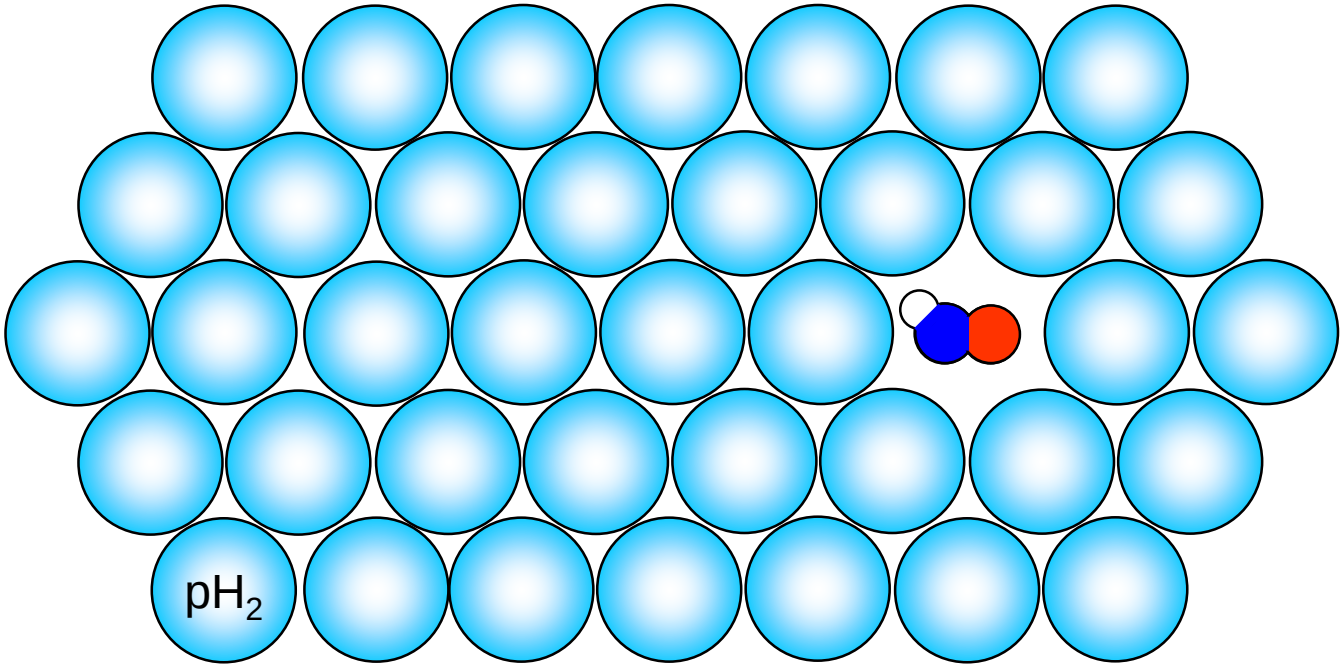
rotational period

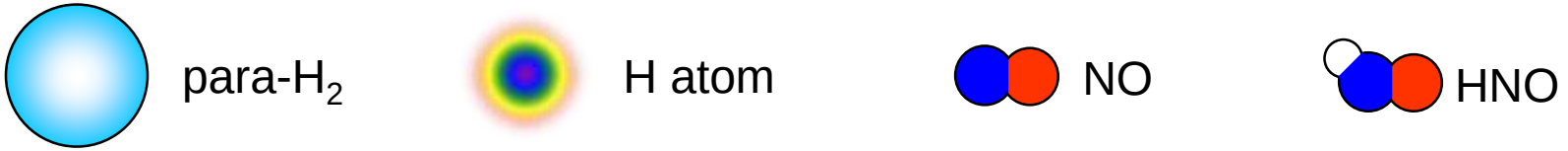
$$t_0 = \frac{h}{2B_0}$$

t_0 = 9.8 ps

1 ps = 1x10^{-12} s

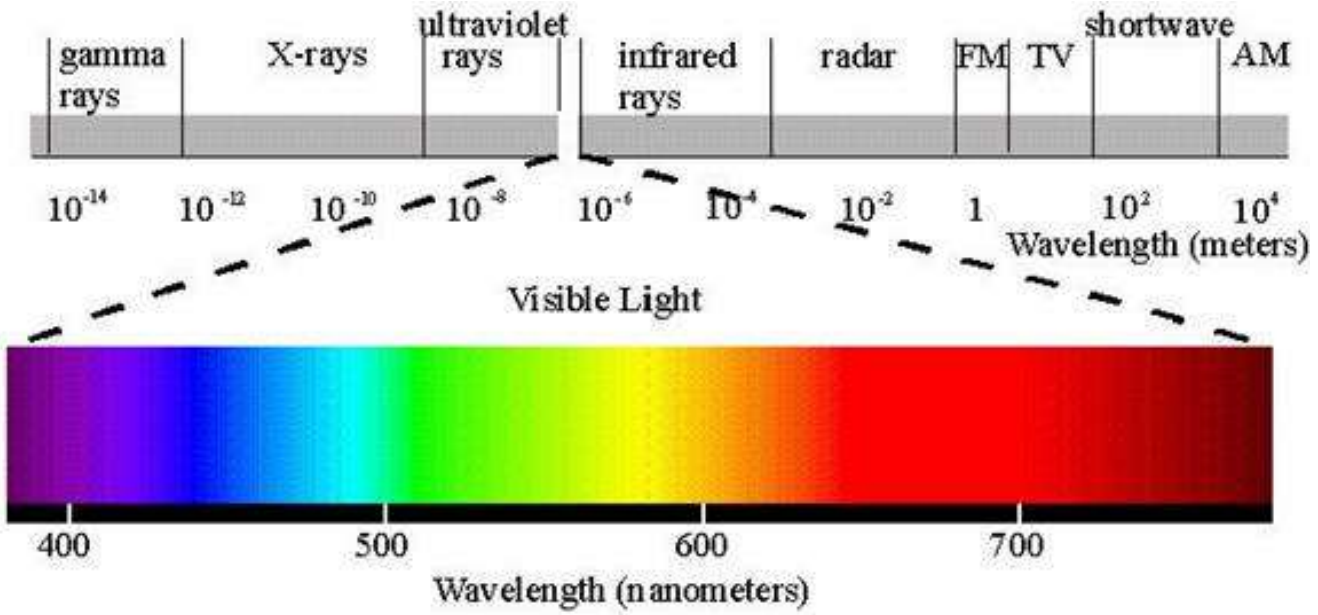
Expected reaction sequence





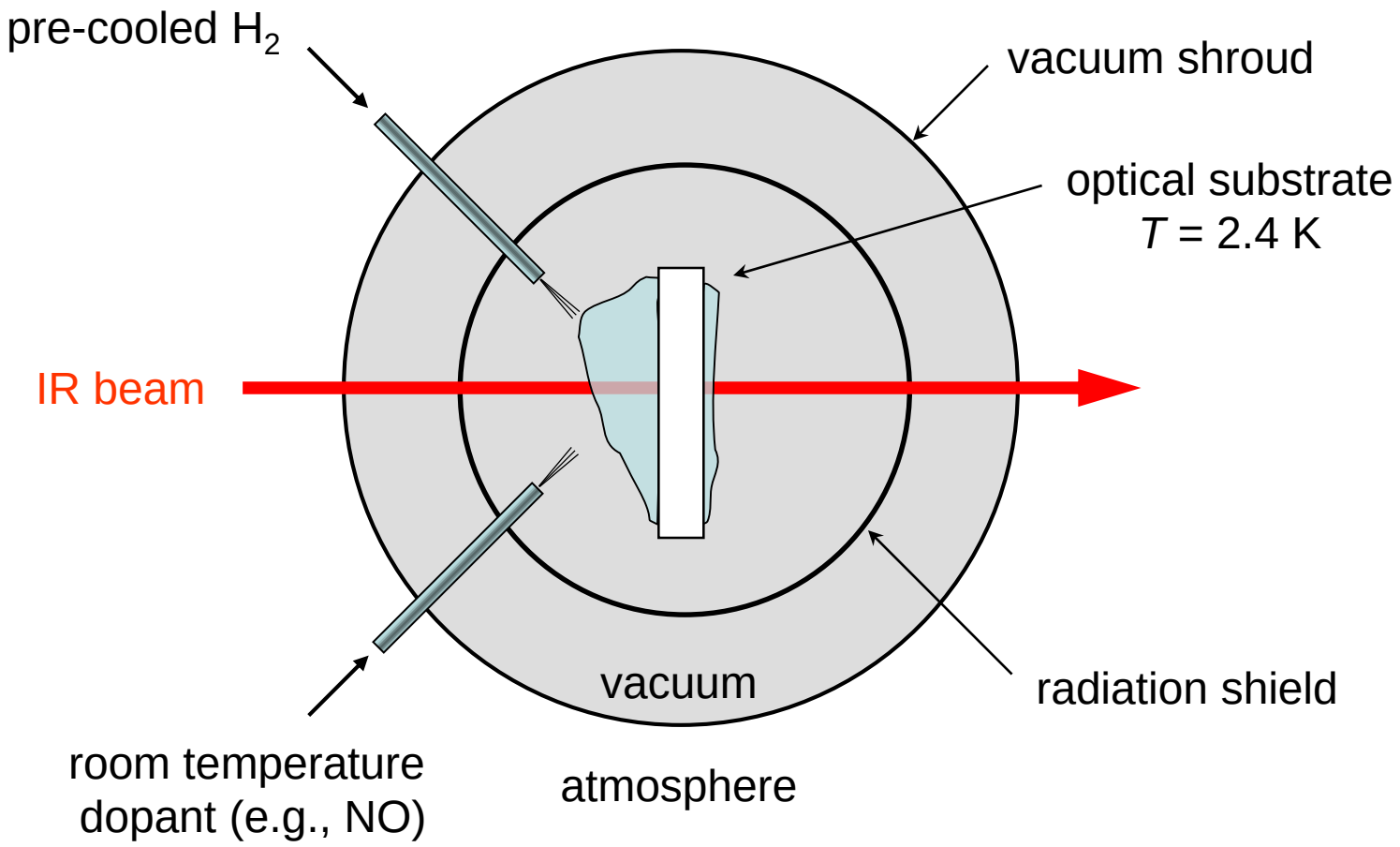
Fourier Transform Infrared (FTIR) Spectroscopy Background

- IR radiation excites vibrational and rotational states
- Detector receives signal from excited molecules



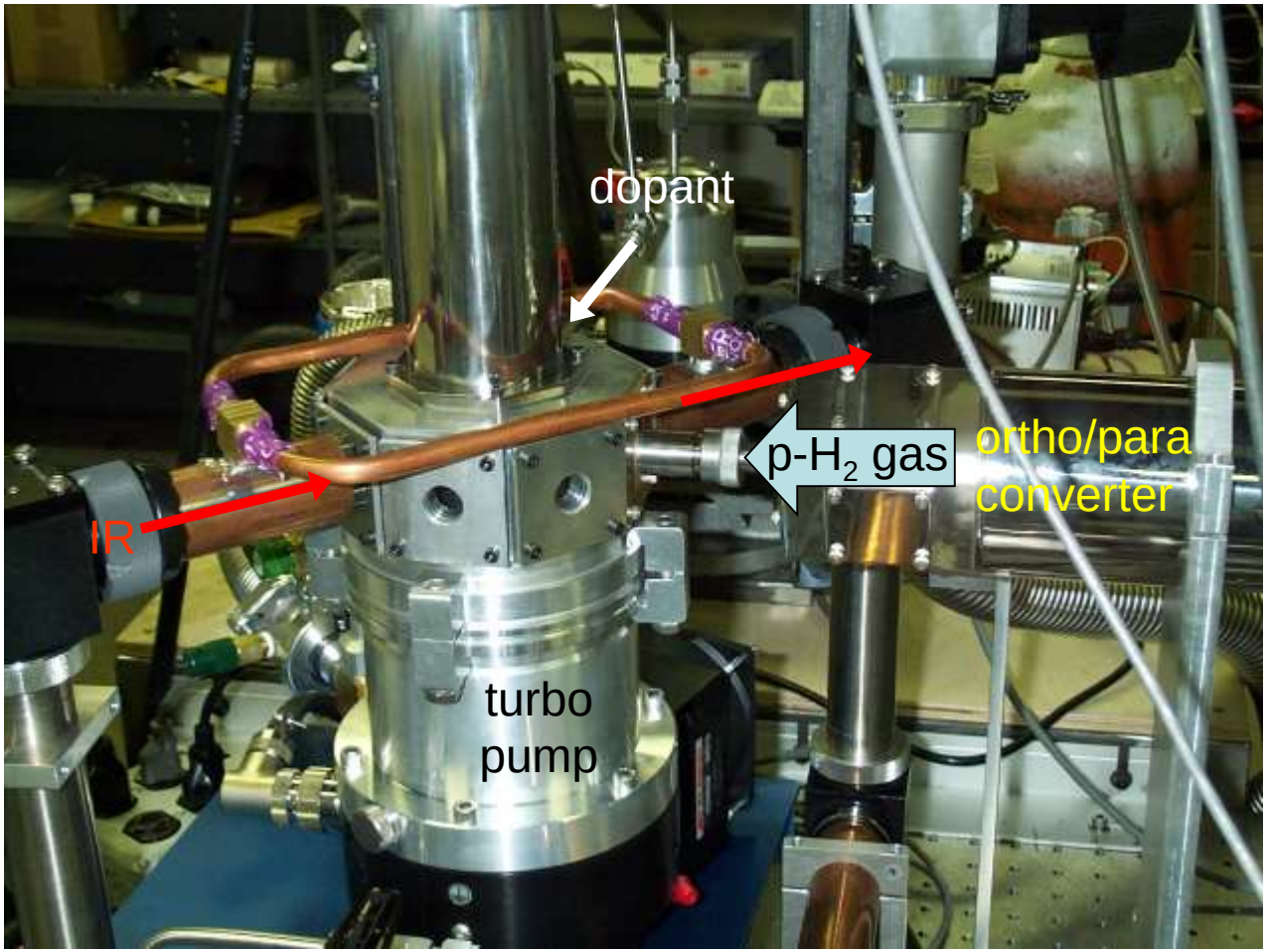
http://www.beercolor.com/color_basics1_files/image002.jpg

Rapid vapor deposition*



*Simon Tam and Mario E. Fajardo, *Rev. Sci. Instrumen.* **70**, 1926 (1999).

Experimental set-up



Specifications

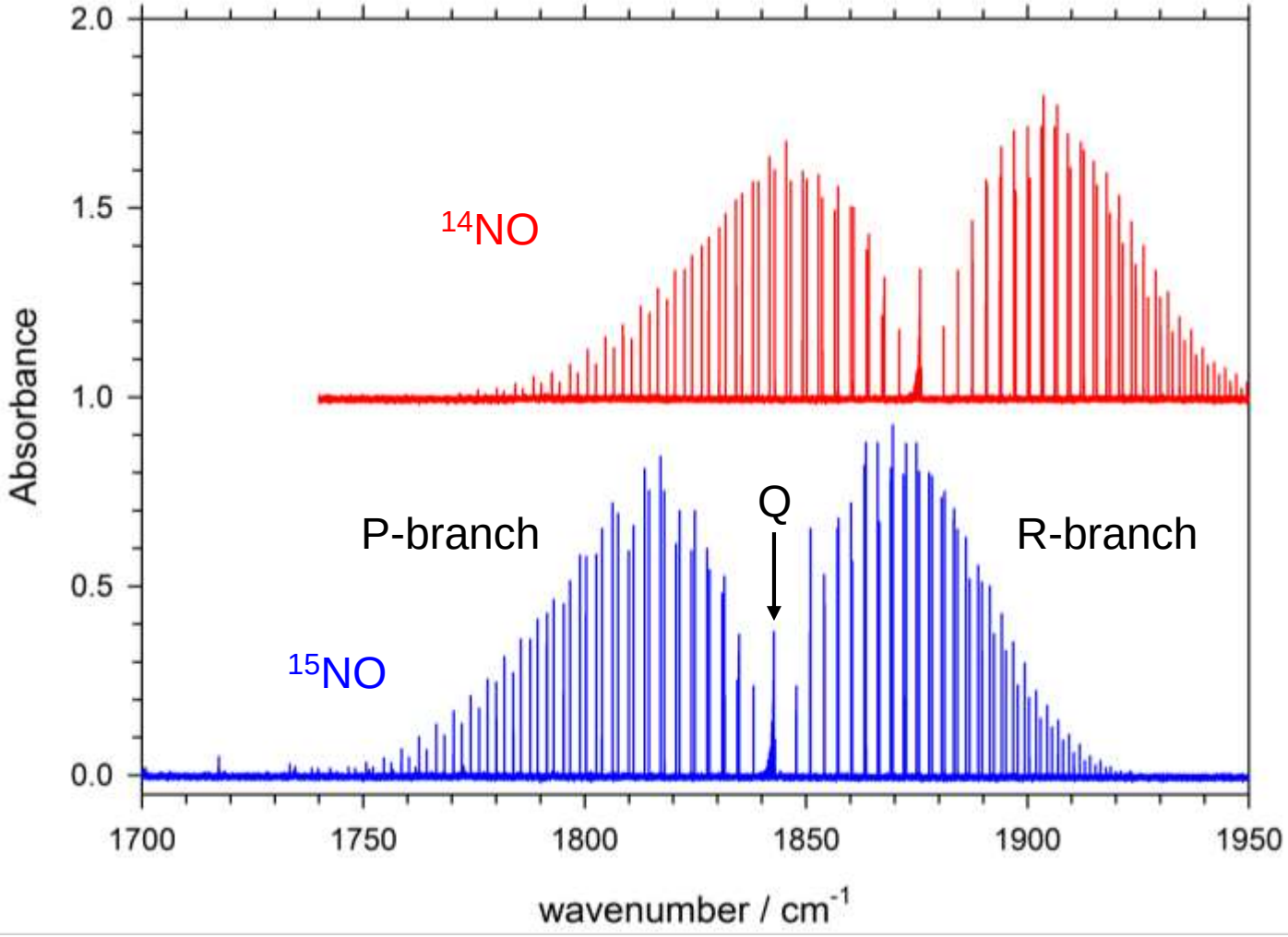
sample-in-a-vacuum liquid helium cryostat (1.7 – 4.5 K)

variable temperature ortho/para converter (10 - 80 K)

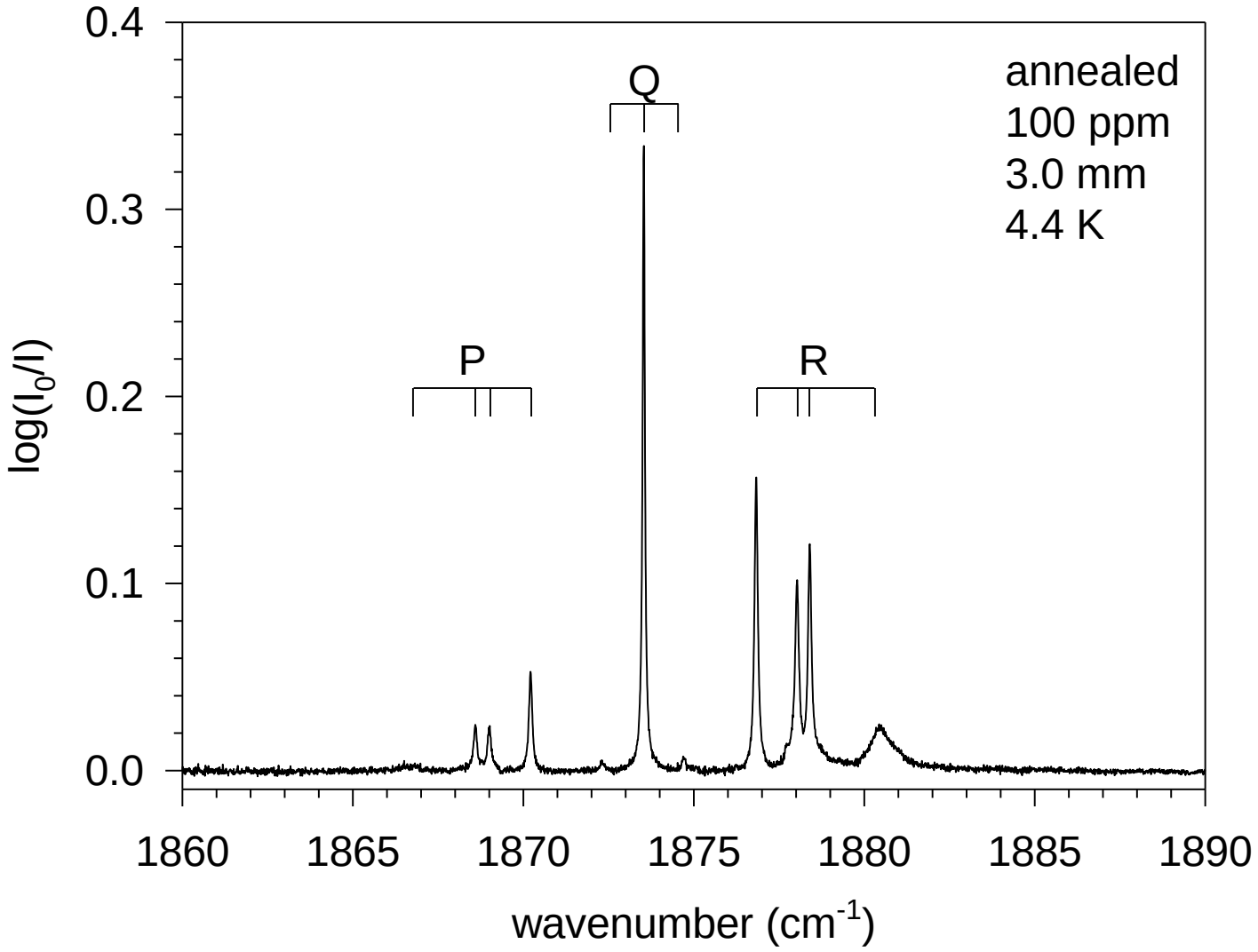
180 L/s turbo pump (<10^{-4} torr during deposition)

IR diagnostics – Bruker IFS120 (0.006 cm^{-1})

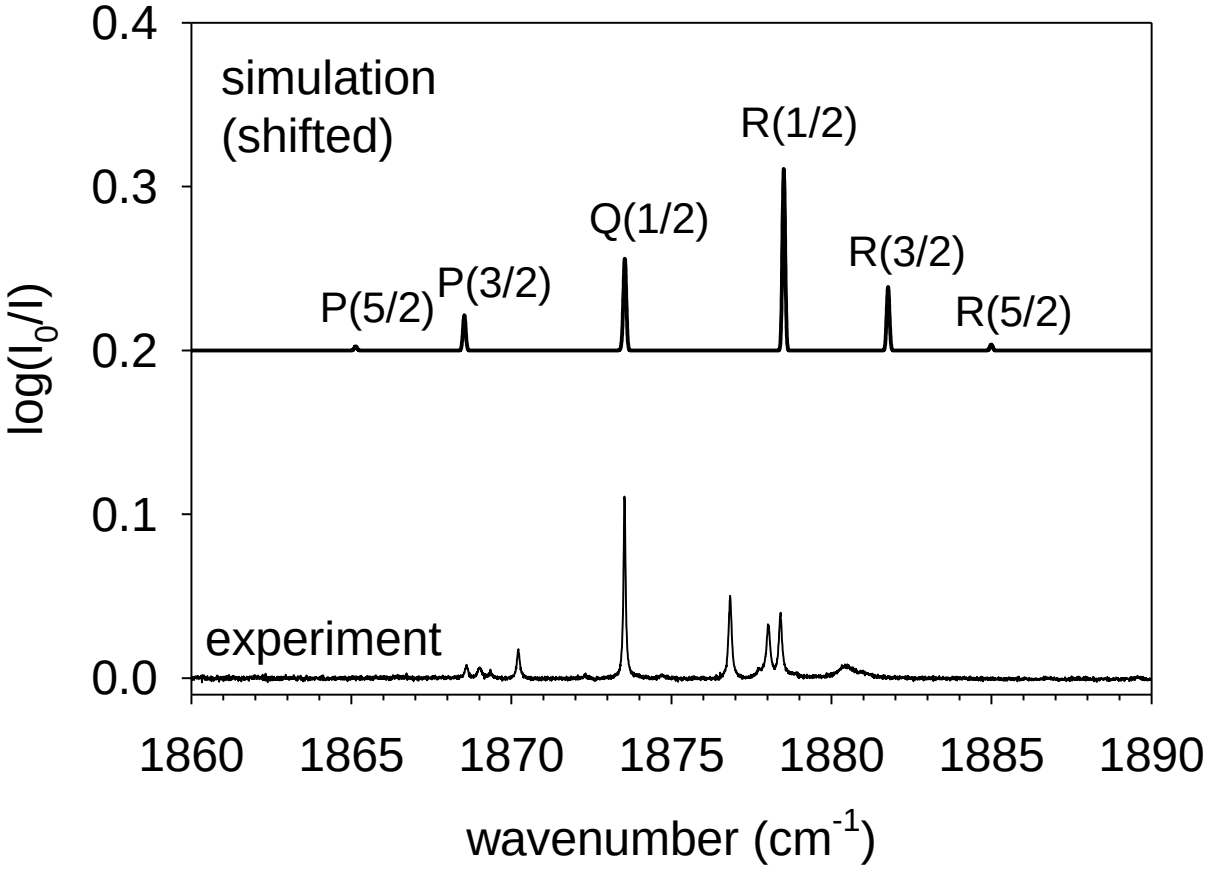
Room temperature gas-phase IR spectra of ^{14}NO and ^{15}NO



Fundamental band of ^{14}NO in solid pH_2



NO rotates in solid pH_2



matrix shift -2.54 cm^{-1}

$B_{NO} \approx 1.37\ cm^{-1}$ (~80%)

significant splitting of J=3/2 rotational state

no observed λ-doublets

Raw Data

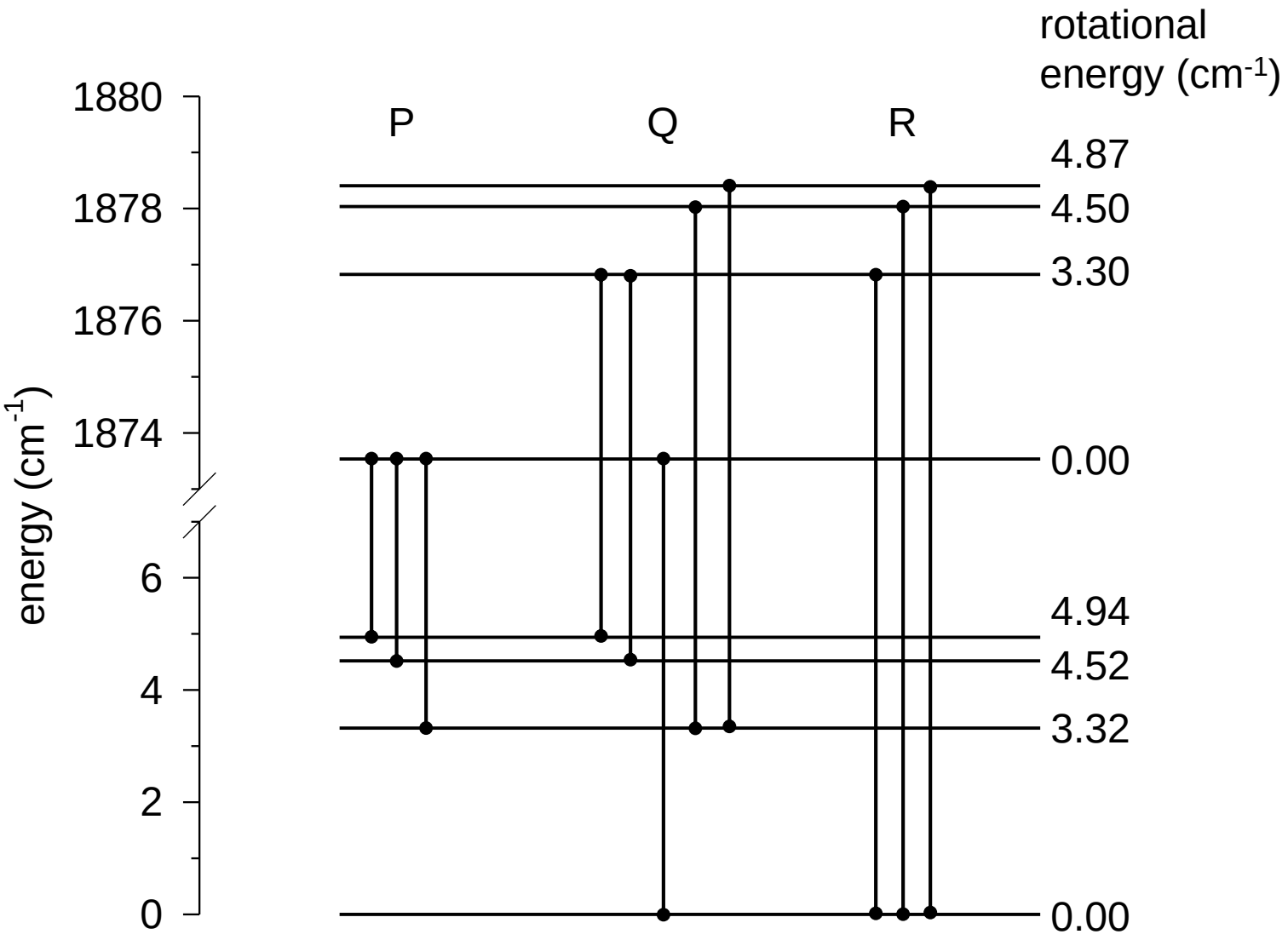
MEB01083MCT	MCT.0004	MCT.0003	MCT.0002	MCT.0001	MCT.0000	AVG	STD	DIFF
P(1.5)	1835.7508	1835.746	1835.7458	1835.7467	1835.7431	1835.74648	0.002776	-4.77422
P(1.5)	1836.0955	1836.0973	1836.1013	1836.1036	1836.1013	1836.0998	0.003305	-4.4209
P(1.5)	1837.2643	1837.2631	1837.2664	1837.2634	1837.261	1837.26364	0.00196	-3.25706
Q(1.5)	1839.3306	1839.3355	1839.334	1839.3355	1839.3154	1839.3302	0.008512	-1.1905
Q(0.5)	1840.5207	1840.5207	1840.5207	1840.5207	1840.5207	1840.5207	2.54E-13	0
Q(1.5)	1841.6456	1841.6623	1841.6456	1841.6459	1841.6745	1841.65478	0.013161	1.13408
R(0.5)	1843.7586	1843.7593	1843.7585	1843.7601	1843.7587	1843.75904	0.000669	3.23834
R(0.5)	1844.9089	1844.9075	1844.9117	1844.9093	1844.9132	1844.90935	0.001746	4.38865
R(0.5)	1845.2266	1845.2252	1845.2242	1845.2237	1845.2219	1845.22432	0.001748	4.70362
R(1.5)	1847.3025	1847.2109	1847.2683	1847.196	1847.2703	1847.2496	0.044574	6.7289

Data Analysis

^{15}NO Data				
$^{15}B_{V=0}$	State	AVG	STD	DIFF
1.6361951	P(1.5)	1835.7195	0.059021	-4.8048
$^{15}B_{V=1}$	P(1.5)	1836.1186	0.040584	-4.4057
1.6195494	P(1.5)	1837.2575	0.005131	-3.2668
	Q(1.5)	1839.3334	0.004469	-1.1909
	Q(0.5)	1840.5243	0.00574	0.0000
	Q(1.5)	1841.6546	0.000283	1.1303
	R(0.5)	1843.7637	0.009232	3.2394
	R(0.5)	1844.8950	0.021137	4.3707
	R(0.5)	1845.2305	0.011235	4.7062
	R(1.5)	1847.2198	0.017068	6.6955

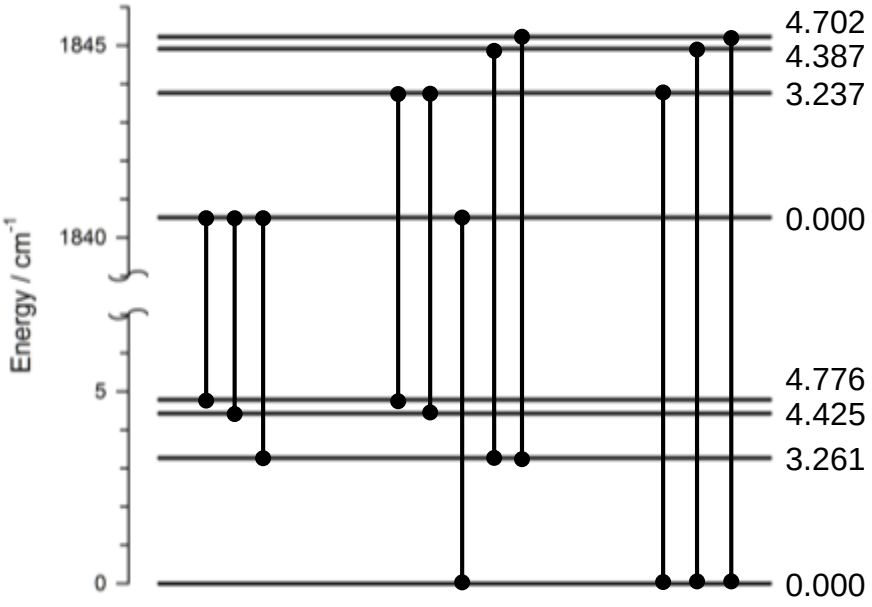
State	^{15}DIFF/B	^{14}DIFF/B	Difference
P(1.5)	-2.936583	-2.91011	-0.0264732
P(1.5)	-2.692652	-2.66909	-0.0235629
P(1.5)	-1.996604	-1.95647	-0.0401304
R(0.5)	2.000173	1.966383	0.0337908
R(0.5)	2.698714	2.668159	0.0305549
R(0.5)	2.905847	2.902852	0.0029949

^{15}NO Energy level diagram

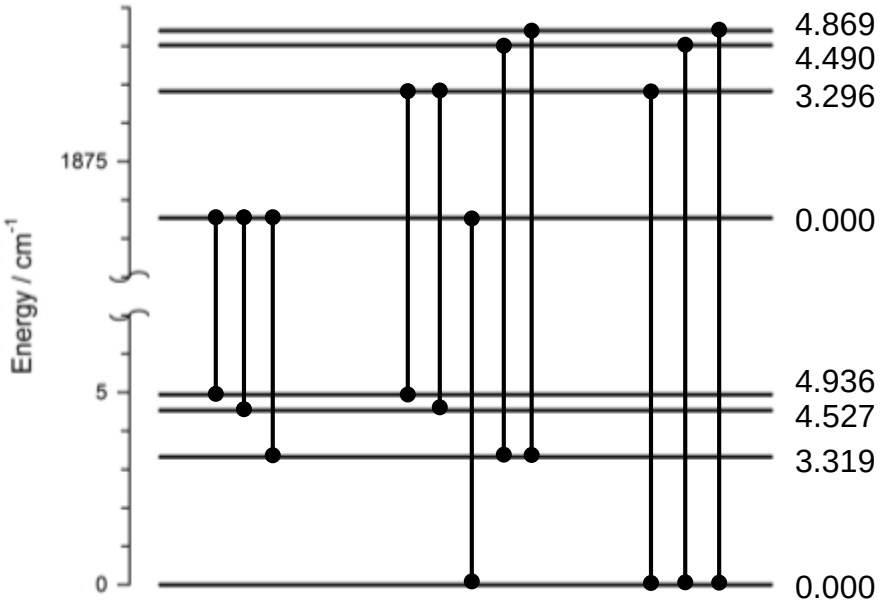


Rotational fine structure consistent with B

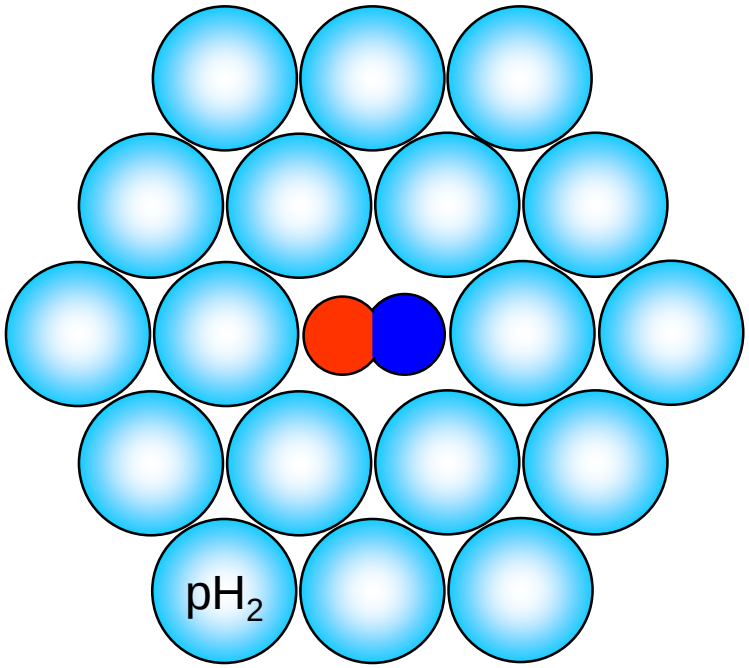
^{15}NO



^{14}NO



NO rotates in solid para-H_2!



NO $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$
A =123 cm^{-1}, B =1.6962 cm^{-1}
ν_0 = 1875.98918 cm^{-1}

Hexagonal closest packed (hcp)
Nearest neighbor = 3.783 Å
Mean displacement = 20% nn

Only barrierless along one specific approach angle!

no barrier

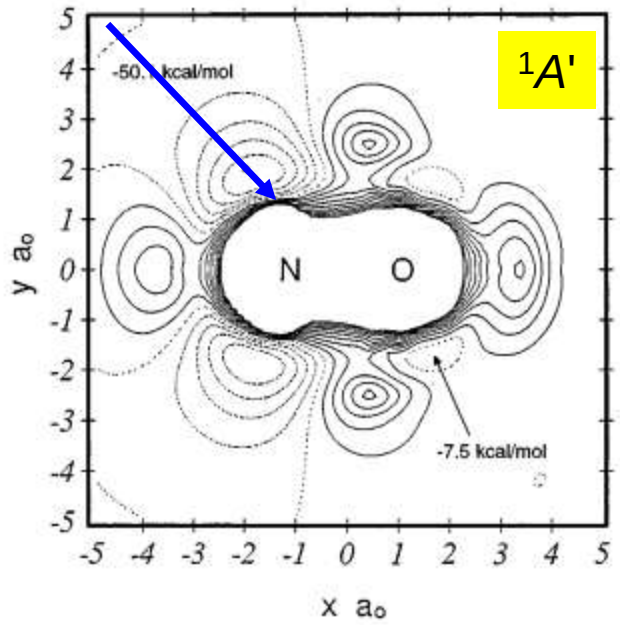


TABLE III. Energies and geometries of saddle points.

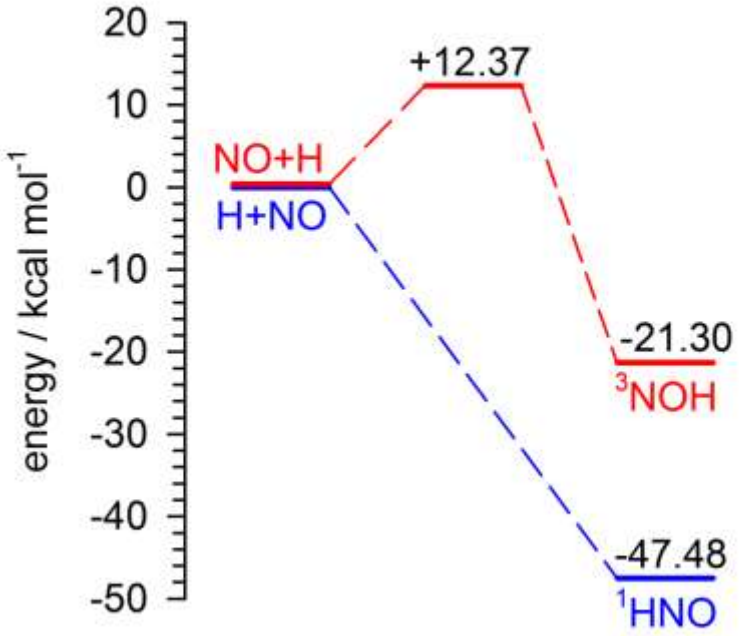
Saddle Point	Surface	Energy[a]		Geometry (present)		
		Present	Previous	NO	NH	OH
H···NO	$^1A'$	0				
	$^3A''$	>4.6	4.1[c]	2.20	3.31	4.73
	$^1A''$	11.1	10.2[c]	2.23	3.01	4.29
H···ON	$^1A'$	3.9	6.7[b]	2.23	4.12	2.53
	$^3A''$	13.5	13.0[b]	2.26	4.33	2.93
	$^1A''$	25.6		2.32	4.25	2.55
Isomerization	$^1A'$	22.4	25.7[b]	2.53	2.41	2.06
	$^3A''$	8.7	14.9[b]	2.54	2.33	2.18
	$^1A''$	33.0		2.54	2.39	2.18

[a]Energies are in kcal/mol relative to H+NO, distances are in a_0.
[b]SOCI results from Ref. 7. Note that we have assumed that the transition state labeled N–OH in Ref. 7 means H···ON.
[c]Reference 8.

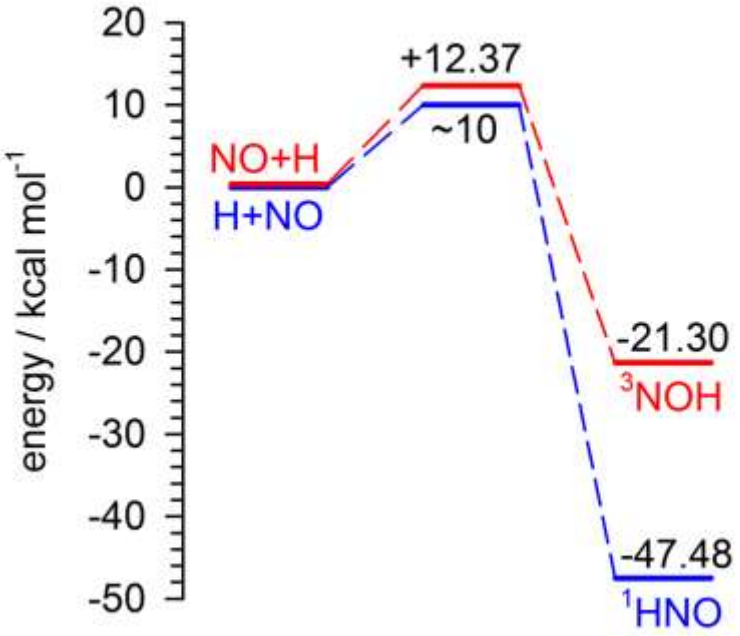
R. Guadagnini, G.C. Schatz, S.P. Walch, *J.Chem.Phys.* **102**, 774 - 783 (1995).

Reaction of H atoms with NO

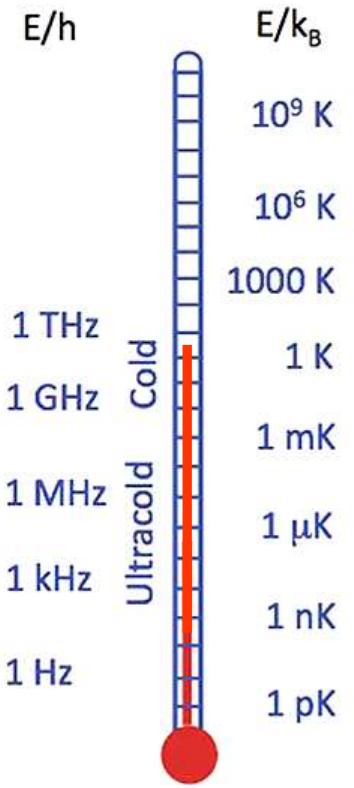
Non-rotating NO

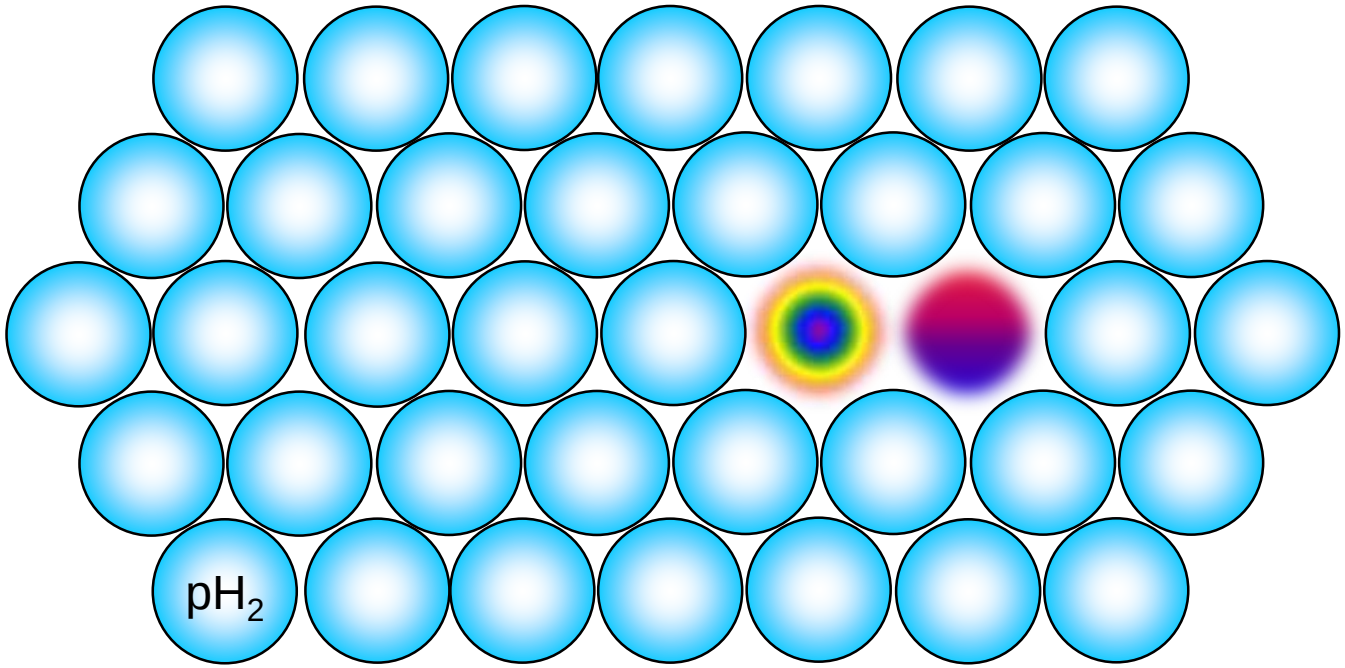


Rotating NO

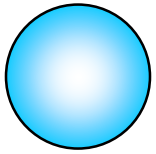


Cold chemistry in a hydrogen crystal

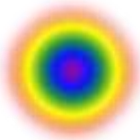




T=4.3 K



para-H_2



H atom

Rotating-NO (J=0.5)

Summary

- Spectral analysis shows NO peaks are reproducible to within ±0.005 cm^{-1}

- ^{15}NO and ^{14}NO rovibrational spectrum in solid pH_2 indicates nearly free rotation

- Well defined NO rotational state influences reactivity and branching ratio

- Need to do more studies with $^{15}N^{18}O$

Acknowledgements

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UNIVERSITY OF WYOMING

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