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Steacie Institute for Molecular Sciences

The $\tilde{B}\,{}^1A_1$ electronic state of SiH_2

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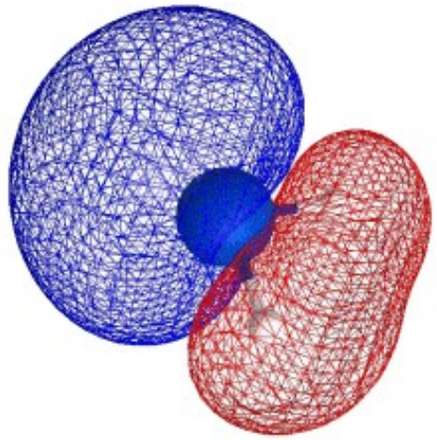
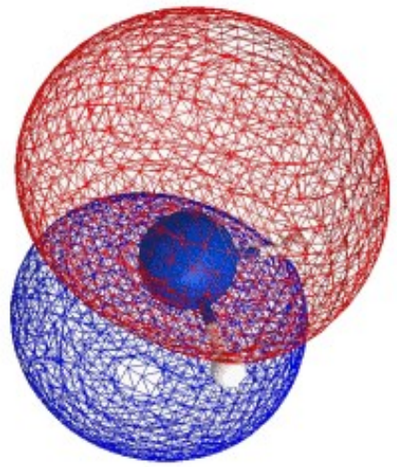
- The four first states of SiH_2 are :

$$\widetilde{X}:^1 A_1 \approx [\text{core}](4a_1)^2(2b_2)^2(5a_1)^2$$
$$\widetilde{B}:^1 A_1 \approx [\text{core}](4a_1)^2(2b_2)^2(2b_1)^2$$
$$\{\tilde{a},\widetilde{A}\}:^{1,3} B_1 \approx [\text{core}](4a_1)^2(2b_2)^2(5a_1)(2b_1)$$

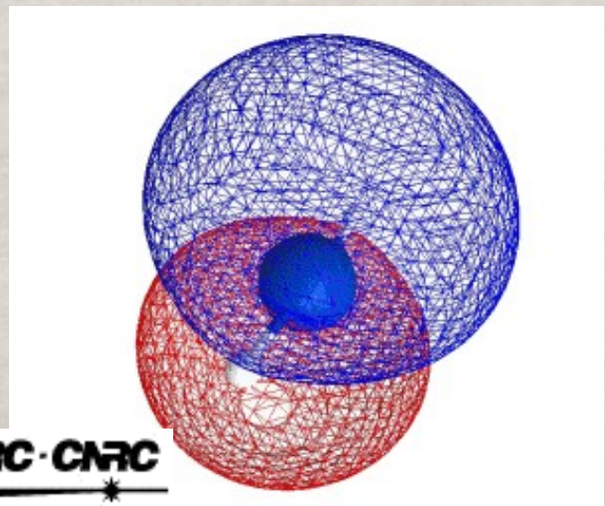
$$[\text{core}] = (1a_1)^2(2a_1)^2(1b_1)^2(1b_2)^2(3a_1)^2$$

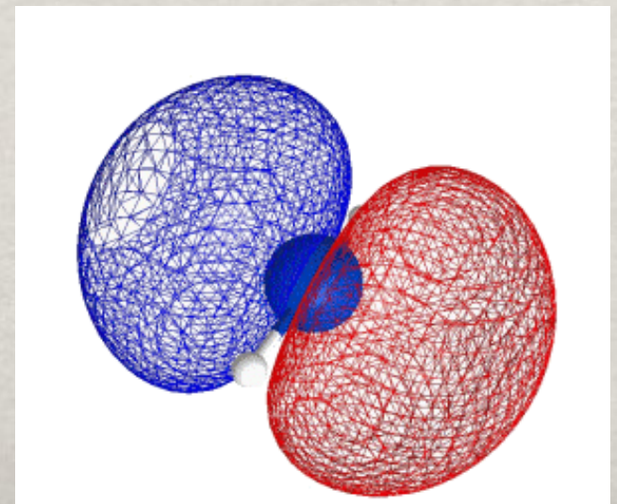


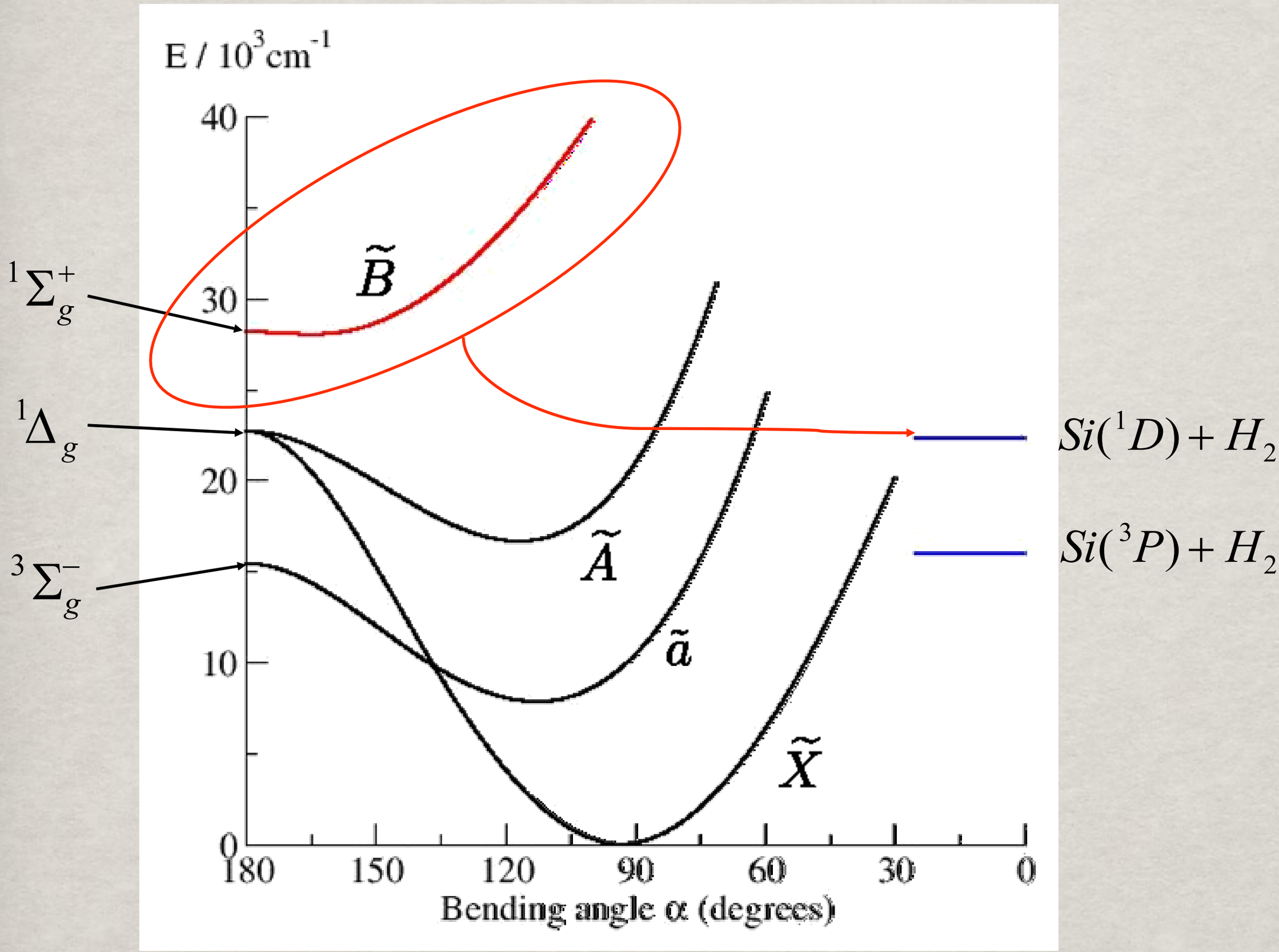


$5a_1$ linearity

$2b_1$ → π_u ; $\{\widetilde{X},\tilde{a},\widetilde{A},\widetilde{B}\}$ → $(\pi_u)^2 : {}^3\Sigma_g^-, {}^1\Delta_g, {}^1\Sigma_g^+$

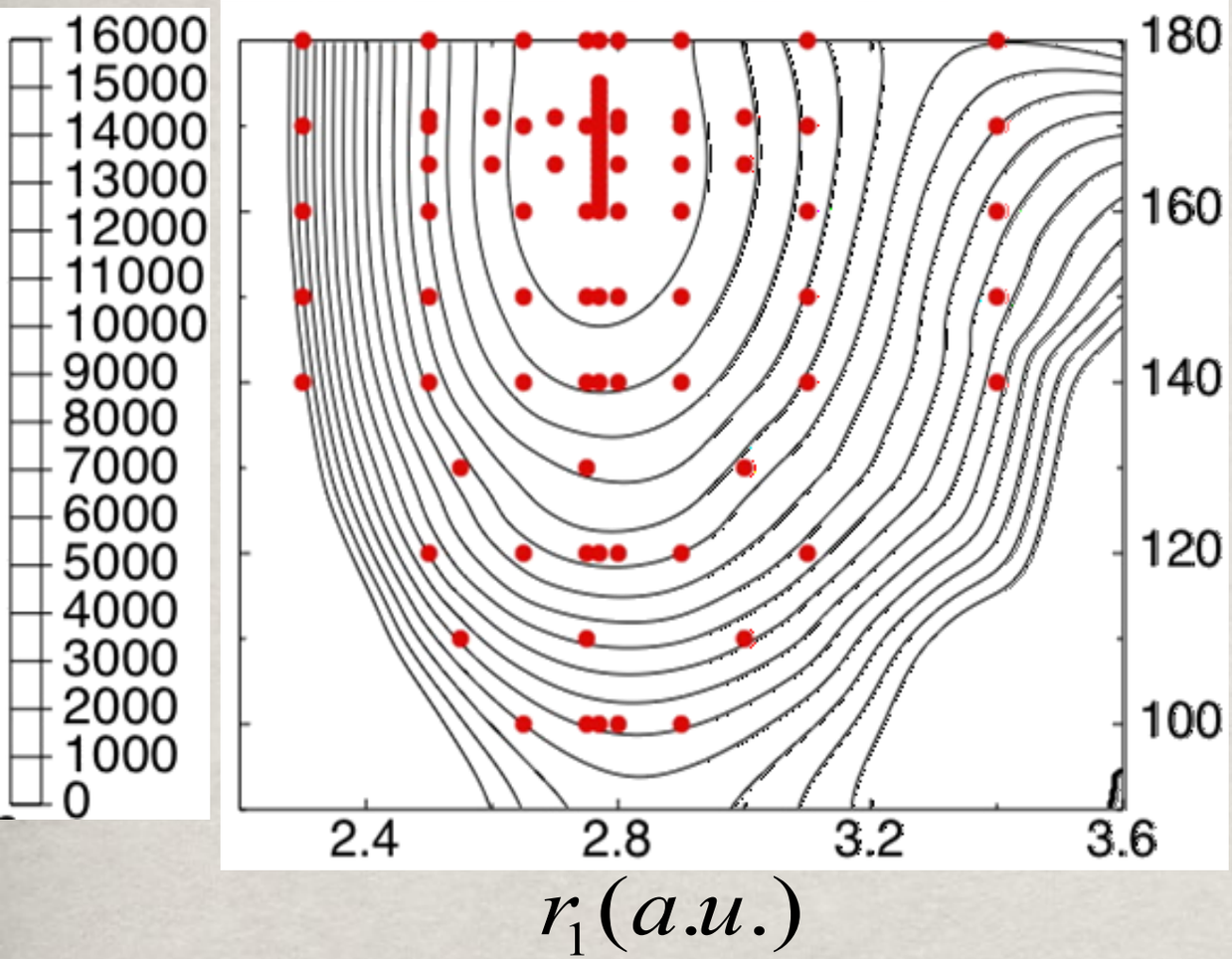




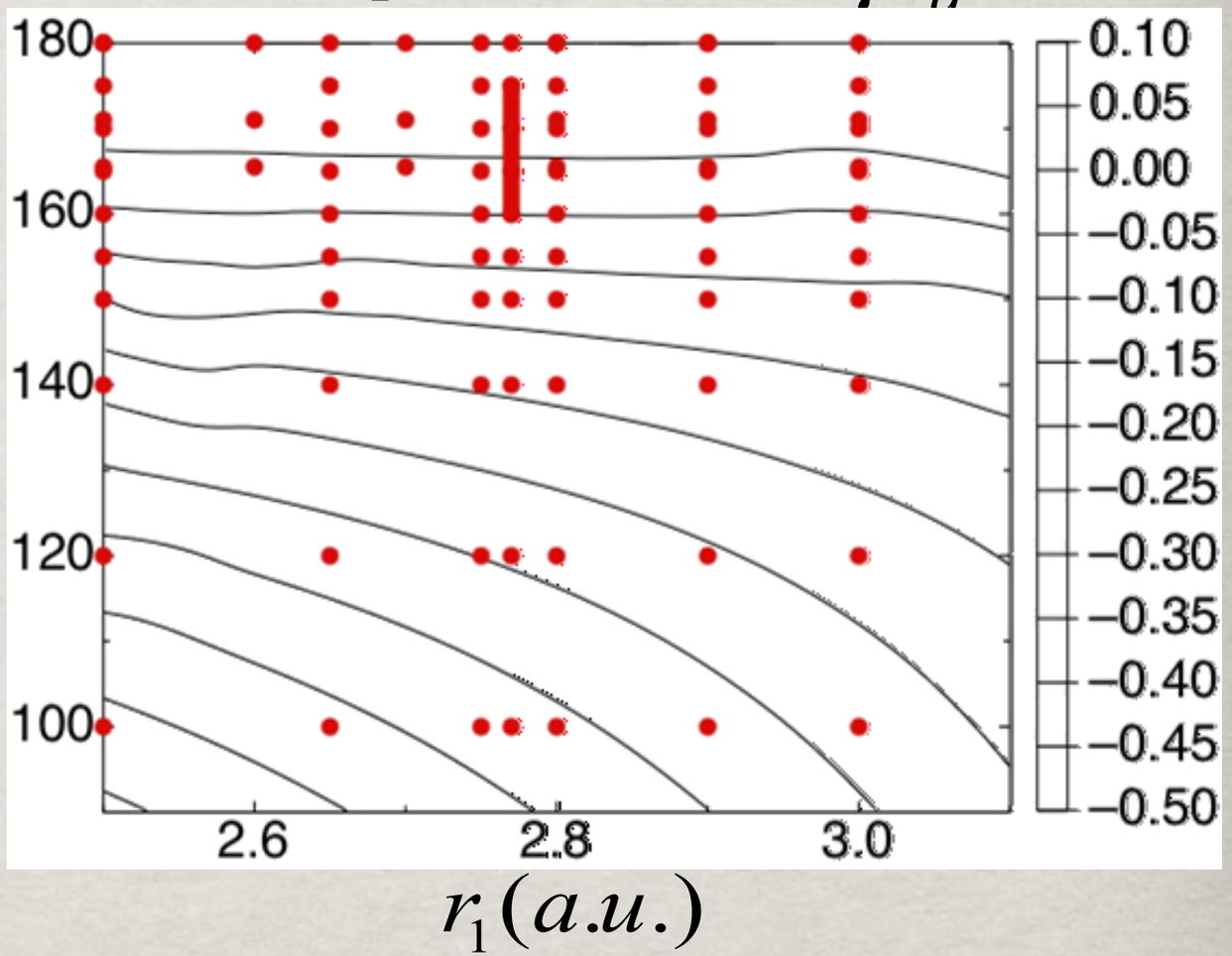

E / 10^3 cm^-1
40
30
20
10
0
180
150
120
90
60
30
0
Bending angle α (degrees)
$^1\Sigma_g^+$
$^1\Delta_g$
$^3\Sigma_g^-$
$\tilde{B}$
$\tilde{A}$
$\tilde{a}$
$\tilde{X}$
$Si(^1D) + H_2$
$Si(^3P) + H_2$

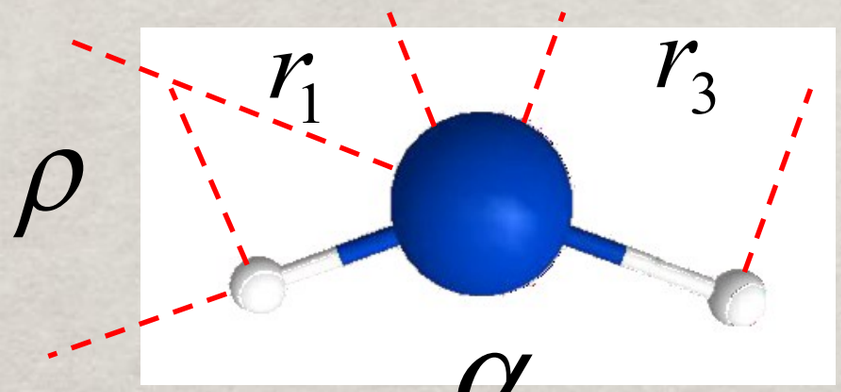
Calculated *ab initio* points

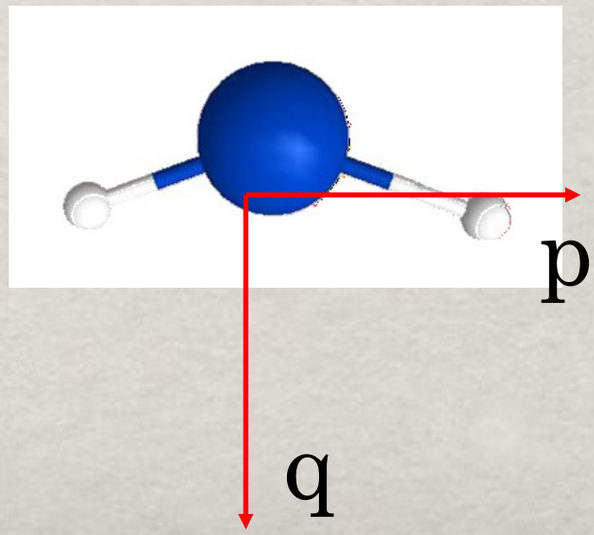
The PES



The dipole moments μ_a







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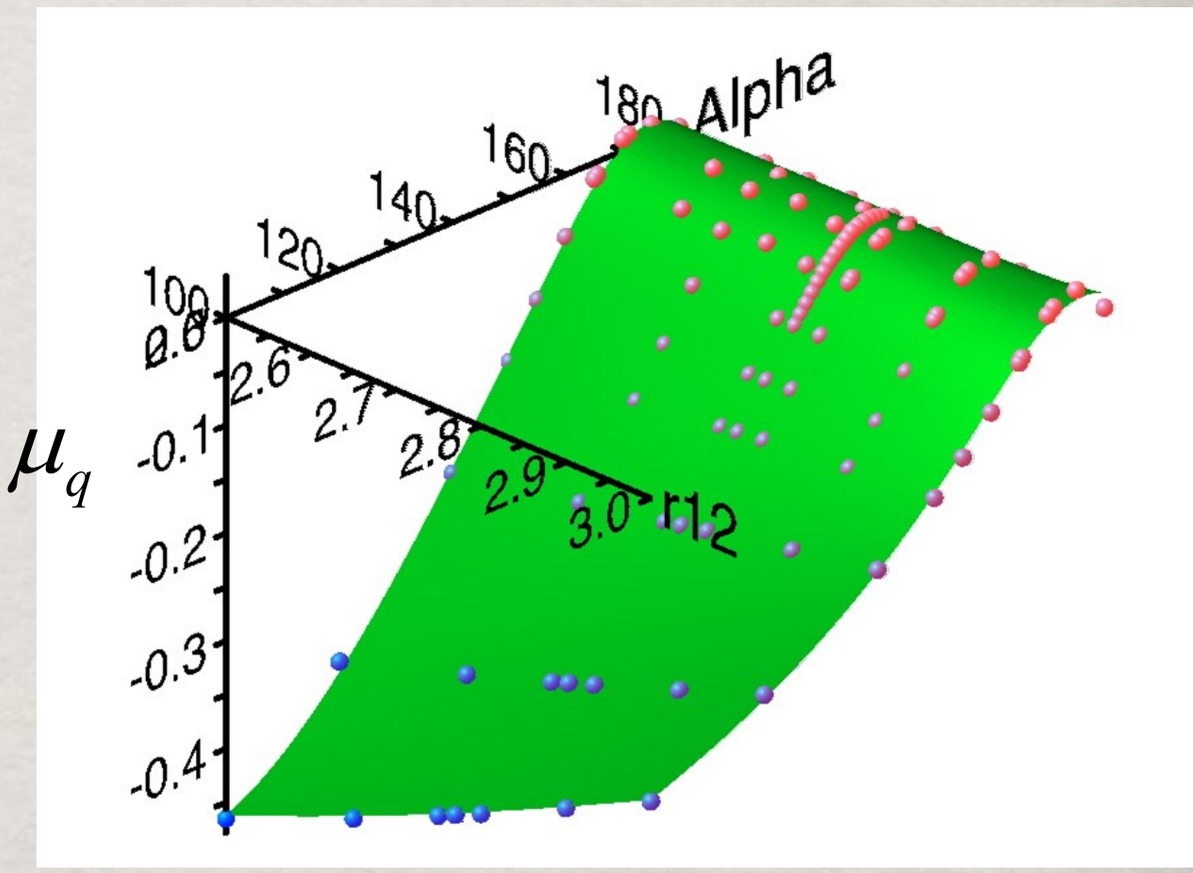
Fitting to analytical function

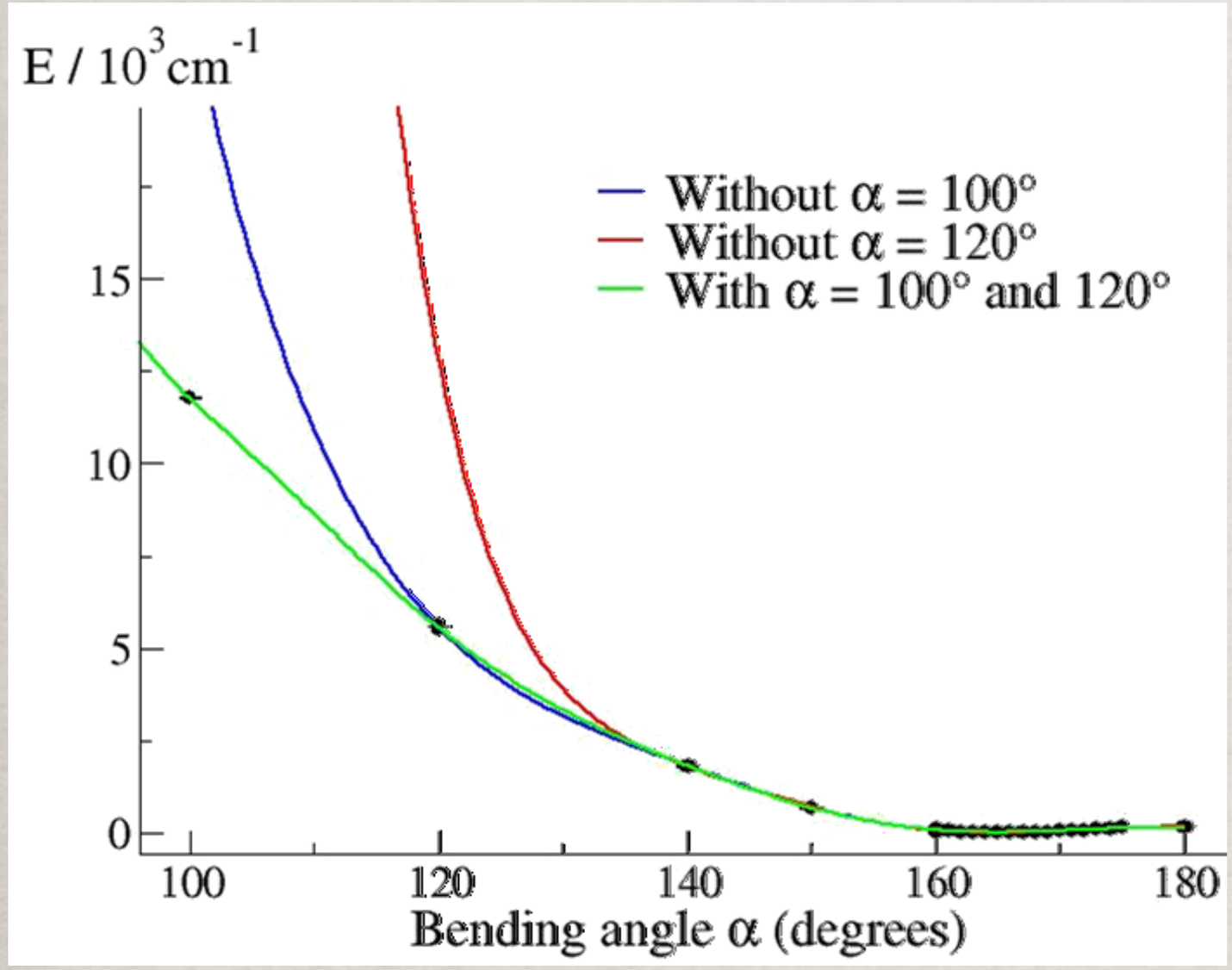
V



85 points
12 parameters

199 points
9 parameters

Details about the fitting



One cannot fit both the equilibrium region and the small angle region.

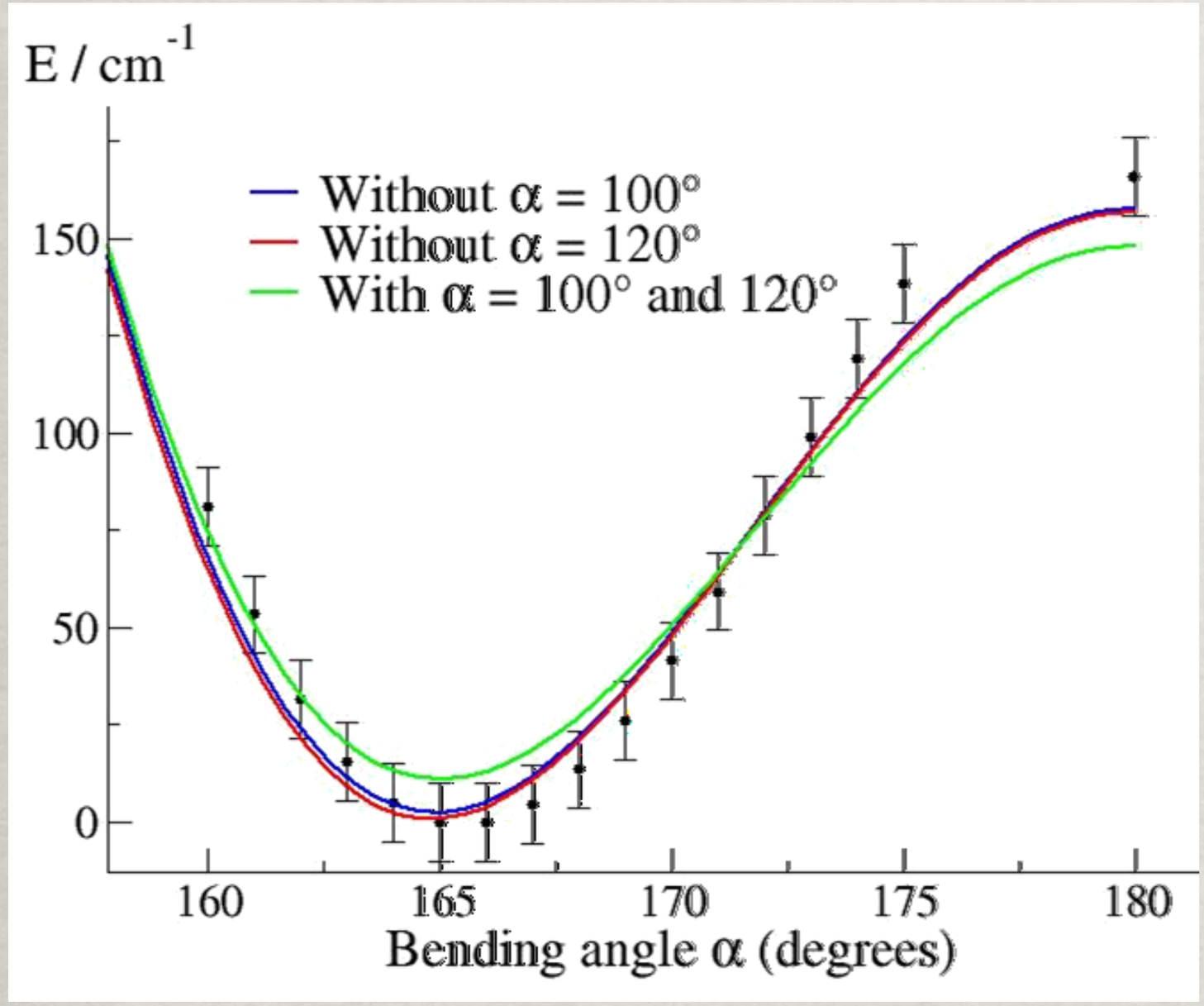
One has to exclude some points from the fit.

Std. Dev. = 31.7 cm^{-1} with 90 points. Spurious inflexion points.

Std. Dev. = 30.1 cm^{-1} with 85 points.

Std. Dev. = 24.6 cm^{-1} with 92 points.

Details about the fitting



Have the better behaviour for small angles but poorly fit the equilibrium region.

Equally describe the equilibrium region.

Although not the smallest std. dev., better compromise.

Fitting to experimental term values

Ab initio points → 1.437 Å, 165.5°, BL ≈ 166 cm^{-1}.

Fitting to these points → 1.466 Å, 164.9°, BL ≈ 155.4 cm^{-1}.

44 lines for SiD_2 → Std. Dev. = 4.6 cm^{-1}

12 lines for SiH_2 → Std. Dev. = 27.1 cm^{-1} (87 cm^{-1} off for level 6000 cm^{-1})

Refined fitting using
5 parameters including
α_e and r_1^e

1.4589 Å, 165.37°, BL ≈ 129 cm^{-1}

SiD_2 → Std. Dev. = 1.6 cm^{-1}

SiH_2 → Std. Dev. = 2.4 cm^{-1}

Calculated term values for SiH_2

			(v_1, v_2, v_3)				
J	K_a	K_c	$(0,0,0)$	$(0,1,0)$	$(0,2,0)$	$(1,0,0)$	$(0,0,1)$
0	0	0	0.00	961.77	2053.97	2155.37	2287.26
1	0	1	7.81	969.64	2061.87	2163.07	2294.93
	1	1	383.78	1485.87	2621.96	2519.84	2654.07
	1	0	383.92	1486.14	2622.34	2519.98	2654.21
2	0	2	23.43	985.39	2077.66	2178.46	2310.27
	1	2	399.32	1501.37	2637.45	2535.07	2669.38
	1	1	399.32	1502.20	2638.60	2535.49	2669.79
	2	1	857.39	2020.64	3190.89	2990.40	3114.71
	2	0	857.39	2020.64	3190.88	2990.40	3114.71
3	0	3	46.86	1009.01	2101.34	2201.54	2333.27
	1	3	422.63	1524.61	2660.68	2557.92	2692.35
	1	2	423.48	1526.27	2663.00	2558.75	2693.16
	2	2	881.00	2044.35	3214.68	3013.54	3138.04
	2	1	881.00	2044.33	3214.64	3013.53	3138.04
	3	1	1383.11	2569.49	3782.85	3510.85	3627.74
	3	0	1383.11	2569.49	3782.85	3510.85	3627.74

$$\alpha_e = 165.3°$$

$$r_1^e = r_3^e = 1.4589 Å$$

$$BL \approx 129\ cm^{-1}$$

$$ZPE = 2599.26\ cm^{-1}$$

$$Std.\ Dev.\ (Obs - Calc) = 2.4\ cm^{-1}$$

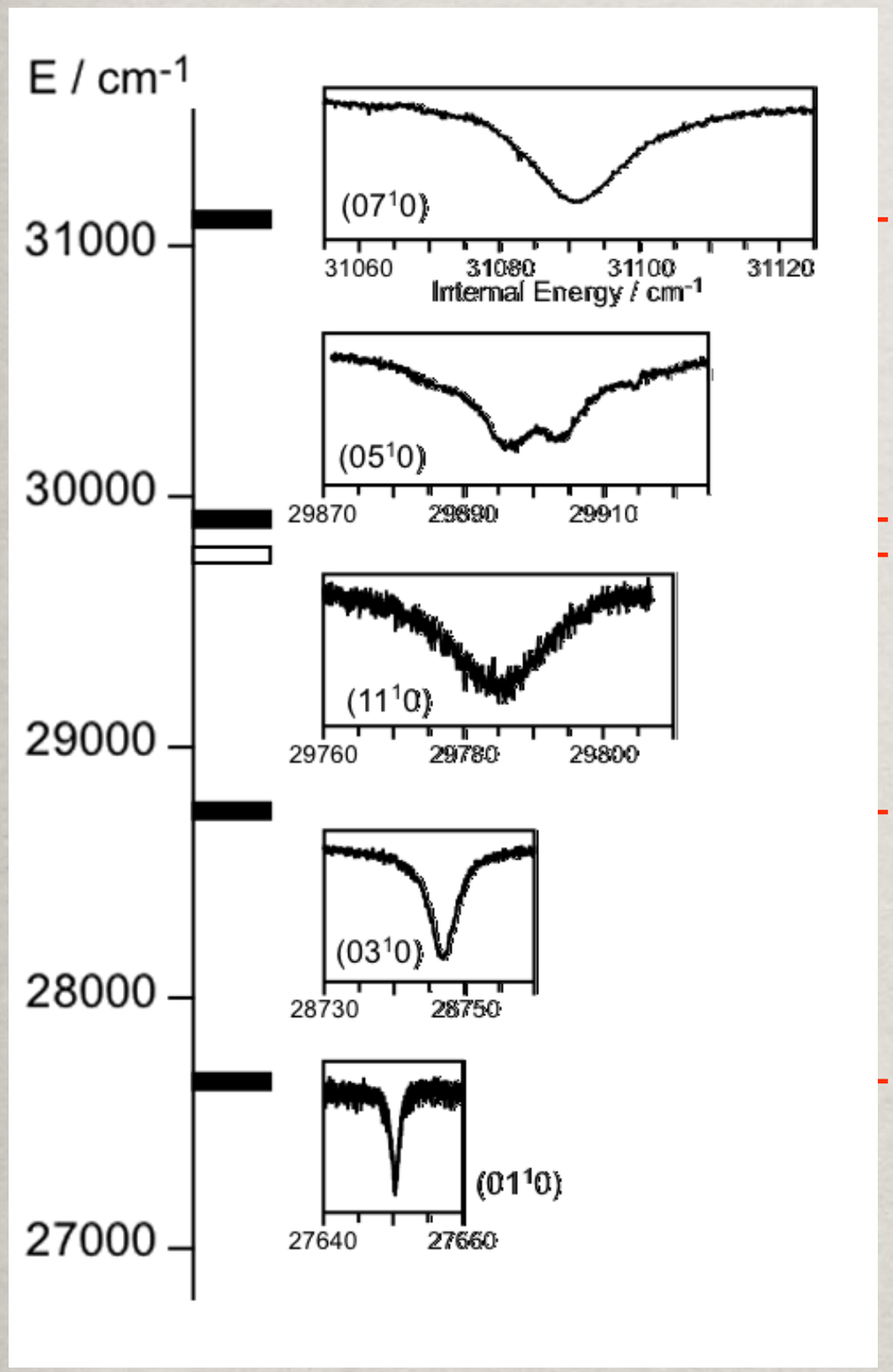
Calculated term values for SiD_2

			(v_1, v_2, v_3)				
J	K_a	K_c	(0, 0, 0)	(0, 1, 0)	(0, 2, 0)	(1, 0, 0)	(0, 0, 1)
0	0	0	0.00	641.74	1415.08	1530.10	1679.57
1	0	1	3.92	645.69	1419.05	1533.97	1683.43
	1	1	242.19	1004.37	1816.96	1762.75	1912.13
	1	0	242.24	1004.46	1817.09	1762.81	1912.18
2	0	2	11.77	653.59	1426.98	1541.72	1691.16
	1	2	250.01	1012.18	1824.79	1770.47	1919.86
	1	1	250.17	1012.47	1825.18	1770.64	1920.01
	2	1	552.83	1377.95	2209.17	2075.34	2215.53
	2	0	552.83	1377.95	2209.17	2075.34	2215.53
3	0	3	23.54	665.43	1438.89	1553.34	1702.76
	1	3	261.74	1023.90	1836.54	1782.05	1931.45
	1	2	262.06	1024.48	1837.31	1782.38	1931.76
	2	2	564.68	1389.84	2221.14	2087.02	2227.27
	2	1	564.68	1389.84	2221.13	2087.02	2227.27
	3	1	906.07	1763.01	2607.38	2428.36	2561.92
	3	0	906.07	1763.01	2607.38	2428.36	2561.92

$$ZPE = 1863.07\ cm^{-1}$$

$$Std.\ Dev. = 1.6\ cm^{-1}$$

Some of the observed spectra of SiH_2



(0,3,0) 1_{10}	3442.14	3440.37		13.3
(0,2,0) 1_{10}	2246.74	2238.42		9.0
(1,0,0) 1_{10}	2135.74	2136.06		
(0,1,0) 1_{10}	1096.39	1102.22		2.4
(0,0,0) 1_{10}	0.00	0.00		1.1
	Obs.	Calc.		FWHM

Y. Muramoto, H. Ishikawa and N. Mikami, *J. Chem. Phys*, 122, 154302 (2005)

Some orders of magnitude…

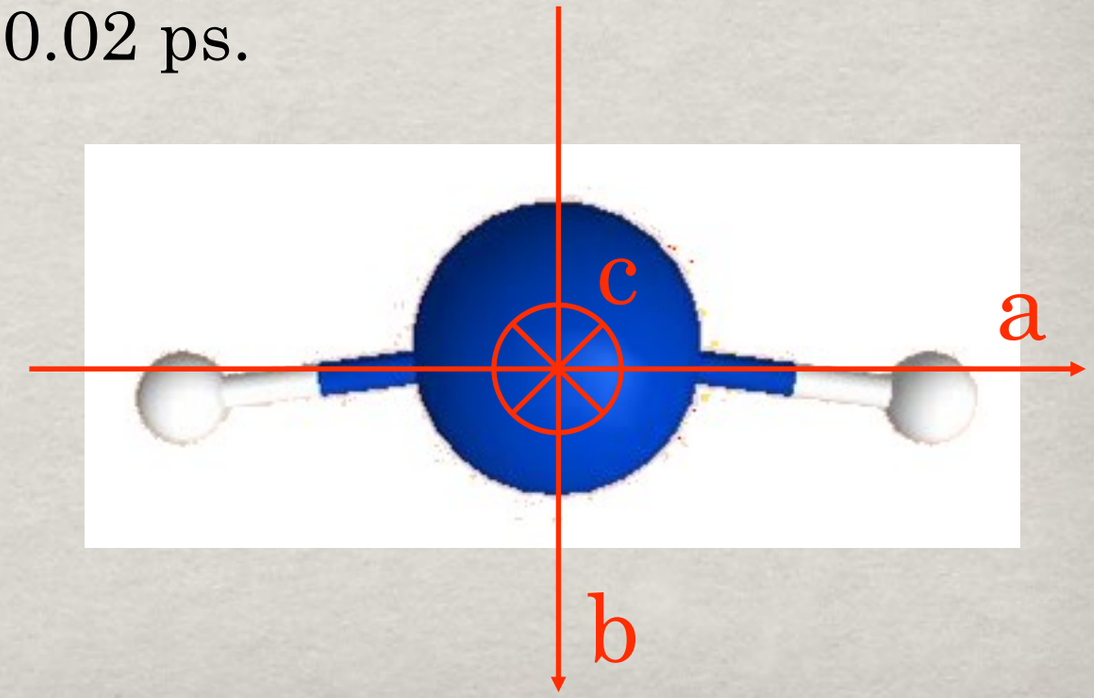
Rule of thumb : width of 10 cm^{-1} → lifetime of 1 ps.

Bending quantum $1\nu_2 \approx 1000\ cm^{-1}$ → 0.01 ps.

Sym/Asym stretching quantum $1\nu_{1,3} \approx 2000\ cm^{-1}$ → 0.005 ps.

End-over-end rotation $B \approx 4\ cm^{-1}$ → 2.5 ps.

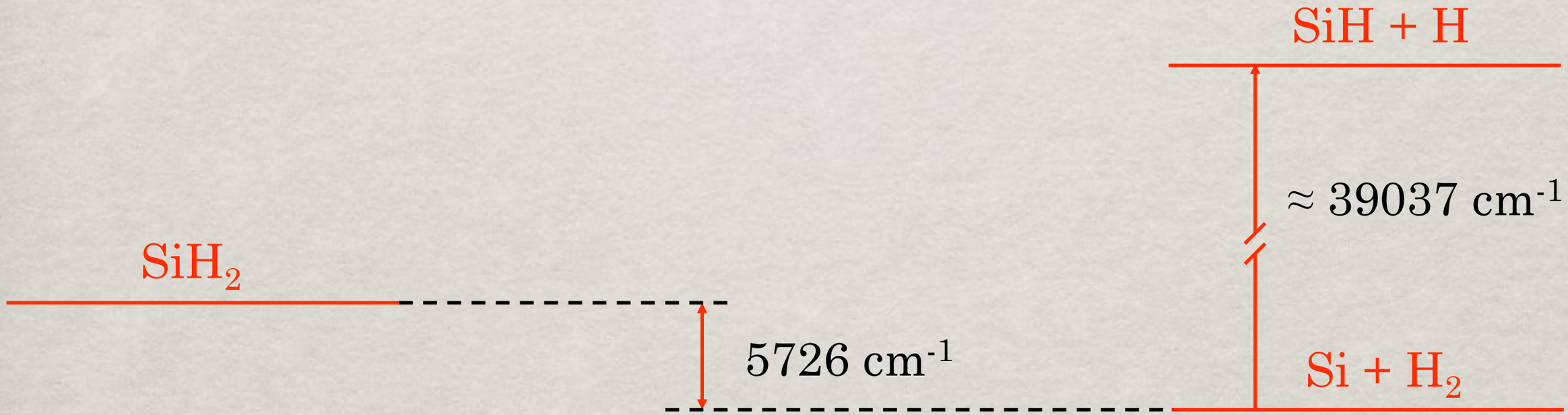
Rotation around the a axis $\approx 500\ cm^{-1}$ → 0.02 ps.



Dissociation path

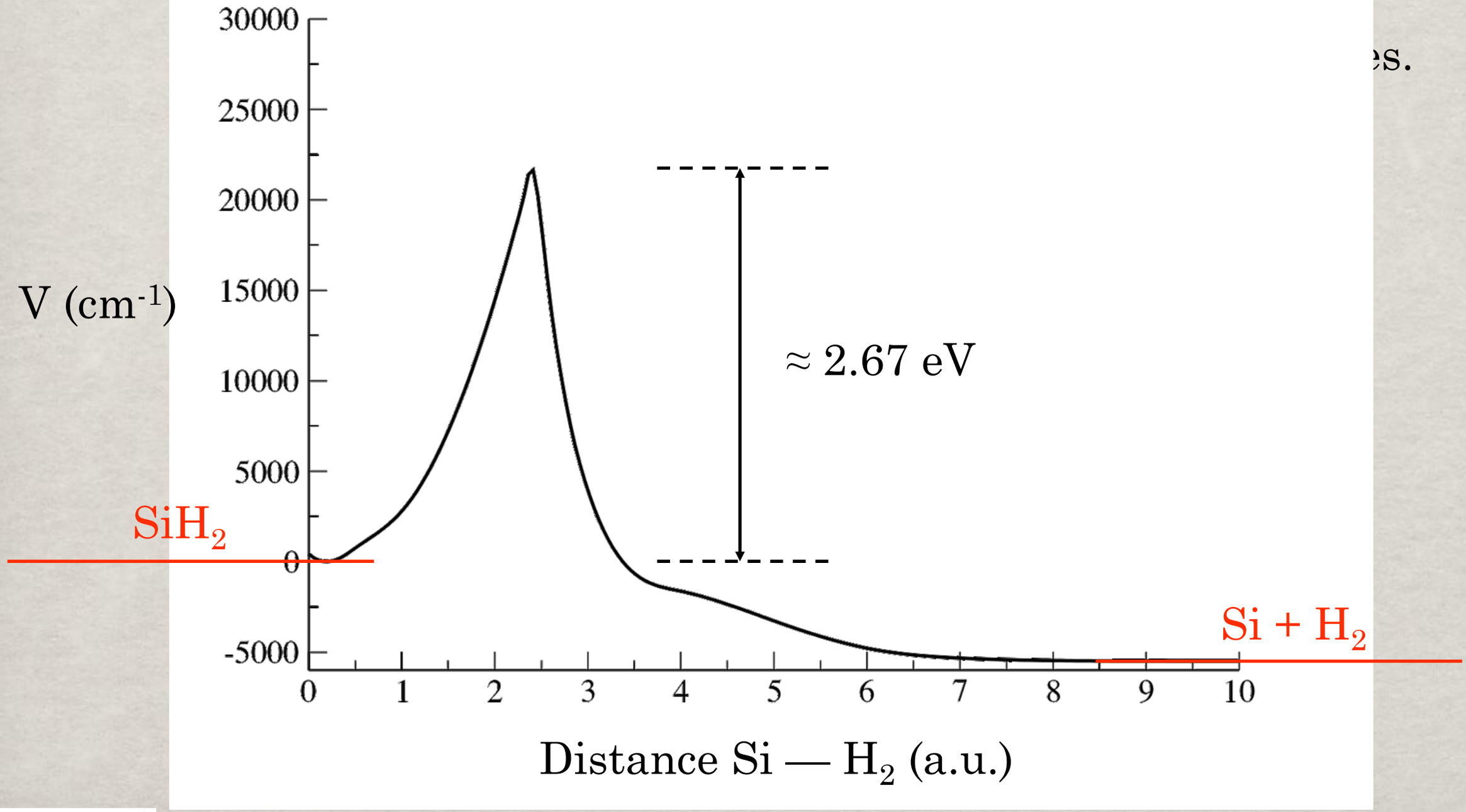
Main dissociation path is : $SiH_2(B\ ^1A_1) \rightarrow Si(^1D) + H_2(^1\Sigma_g^+)$.

Dissociation to $SiH_2(B\ ^1A_1) \rightarrow SiH(^2\Delta) + H(^2S)$ impossible.

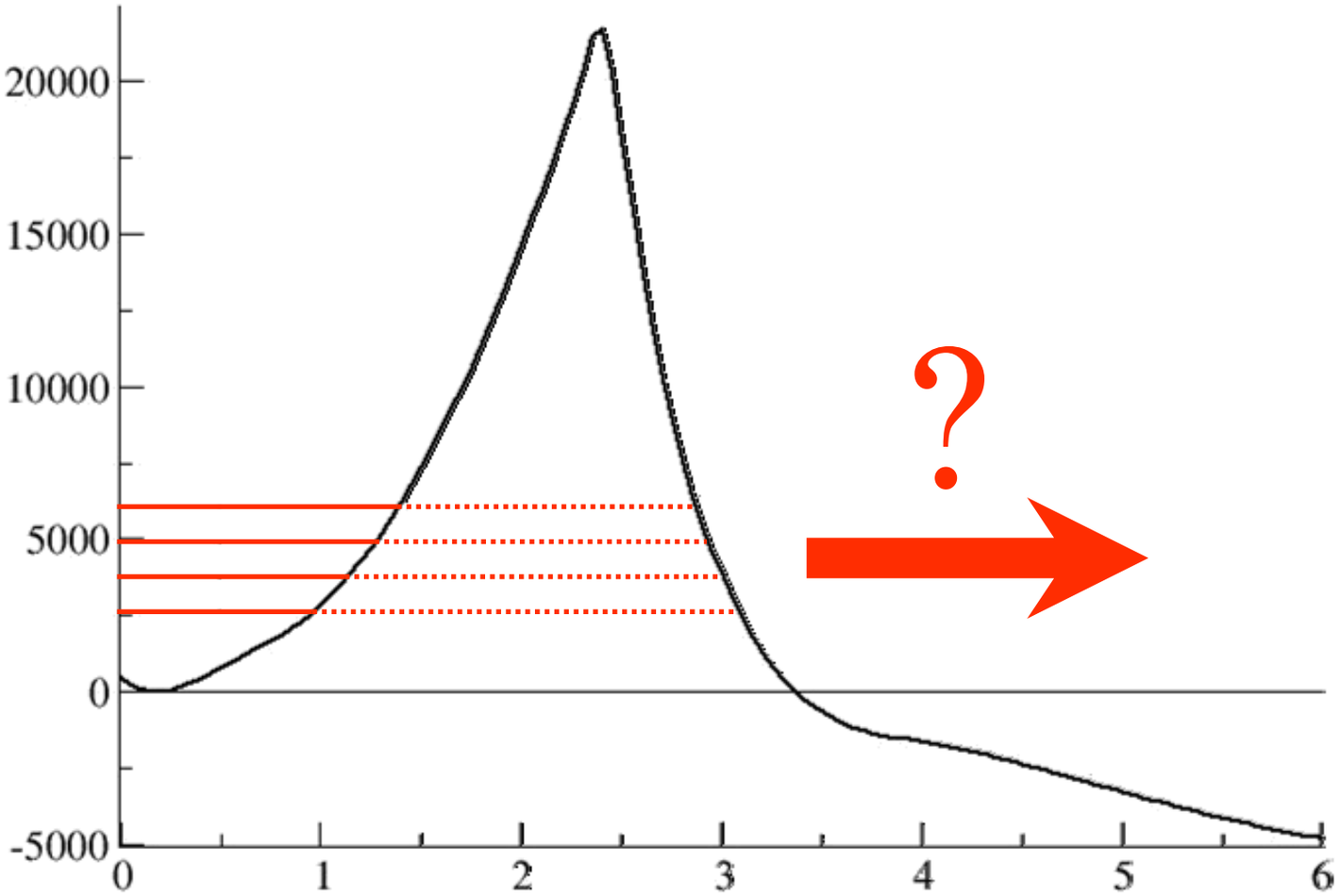


Calculated dissociation path

Main dissociation path is : $SiH_2(B\ ^1A_1) \rightarrow Si(^1D) + H_2(^1\Sigma_g^+)$.



Concluding remarks



Can experimental lifetimes be explained by tunnelling probabilites ?

No crossing state which could lower the barrier.

Summary

- *Ab initio* calculations.
- Fitting to an analytical function of nuclear coordinates.
- Refined fitting to a few experimental term values.
- Discussion about dissociation.

Thank you for your attention !

Questions ???

Fitting to experimental term values

Ab initio points → 1.437 Å, 165.5°, BL ≈ 166 cm^{-1}.

Fitting to these points → 1.466 Å, 164.9°, BL ≈ 155.4 cm^{-1}.

Calculation of rovibrational levels with this fit and comparison with a few existing experimental lines.

44 lines for SiD_2 → Std. Dev. = 4.6 cm^{-1}

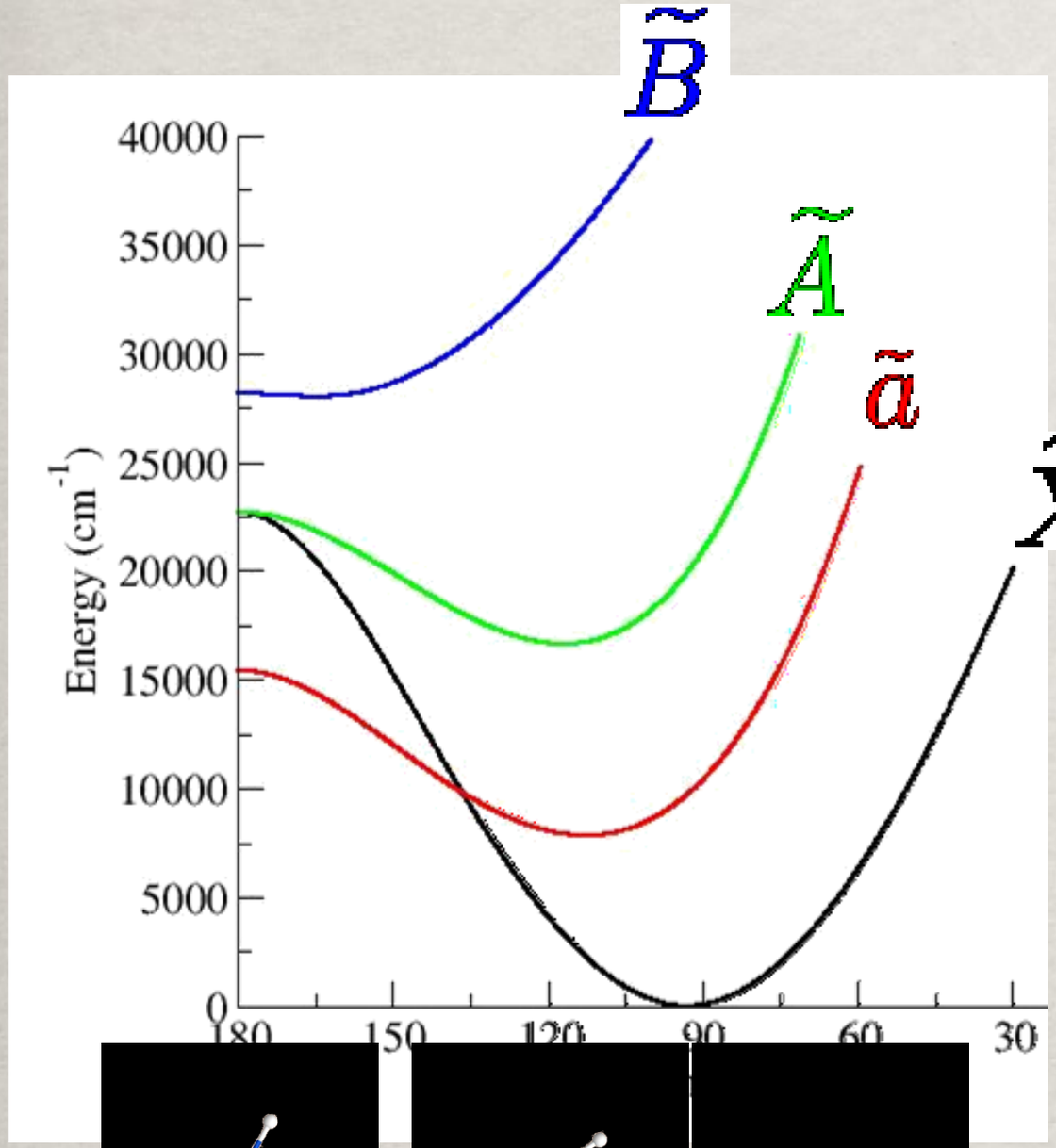
12 lines for SiH_2 → Std. Dev. = 27.1 cm^{-1} (87 cm^{-1} off for level 6000 cm^{-1})

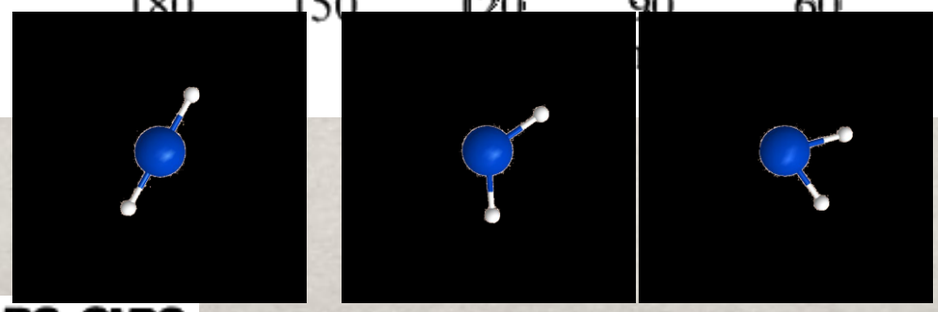
1.4589 Å, 165.37°, BL ≈ 129 cm^{-1}

SiD_2 → Std. Dev. = 1.6 cm^{-1}

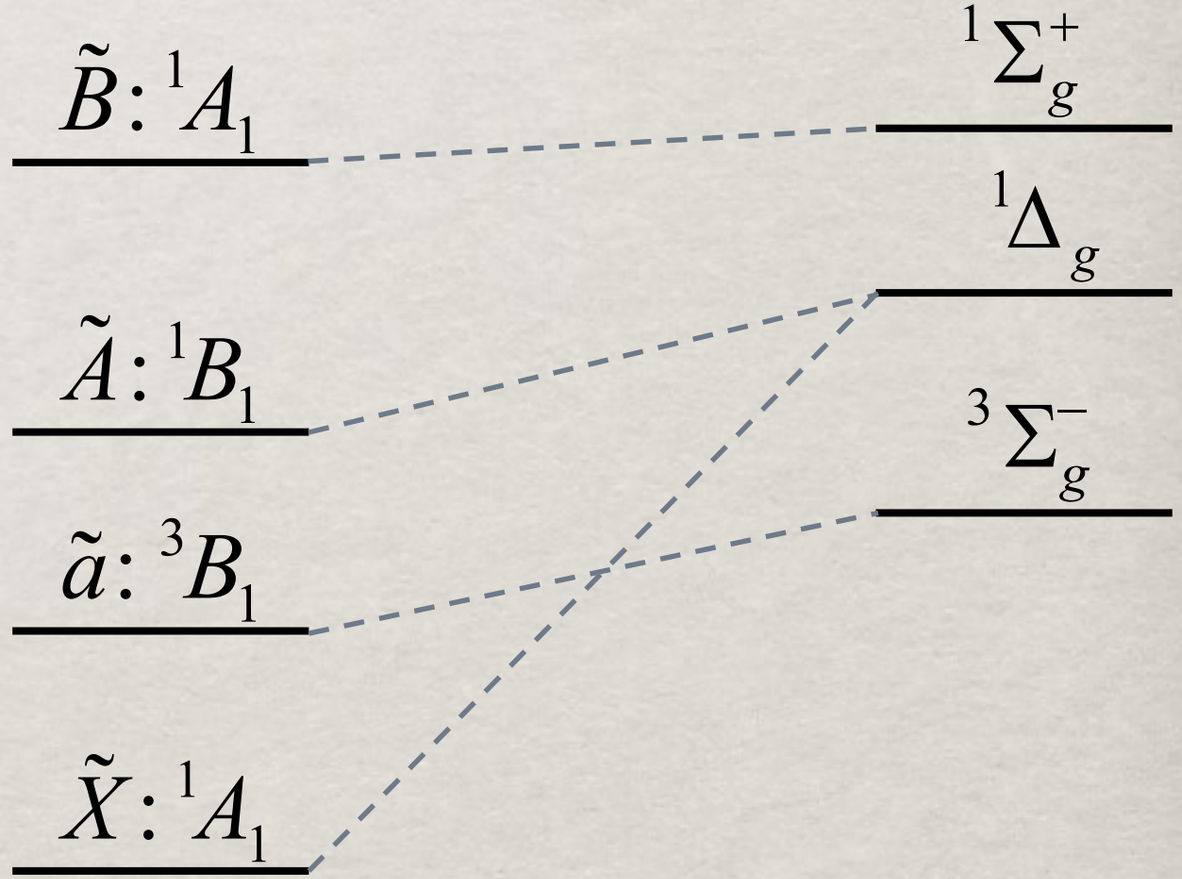
SiH_2 → Std. Dev. = 2.4 cm^{-1}

Bending potentials

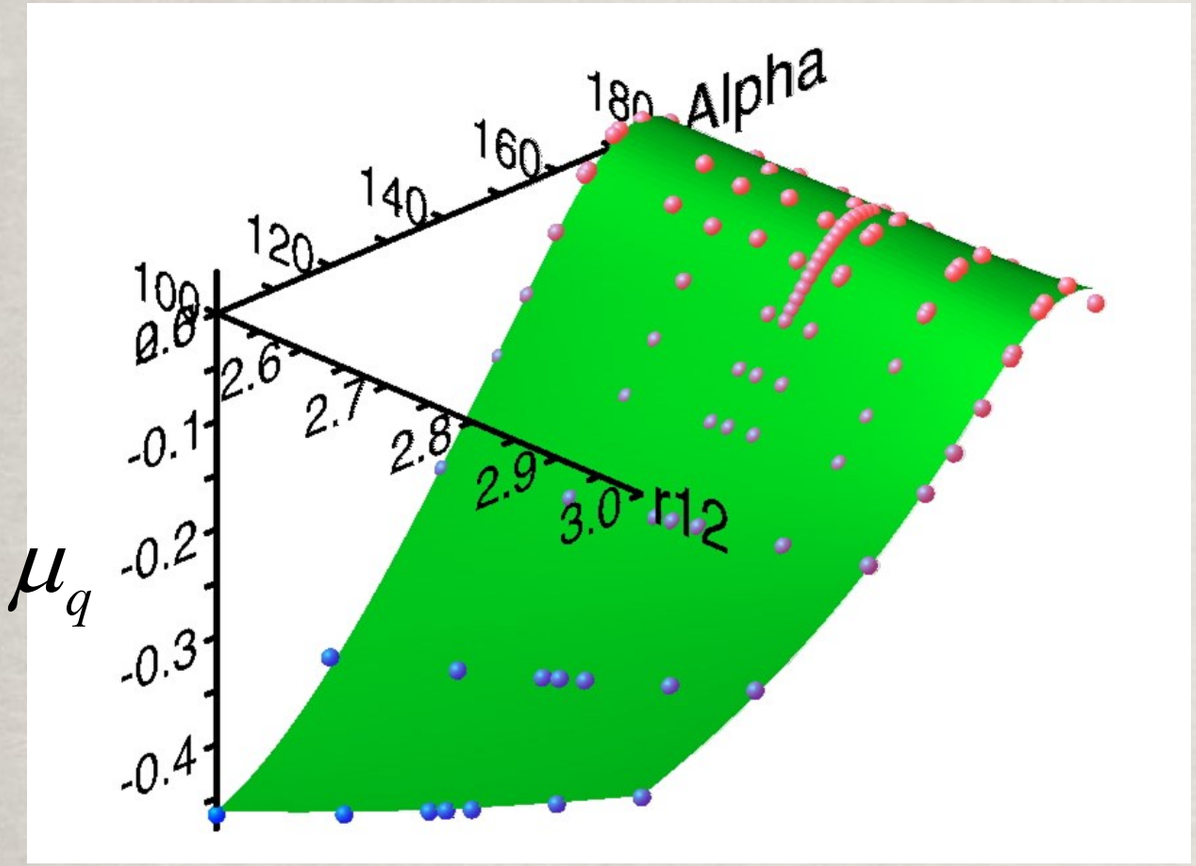


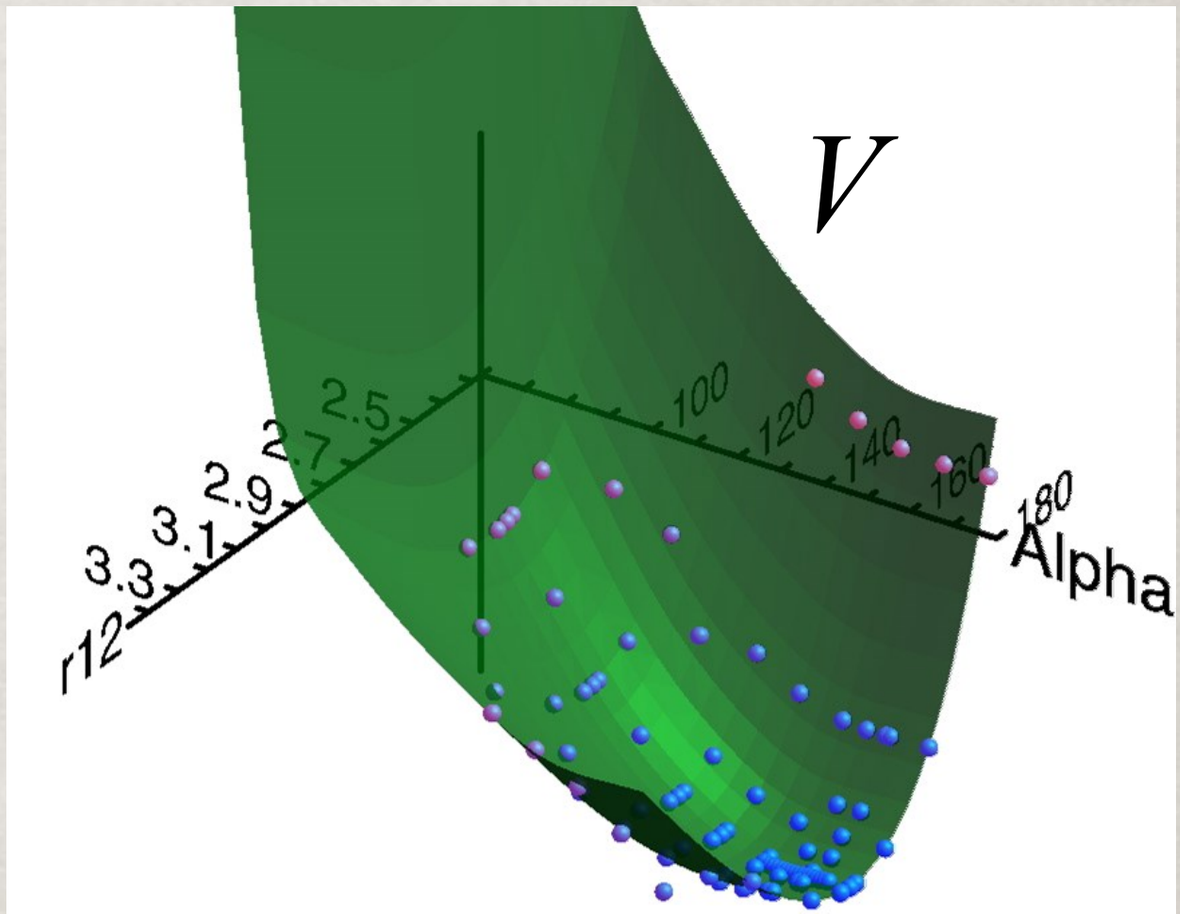


Correlation diagram between bent and linear configurations



Fitting to analytical function



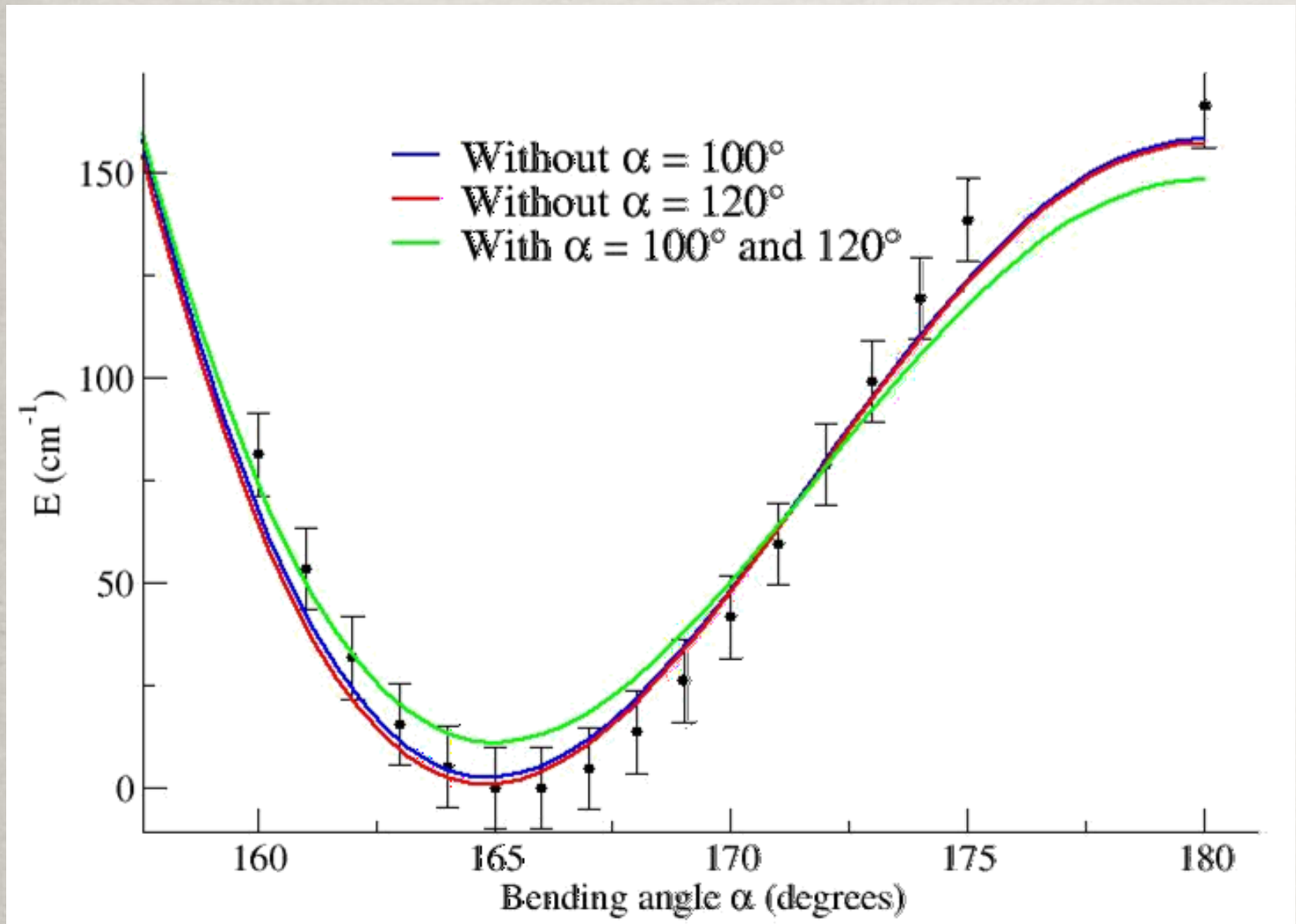


$$V(r_1, r_3, \rho) = \sum_{jkm} Y_{jkm} y_1^j y_3^k (\cos\rho_e - \cos\rho)^m$$

$$\mu_q(\Delta r_1, \Delta r_3, \rho) = \sin\rho \sum_{jkm} q_{jkm} \Delta r_1^j \Delta r_3^k (\cos\rho_e - \cos\rho)^m$$

$$y_i = 1 - \exp(-a_i \Delta r_i) \quad ; \quad \Delta r_i = r_i - r_e$$

Details about the fitting



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Equally describe the equilibrium region.

Although not the smallest std. dev., better compromise.

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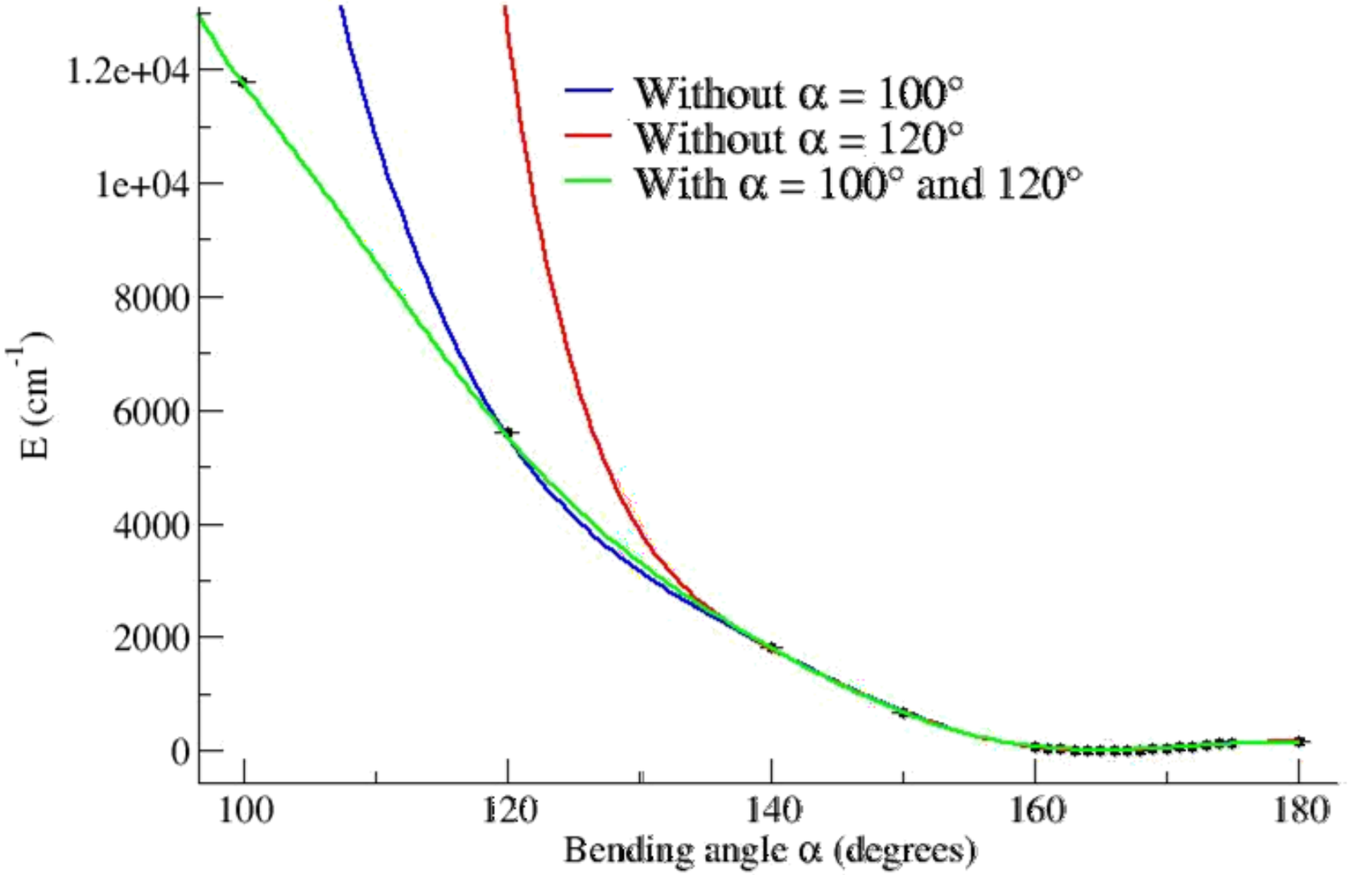

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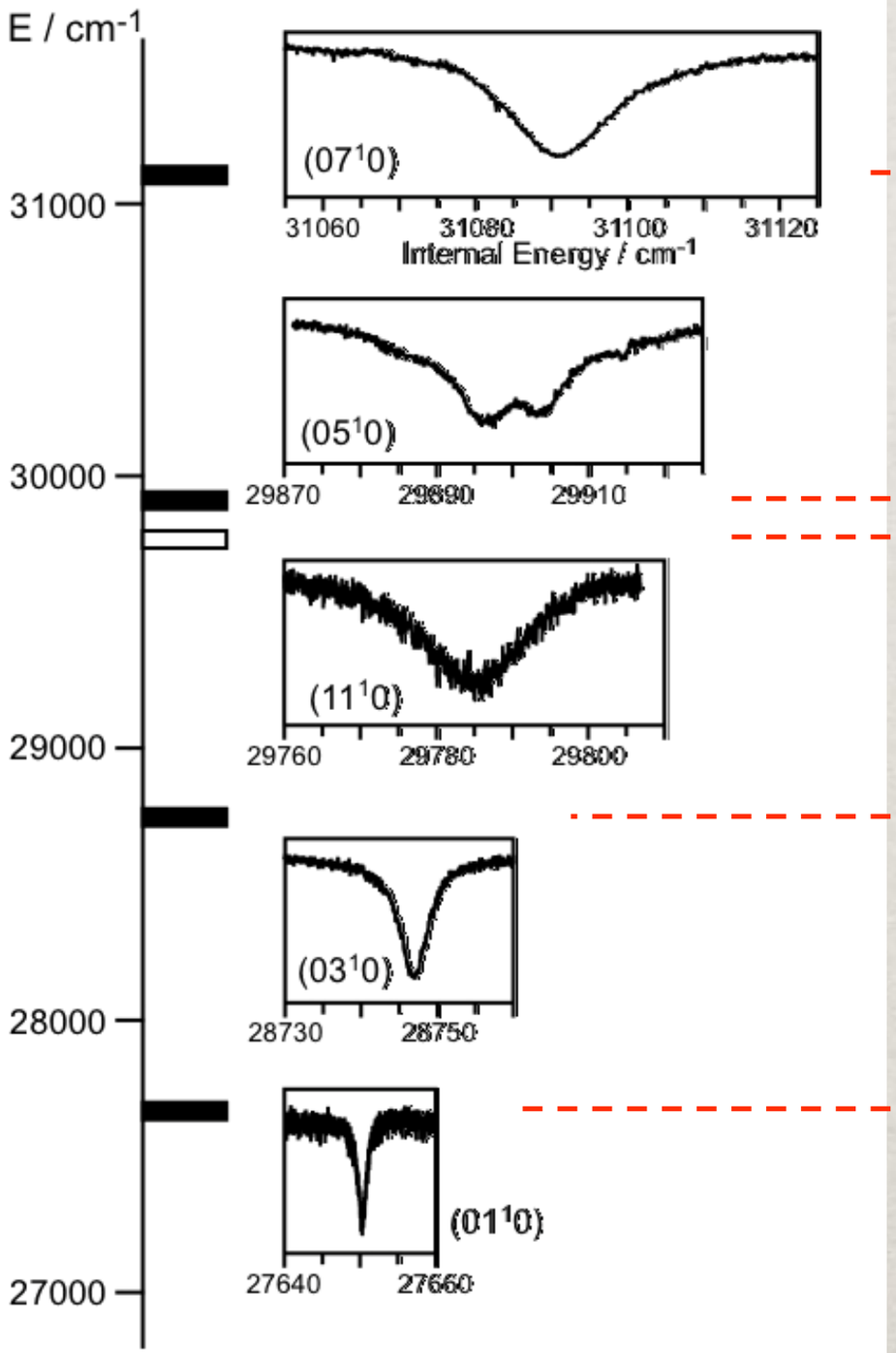

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	Obs.	Calc.	FWHM

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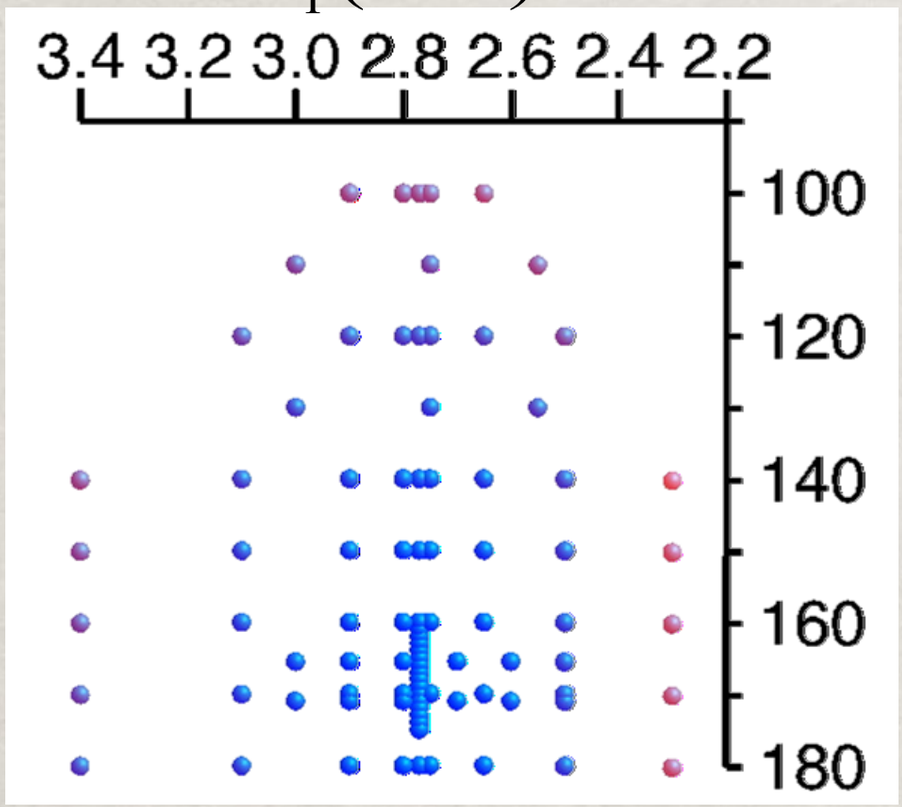
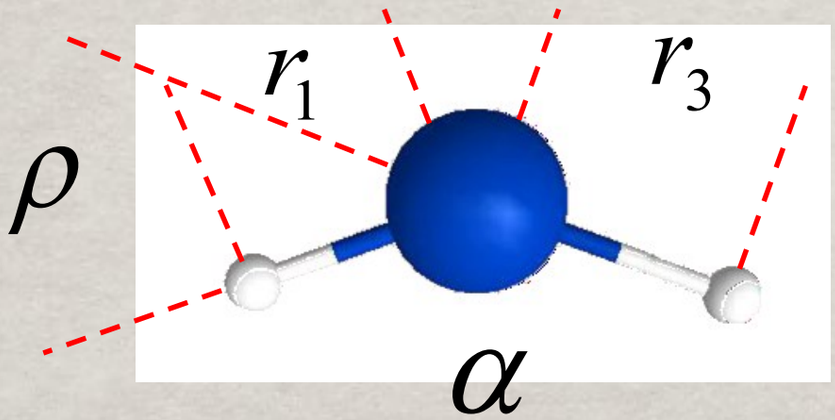
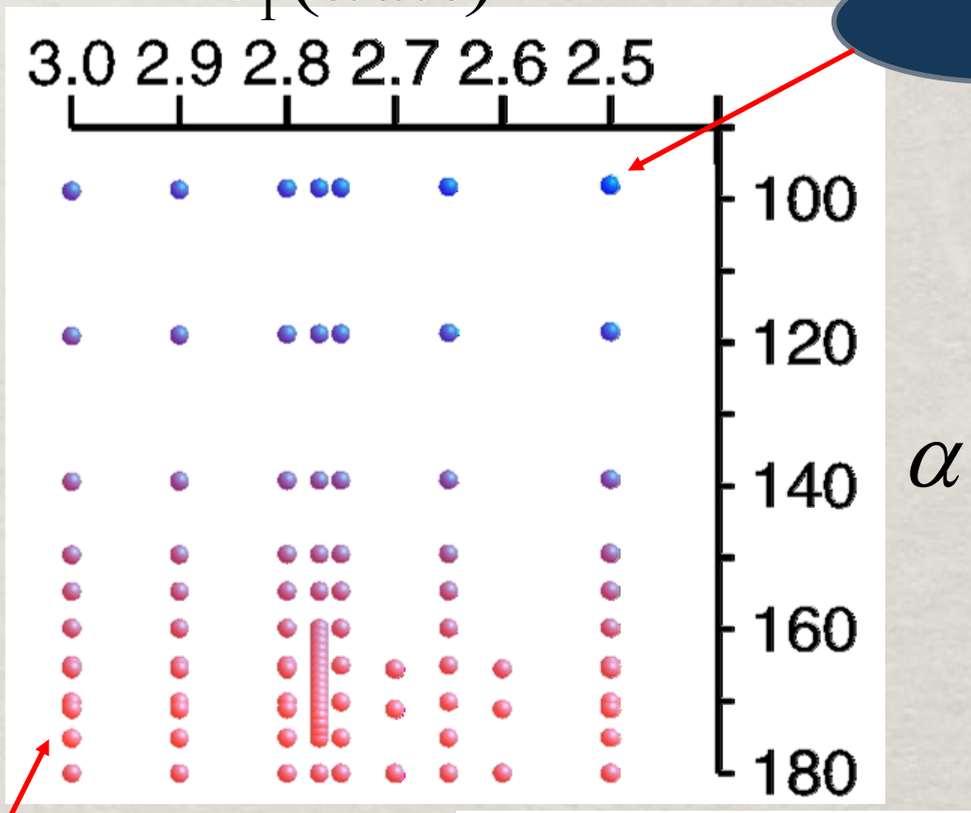
Calculated *ab initio* points

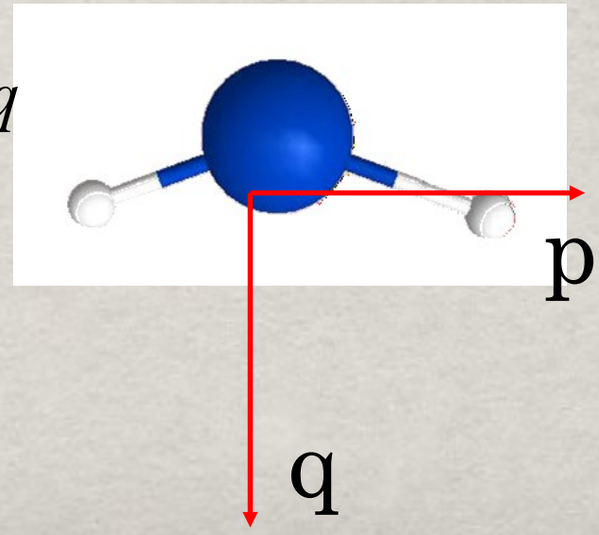
The PES



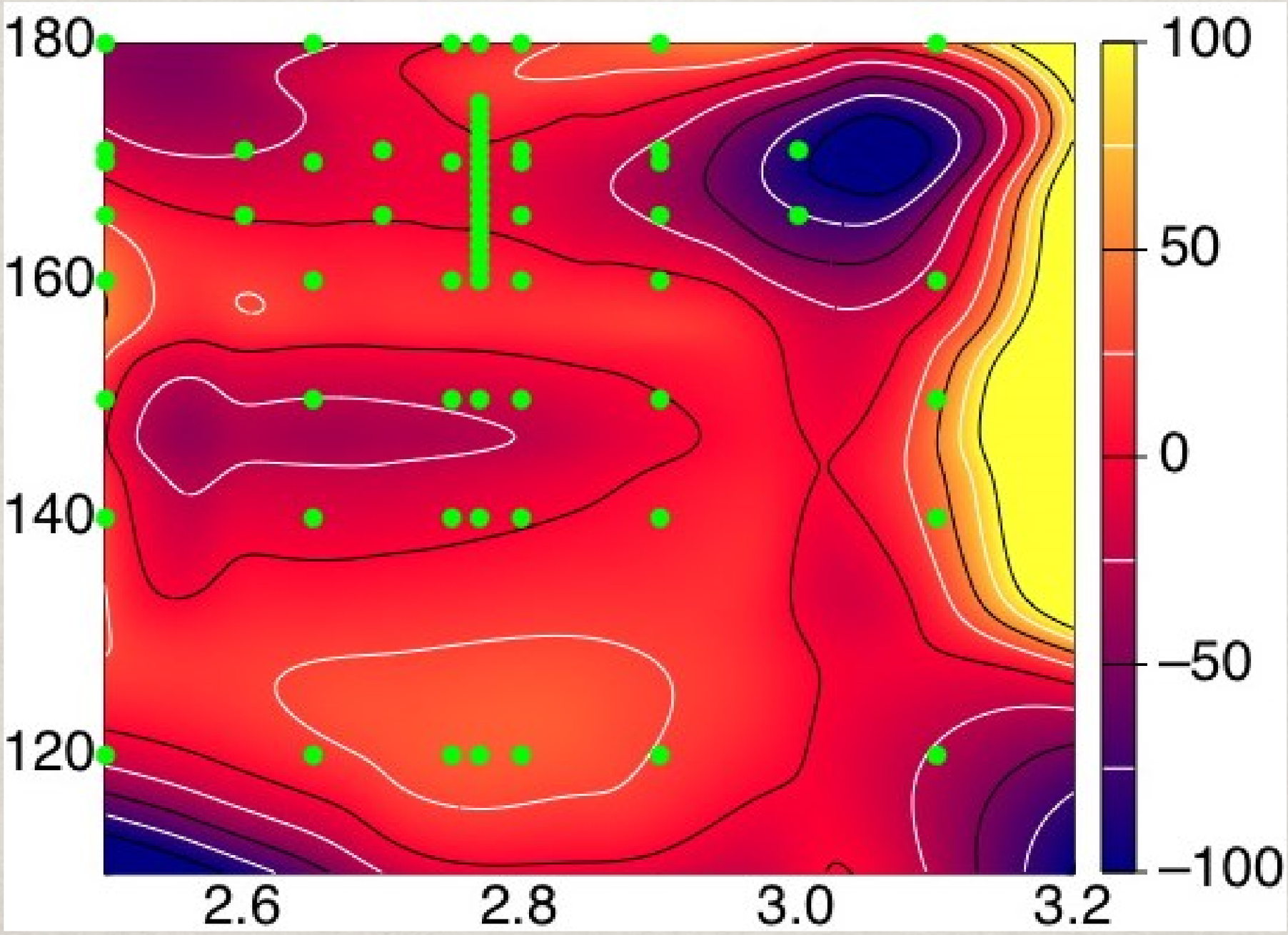


The dipole moments





Fitting to analytical function



Obs-calc (cm^{-1})