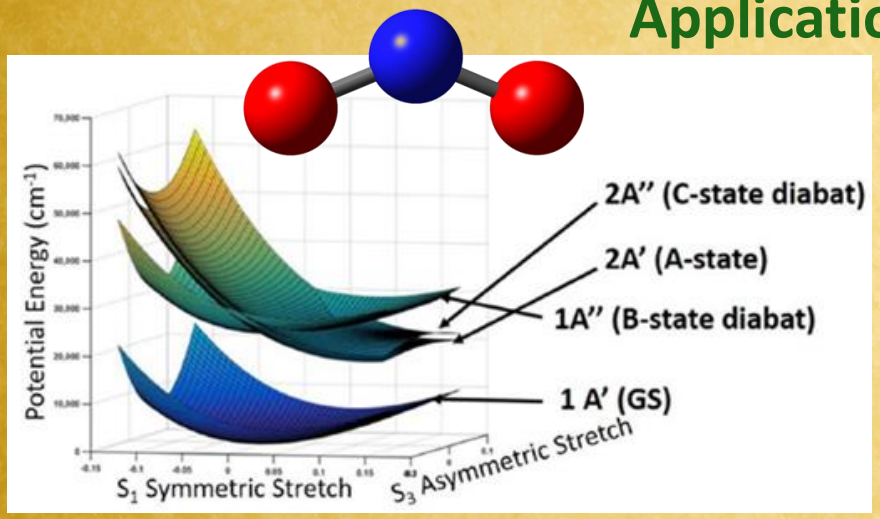
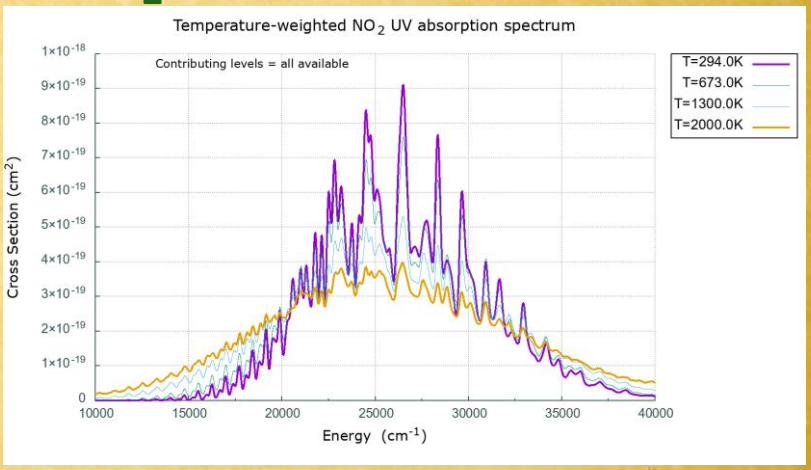
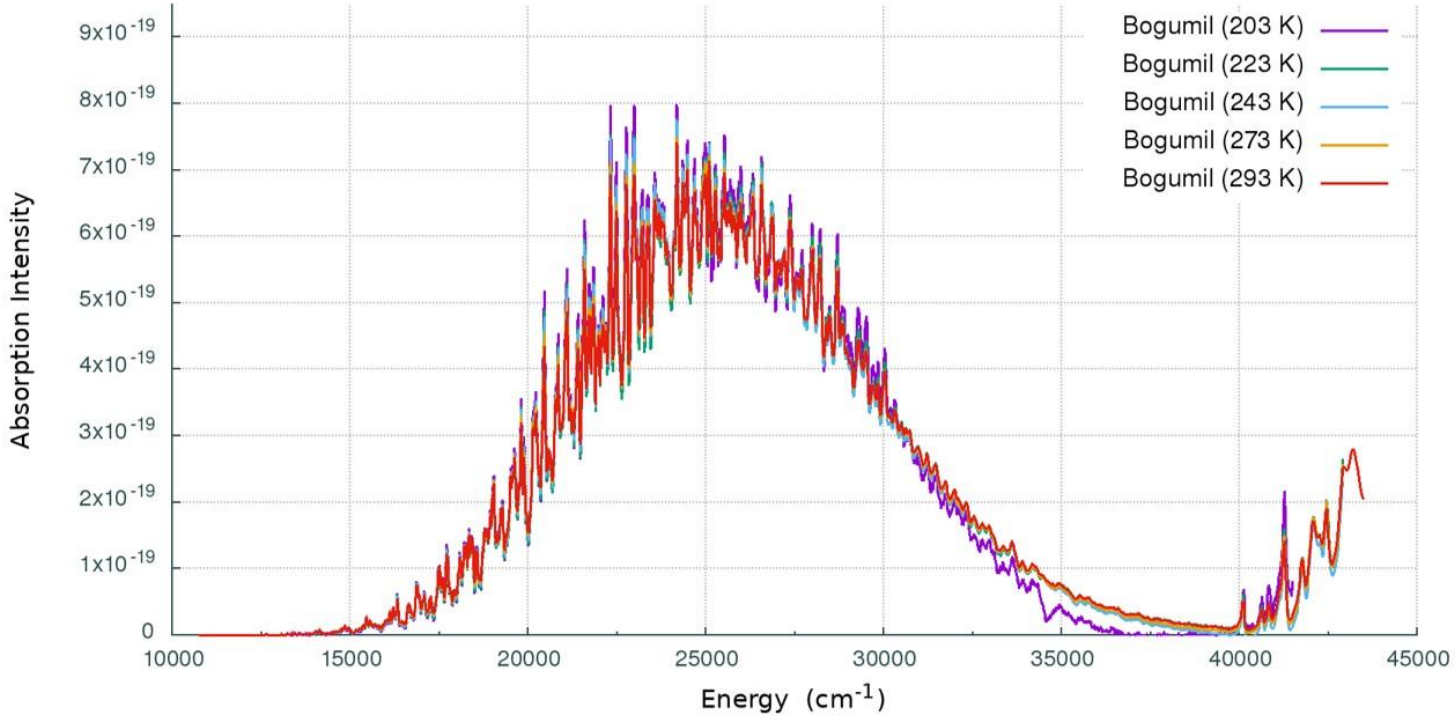
Development of a tool for the complete first-principles prediction of finite-temperature and generalized initial-state UV absorption spectra: Application to NO_2





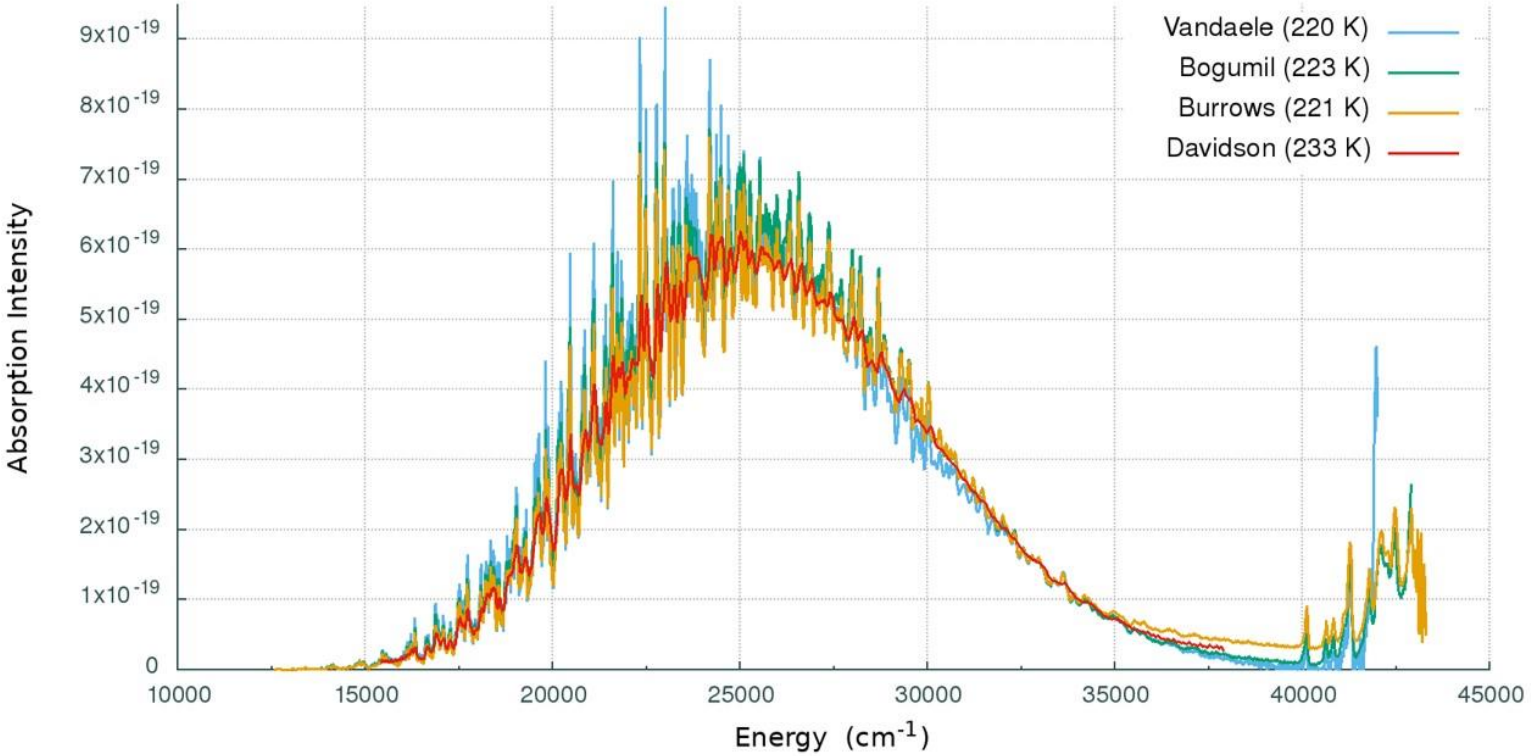
Richard Dawes, Ernesto Quintas-Sánchez, Steve Ndengué

NO_2 has a notoriously complex UV absorption spectrum



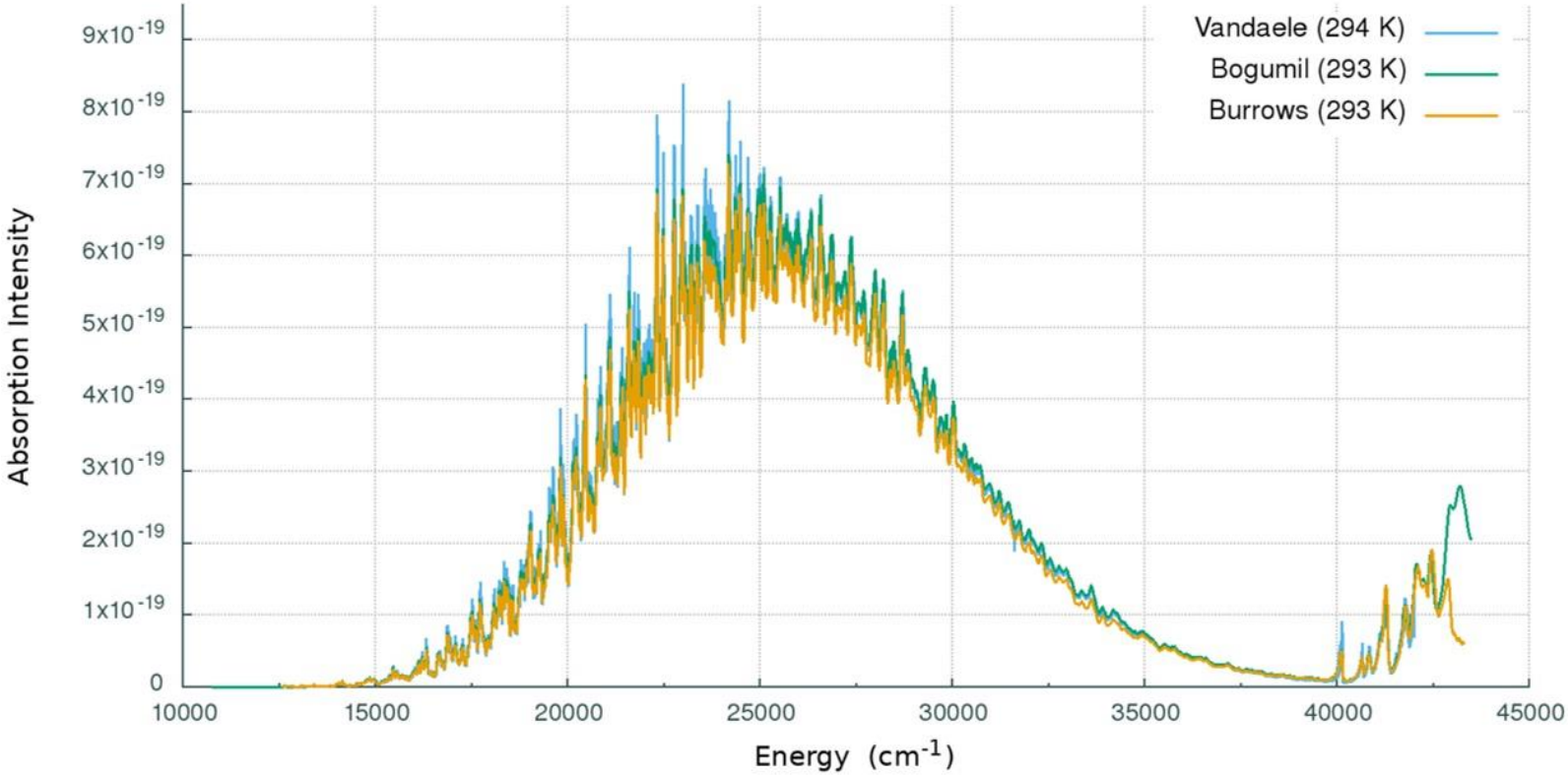
- First explore consistency of available data
- Experiments are challenging due to photodissociation to NO + O beginning at ~25000 cm^{-1} and equilibrium with N_2O_4.
- Mainz database has several spectra recorded by different people, temperatures, resolution etc. http://satellite.mpic.de/spectral_atlas/cross_sections/Nitrogen%20oxides/NO2.spc
- Data recorded by Bogumil in 2003 includes the lowest temperature available (203 K).

NO_2 has a notoriously complex UV absorption spectrum



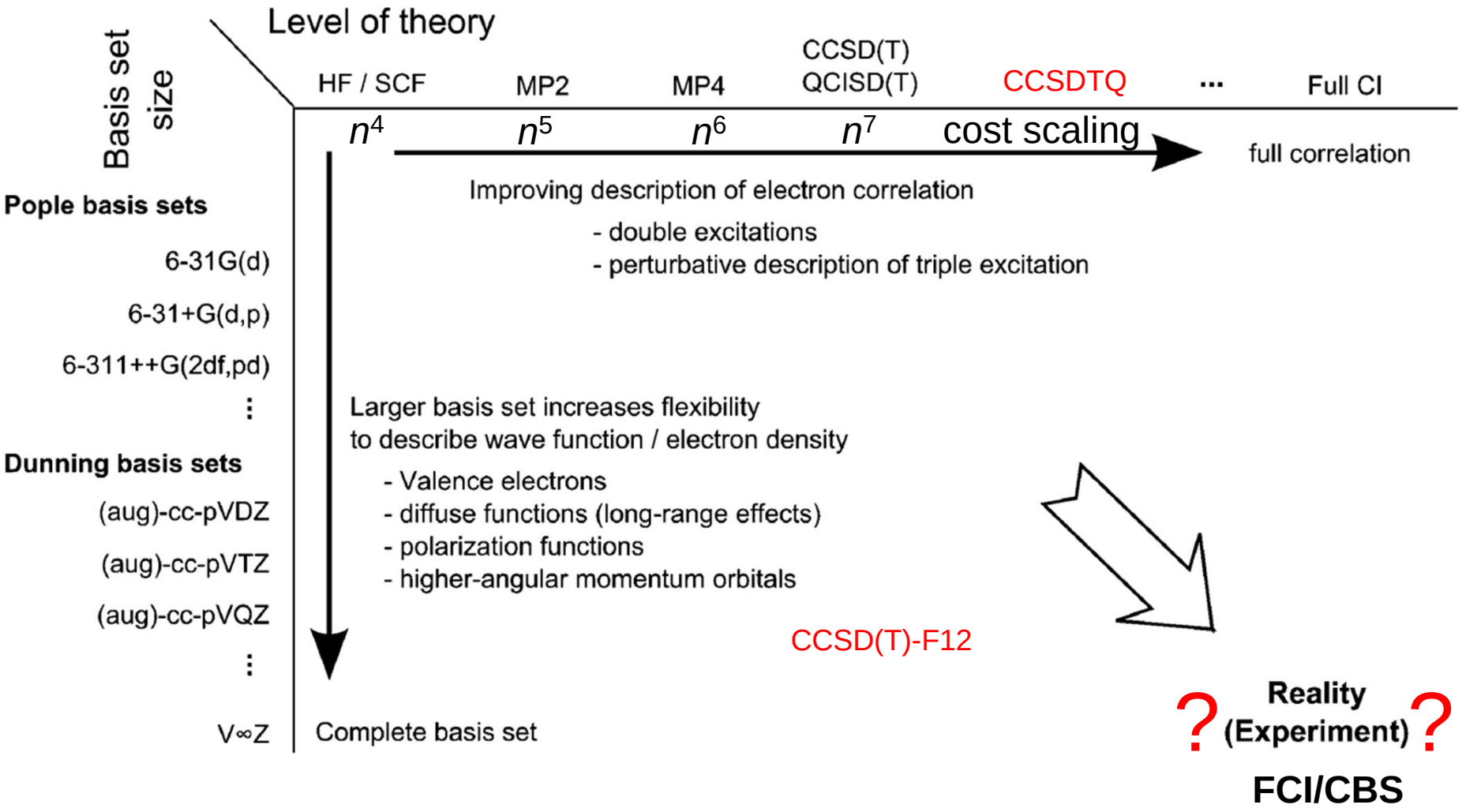
- Several datasets are available near 220 K and are fairly consistent except for differences in resolution

NO_2 has a notoriously complex UV absorption spectrum



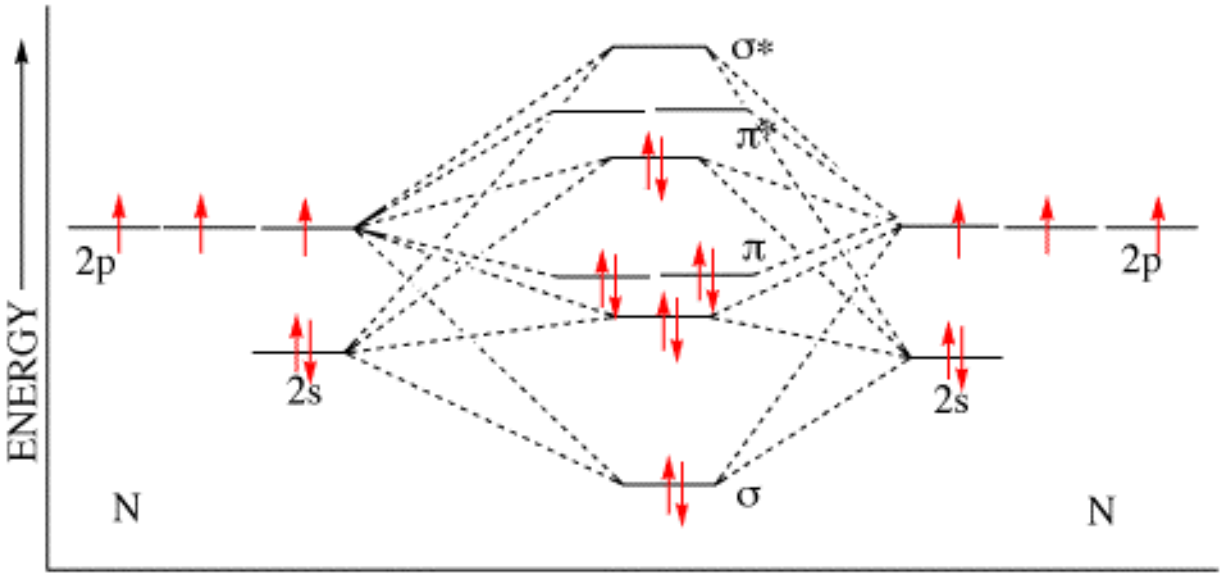
- Several datasets are available around 294 K and are more consistent, with that by Vandaele (1998) having the highest resolution (2 cm^{-1}). A.C. Vandaele, C. Hermans, P.C. Simon, M. Carleer, R. Colins, S. Fally, M.F. Mérienne, A. Jenouvrier, and B. Coquart, "Measurements of the NO_2 absorption cross-sections from 42000 cm^{-1} to 10000 cm^{-1} (238-1000 nm) at 220 K and 294 K", J. Quant. Spectrosc. Radiat. Transfer 59, 171-184 (1998); DOI: 10.1016/S0022-4073(97)00168-4

Electronic Schrödinger Equation: Single reference method hierarchy

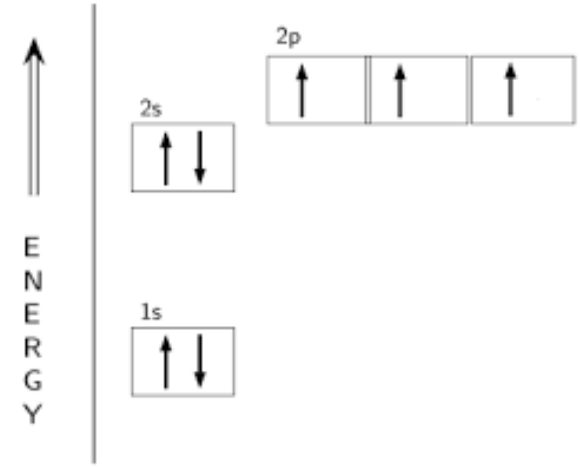


Chem. Soc. Rev. 2012, **41**, 6259

Molecular nitrogen: N_2



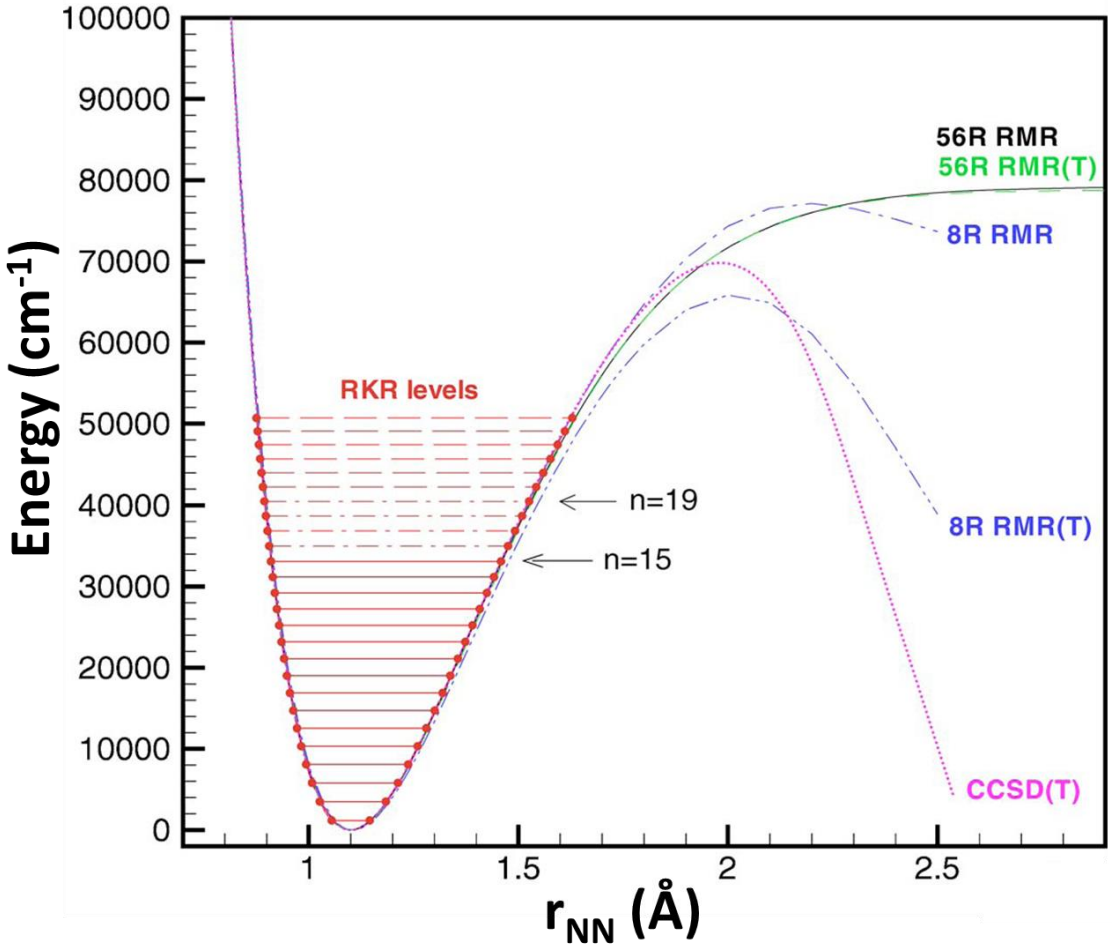
MO diagram of N_2



Atomic Nitrogen electron configuration

What happens if we don't account for changing of important electron configurations in N_2 as it dissociates?

Single-reference breakdown



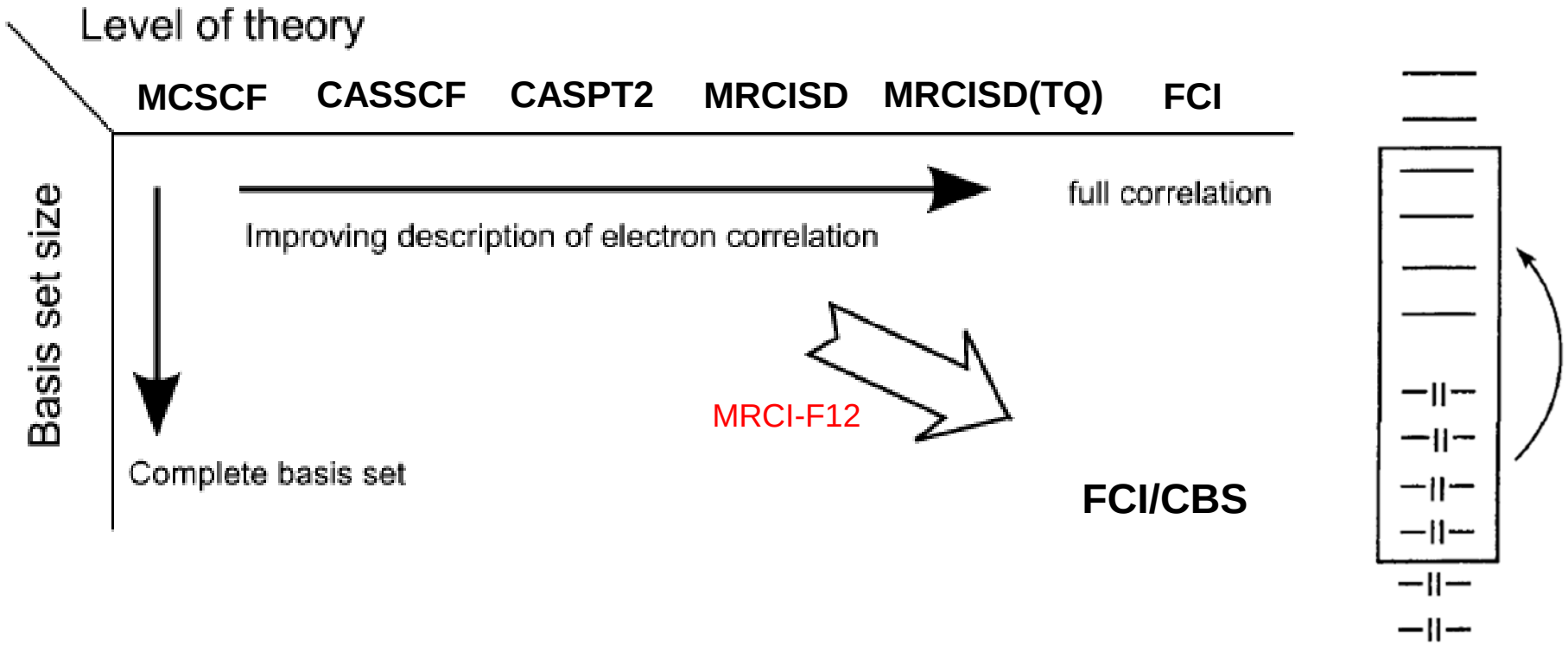
Divergence of CCSD(T) occurs for r_{NN} > 2 Å.

X. Li and J. Paldus, *J. Chem. Phys.* **129**, 054104 (2008).

Multireference Calculations

- **Multi-reference methods** (e.g. MRCI) are usually required when forming/breaking bonds, or even at particular minima when the electronic structure is not well-described by a single configuration (e.g. Ozone)
- Most convenient way to describe multiple states of the same symmetry and spin
- Multireference explicitly correlated F12 methods are available (CASPT2-F12, MRCI-F12).
- No common cost-effective strategies for higher-order correlation
  - Davidson correction to approximately restore size-consistency and extensivity is sometimes said to account for higher-order correlation, but often is not as accurate for thermochemistry as CCSD(T)
- Internal contraction used in Molpro to greatly reduce cost has been shown to affect the attractiveness of some PESs in dynamically important ways (e.g. HO_2, Harding, Klippenstein, Lischka, Shepard-*Theo. Chem. Acc.* **133** 1 (2014), O_3, A. Powell, N.S. Dattani, RFK Spada, FBC Machado, H. Lischka, R. Dawes, J. Chem. Phys. **147**, 094306 (2017).)

Electronic Schrödinger Equation: Multireference method hierarchy



Adapted from *Chem. Soc. Rev.* 2012, **41**, 6259

Dynamically-weighted state-averaged multireference electronic structure theory

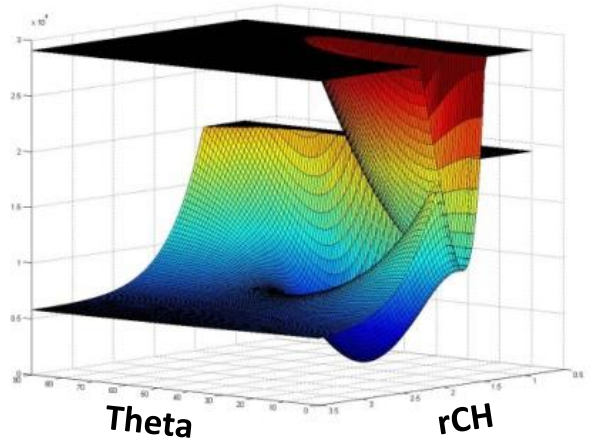
$$\overline{E}^{SA-MCSCF} = \sum_{i=0}^{n} \frac{w_i}{W} E_i^{MCSCF} \qquad W = \sum_{i=0}^{n} w_i$$

Dynamic weighting[1]

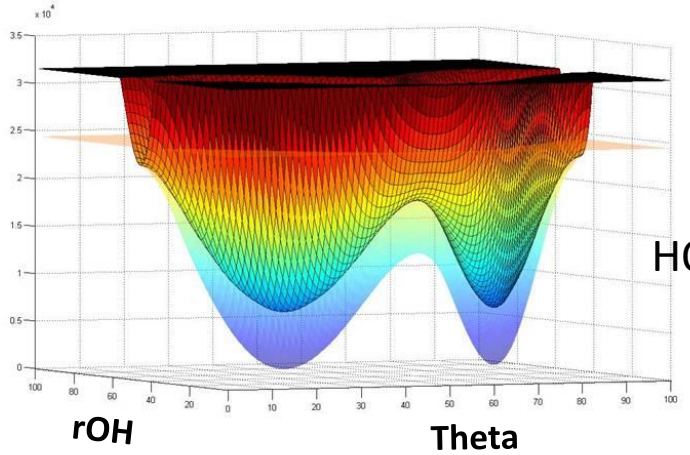
$$w_i = \cosh^2(\Delta E_{i0} / \beta) \qquad \Delta E_{i0} = E_i - E_0$$

Generalized dynamic weighting[2]

$$w_i = \cosh^2(\Delta E_{ij} / \beta) \qquad \Delta E_{ij} = |E_i - E_j|$$



HCO



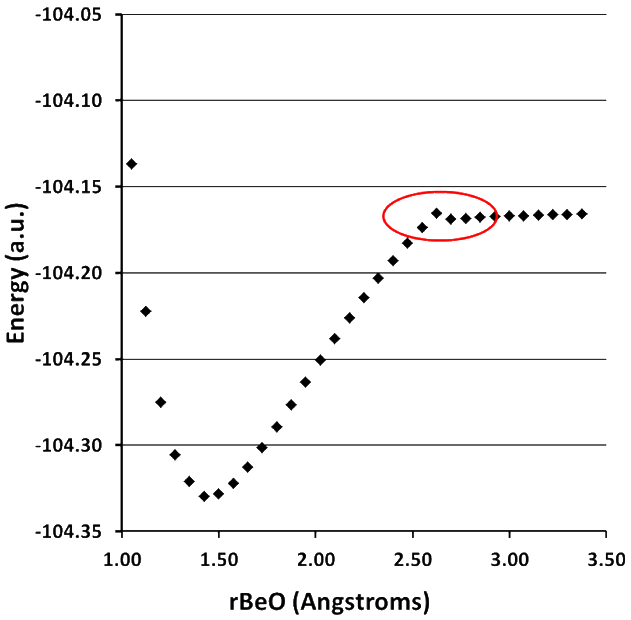
HO_2

[1]M.P. Deskevich, D.J. Nesbitt and H-J. Werner, JCP **120** 7281 (2004)

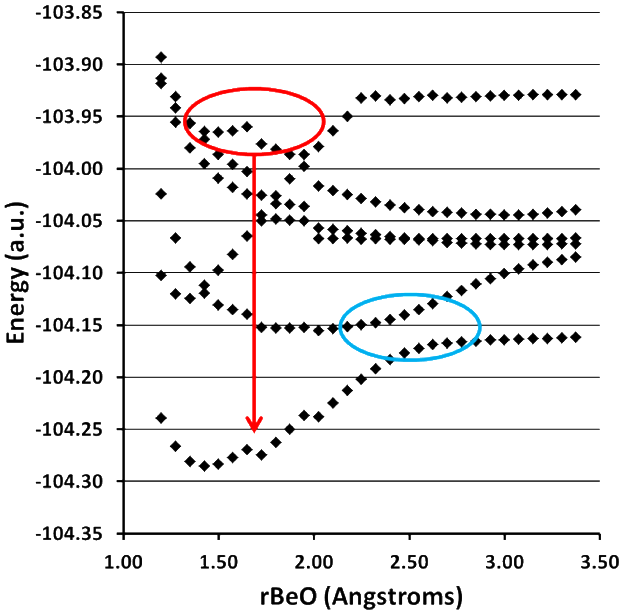
[2]R. Dawes, A.W. Jasper…S.A. Reid *et al.* J. Phys. Chem. Lett. **1** 641 (2010)

Importance of Dynamic Weighting: BeOBe → BeO + Be

1 state



23 states equal weights



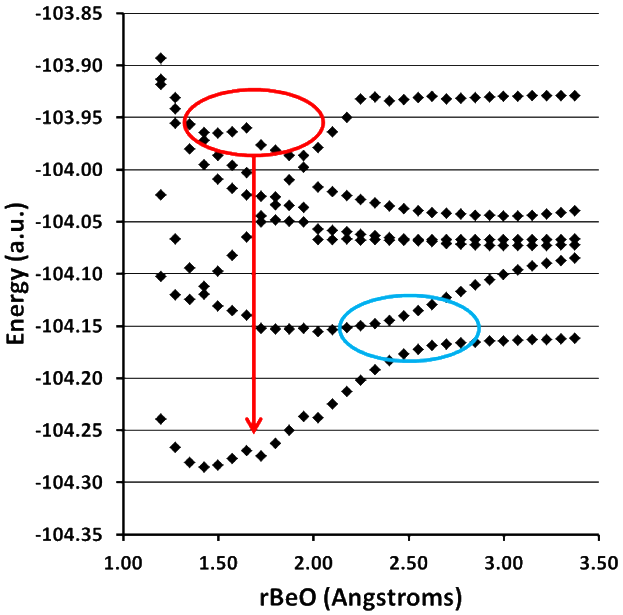
In single state calc (at left), avoided crossing with higher lying state (blue oval, at right) causes discontinuity.

In fixed weights calc (at right) crossing with higher lying state (red oval) causes discontinuity cascade affecting ground state.

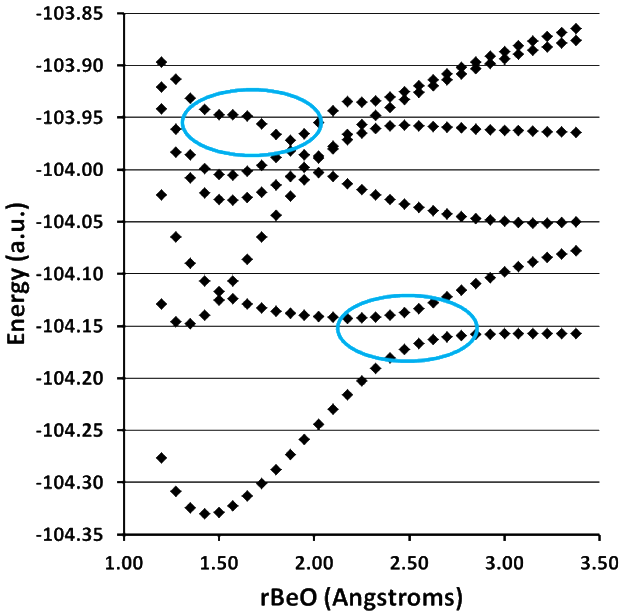
Six lowest A_1 states (co-linear asymmetric stretch C_{2V})

Importance of Dynamic Weighting: BeOBe → BeO + Be

23 states equal weights



23 states dynamic weights

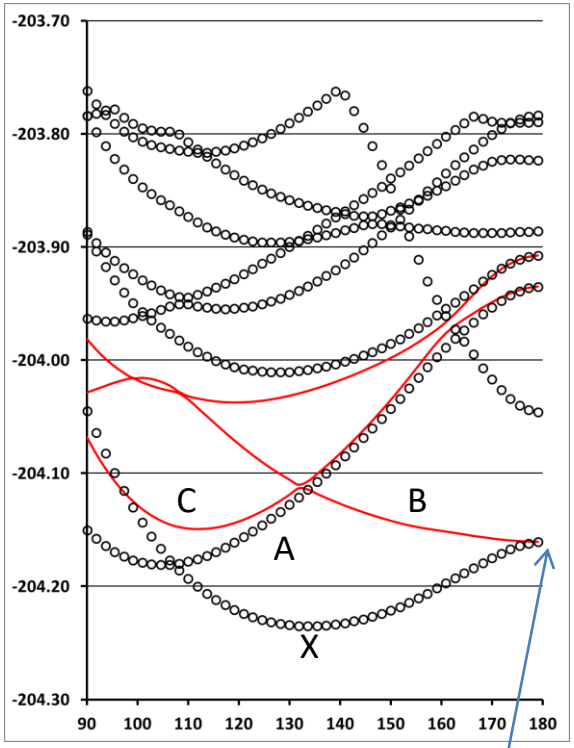


With dynamic weights (at right), crossing still occurs (blue oval), but due to negligible weight, no disruption results.

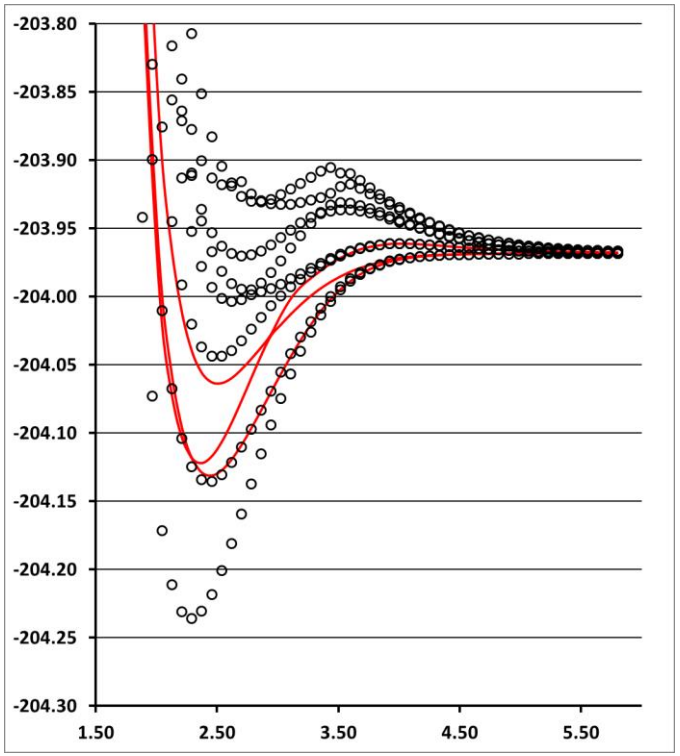
R.Dawes and S. Ndengué, "Single- and multireference electronic structure calculations for constructing potential energy surfaces", *International Reviews in Physical Chemistry* **35**, 441 (2016).

Dynamic weighting applied to 18 doublet states of NO_2

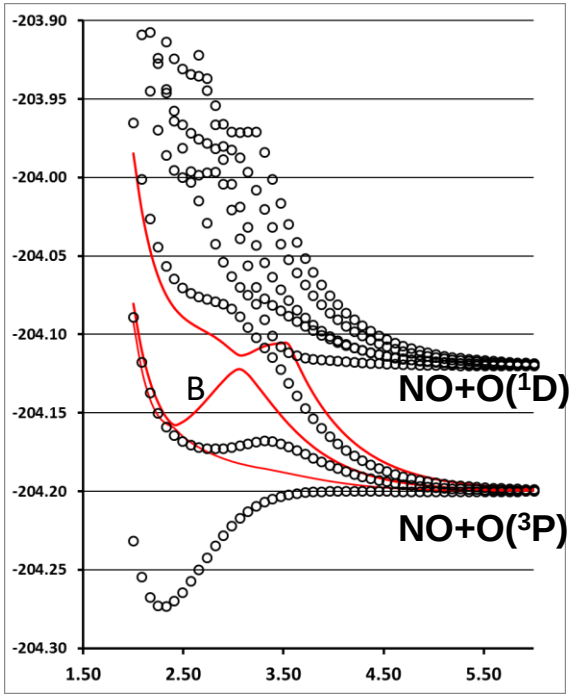
Each plot shows a different cut through the PESs
Calculations include 8 A’ and 10 A’’ states
Plot only show 8 A’ (open symbols) and lowest 3 A’’ states (red)



Bend: bond distances held at equilibrium
-X and A states cross around 107°
-X and B states form RT pair at 180°
2 A’’ states cross in vicinity of FC region



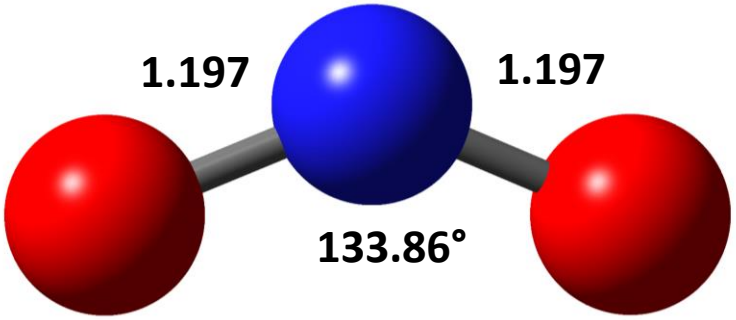
Symmetric stretch: angle held at equilibrium, 133°
-all 18 included states are degenerate at separate atoms asymptote (ground state atoms) as expected



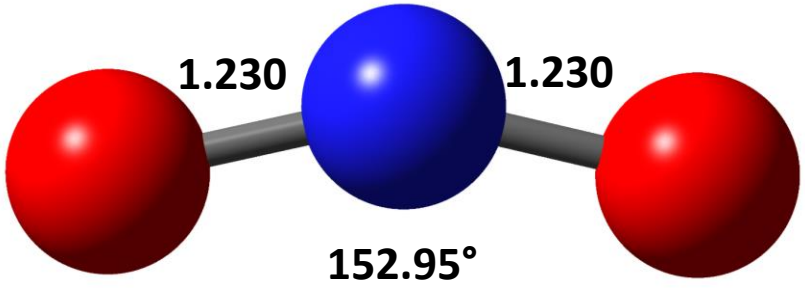
Asymmetric stretch: one distance and angle held at equilibrium
-states form two blocks at NO + O limit

Normal mode displaced geometries for MRCI-F12(Q)/VTZ-F12 method

EQ

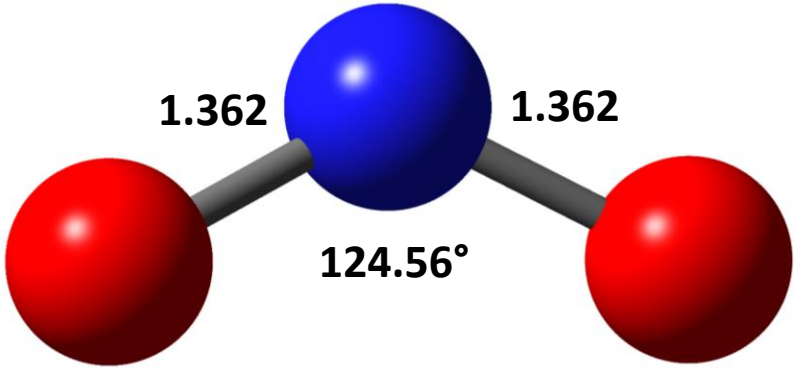


Bend : Q1 = -0.2 Å

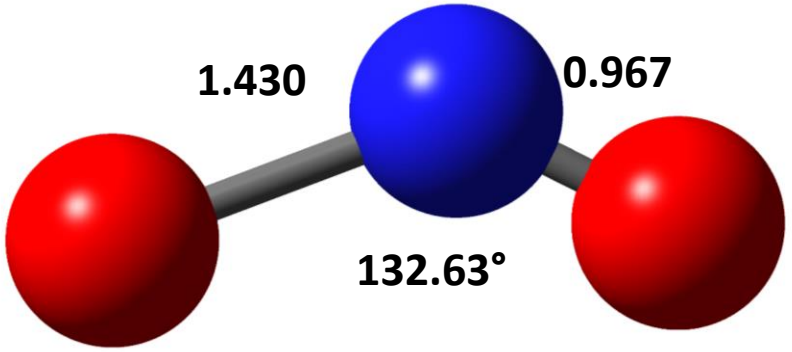


Note – phase of bend is such that positive displacement *contracts* the angle

Symmetric Stretch : Q2 = 0.2 Å

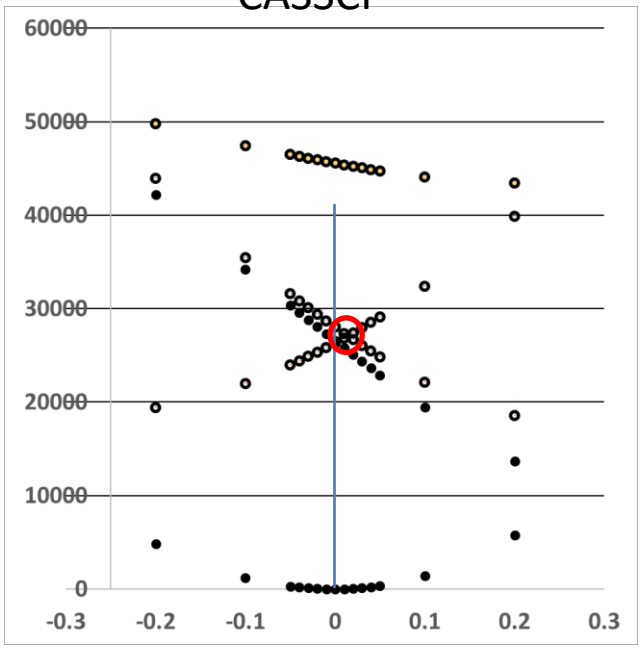


Asymmetric Stretch : Q3 = -0.2 Å

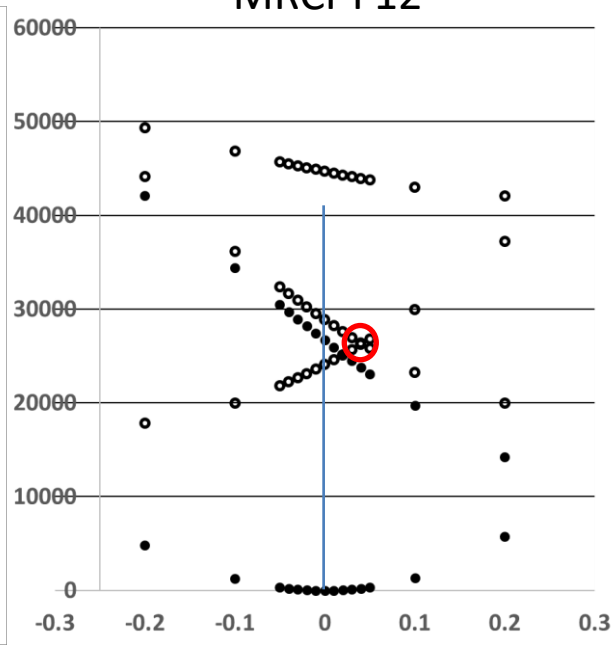


Effect of dynamic correlation on state gaps and crossing points

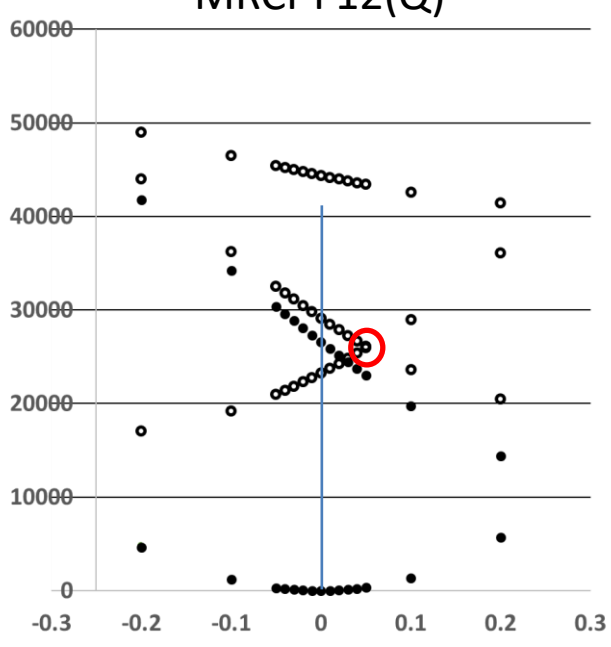
CASSCF



MRCI-F12



MRCI-F12(Q)



Dynamic electron correlation significantly affects energies of A'' states and the location of their crossing

Crossing point

Vertical excitation

Filled symbols – A' states

Open symbols – A'' states

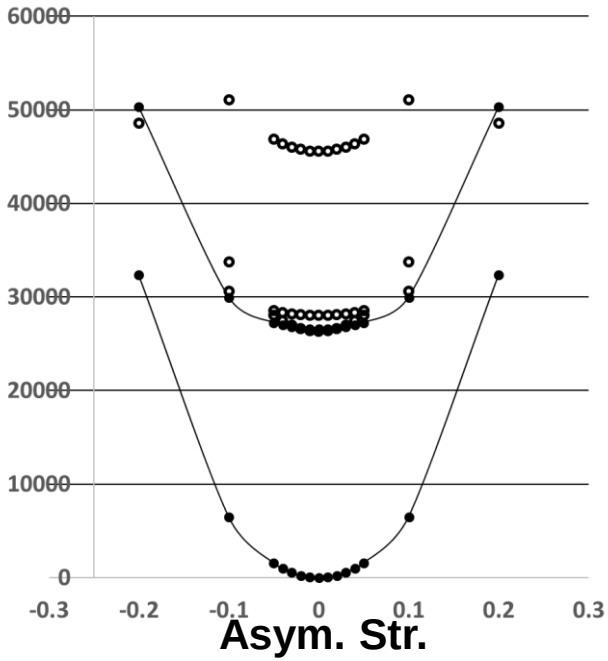
Vertical gaps CASSCF level 26588, 26375, 28747

Vertical gaps MRCI level 26694, 24104, 28883

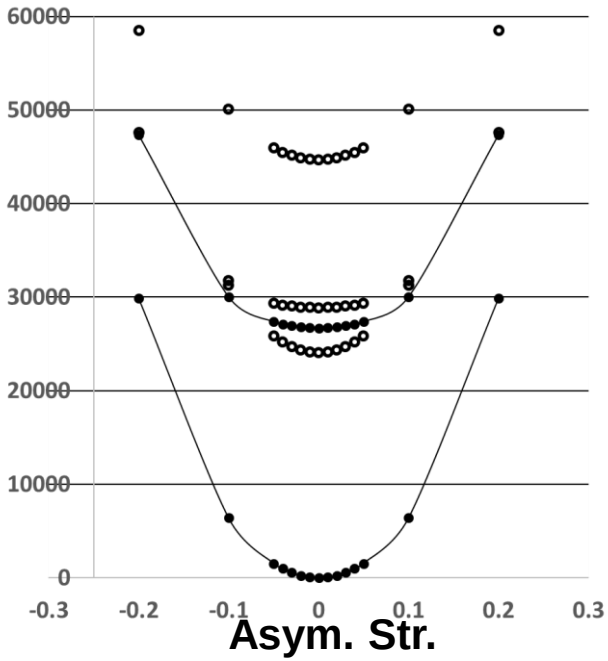
Vertical gaps MRCI(Q) level 26593, 23283, 29145

Effect of dynamic correlation on state gaps and crossing points

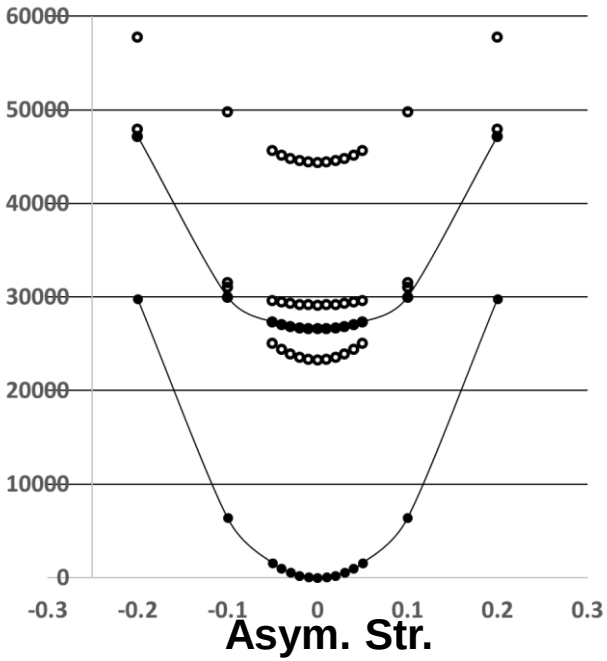
CASSCF



MRCI-F12

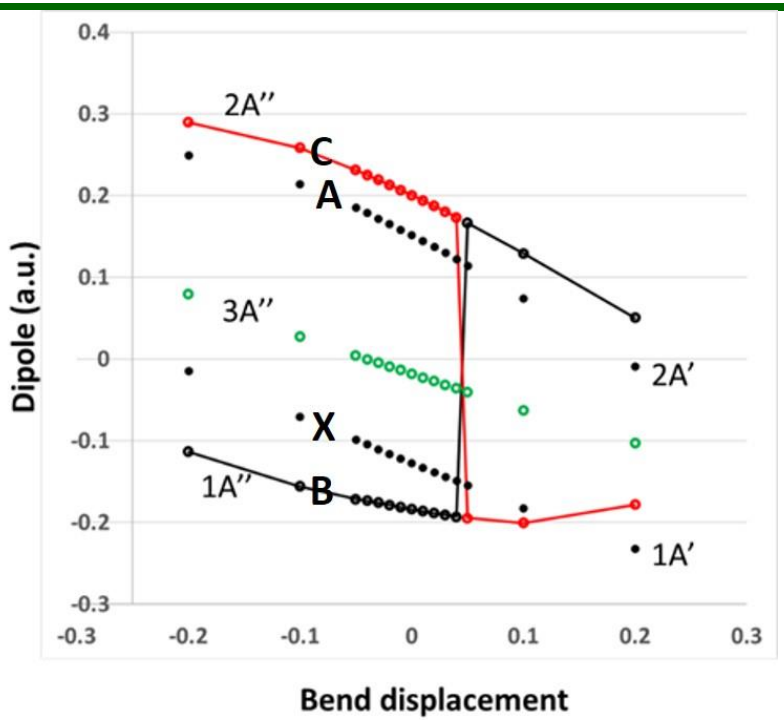


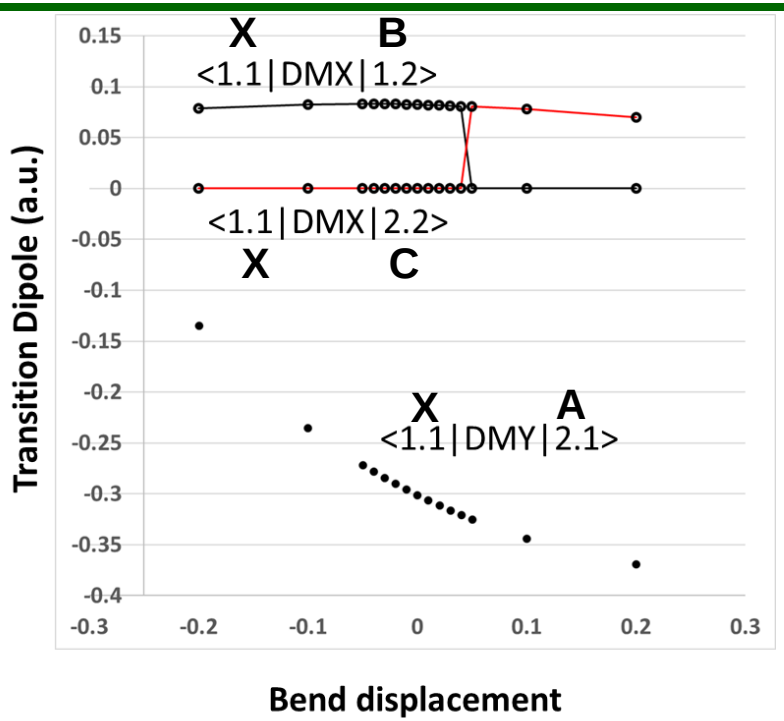
MRCI-F12(Q)



Energies along asymmetric stretch coordinate are symmetric with respect to positive/negative displacement. The two most relevant A'' states don't cross along this coordinate. The A'' energies and spacing are sensitive to dynamic electron correlation

Dipoles and Diabatization





Dipoles of the two A'' states which cross, abruptly switch character (and sign) making for a convenient properties based diabatization.

$$\mathbf{U} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix},$$

$$\theta = \frac{1}{4}\tan^{-1}\left(\frac{G}{-F}\right),$$

$$F = |\boldsymbol{\mu}^0_{12}|^2 - |\boldsymbol{\mu}^0_{11} - \boldsymbol{\mu}^0_{22}|^2/4,$$

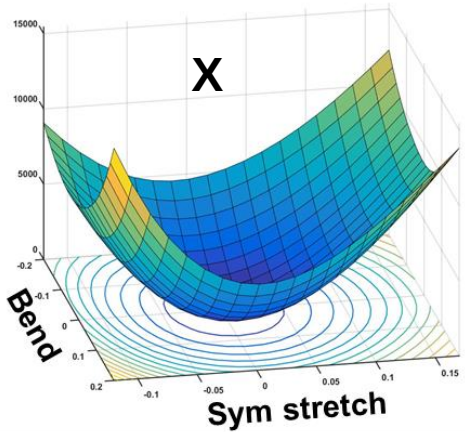
$$G = \boldsymbol{\mu}^0_{12} \cdot (\boldsymbol{\mu}^0_{11} - \boldsymbol{\mu}^0_{22}),$$

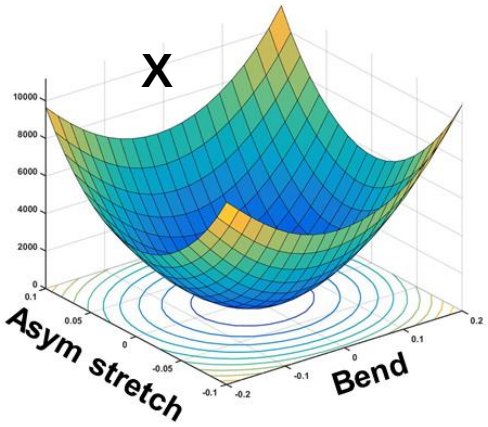
$$\boldsymbol{\mu}^0_{JK} = \langle \Phi_J | \hat{\boldsymbol{\mu}} | \Phi_K \rangle.$$

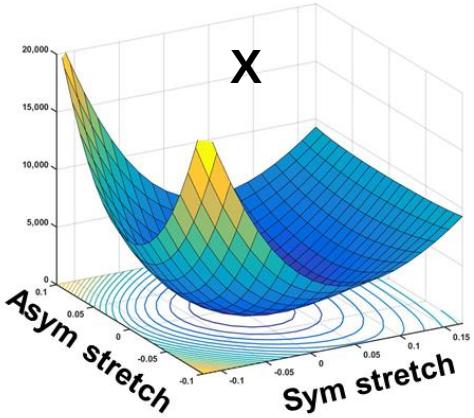
Samanta K, Beames JM, Lester MI, Subotnik JE. JCP 2014;141(13):134303.

Fitted Surfaces: Energies

~1500 symmetry unique data fit with committee of neural networks
Energies at MRCI-F12(Q):GDW(18)-CASSCF(13*e*,10*o*)/VTZ-F12 level

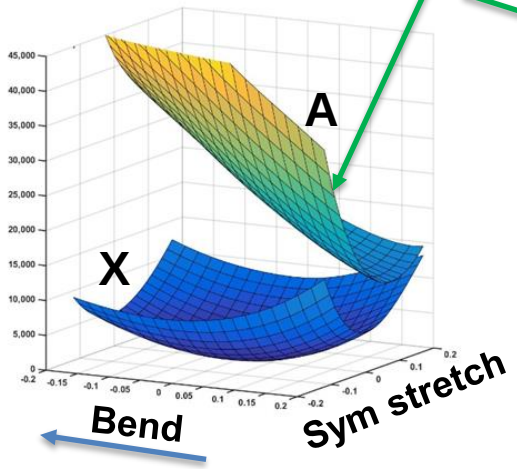


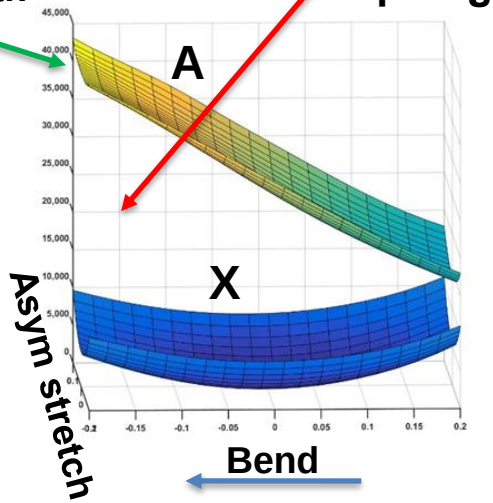


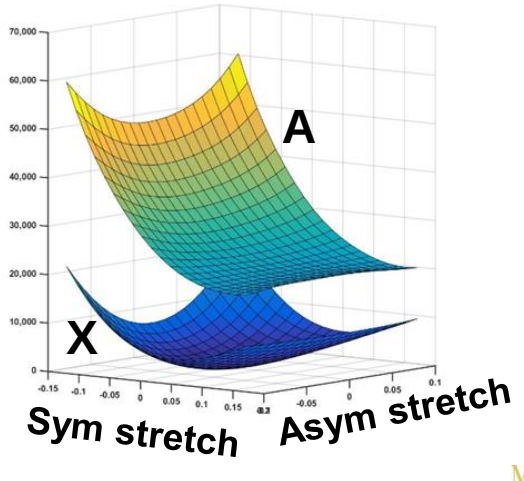


A-state varies much more with sym str.

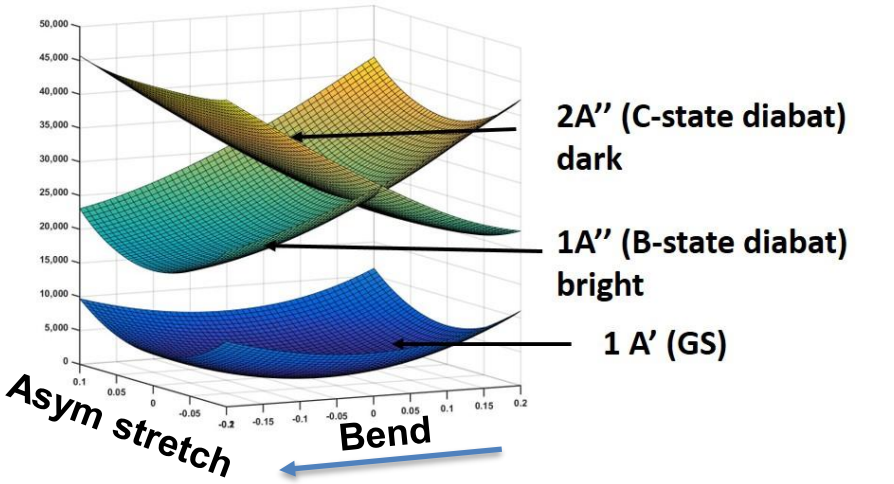
Gap larger for larger angles…

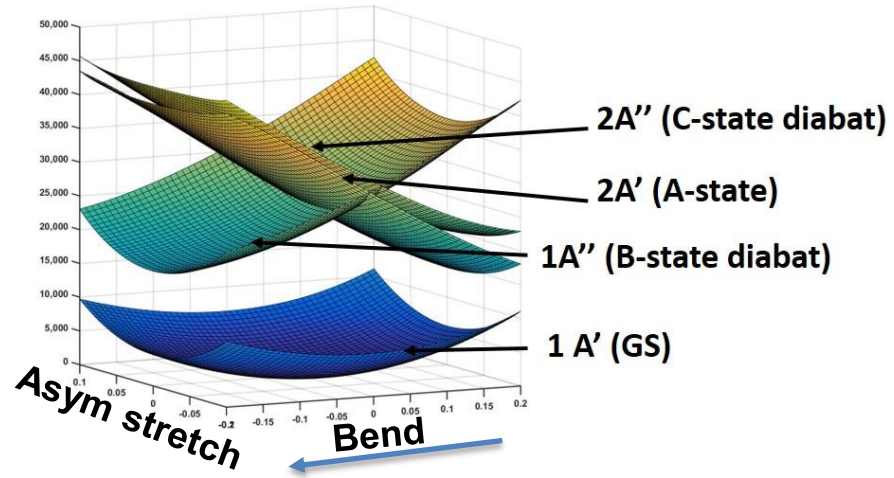


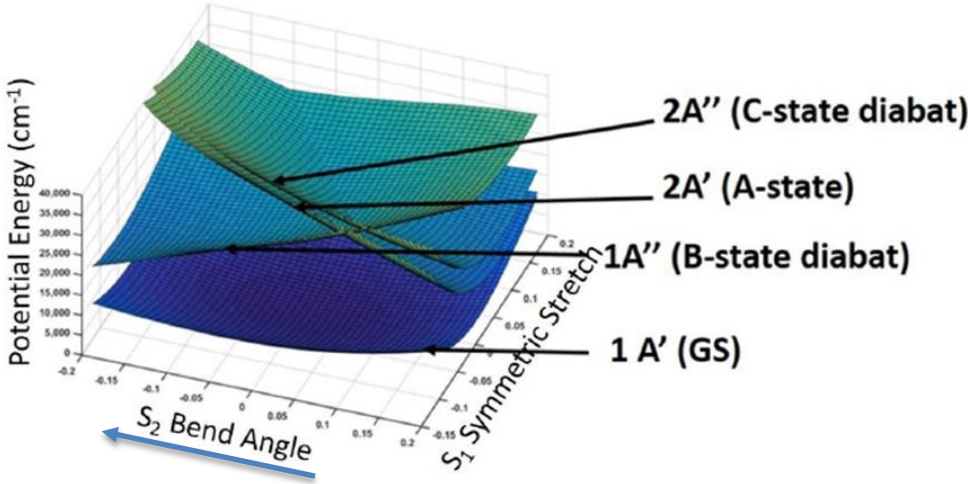


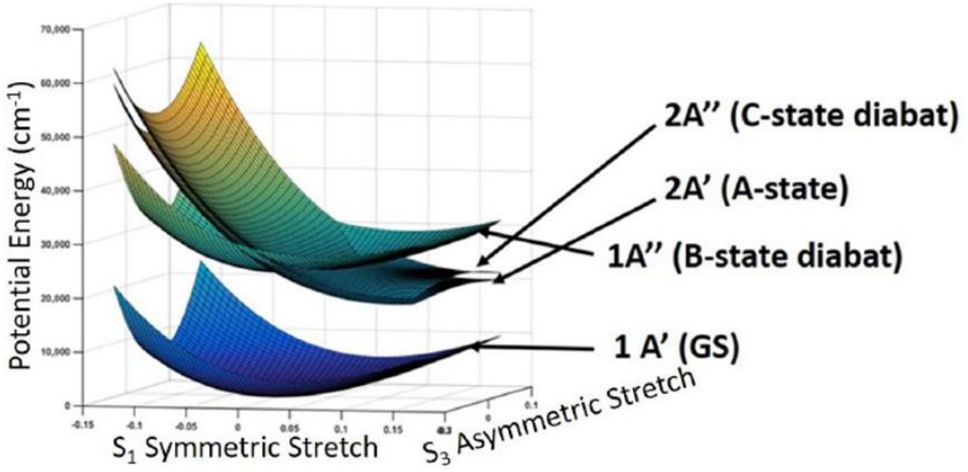


Fitted Surfaces: Energies

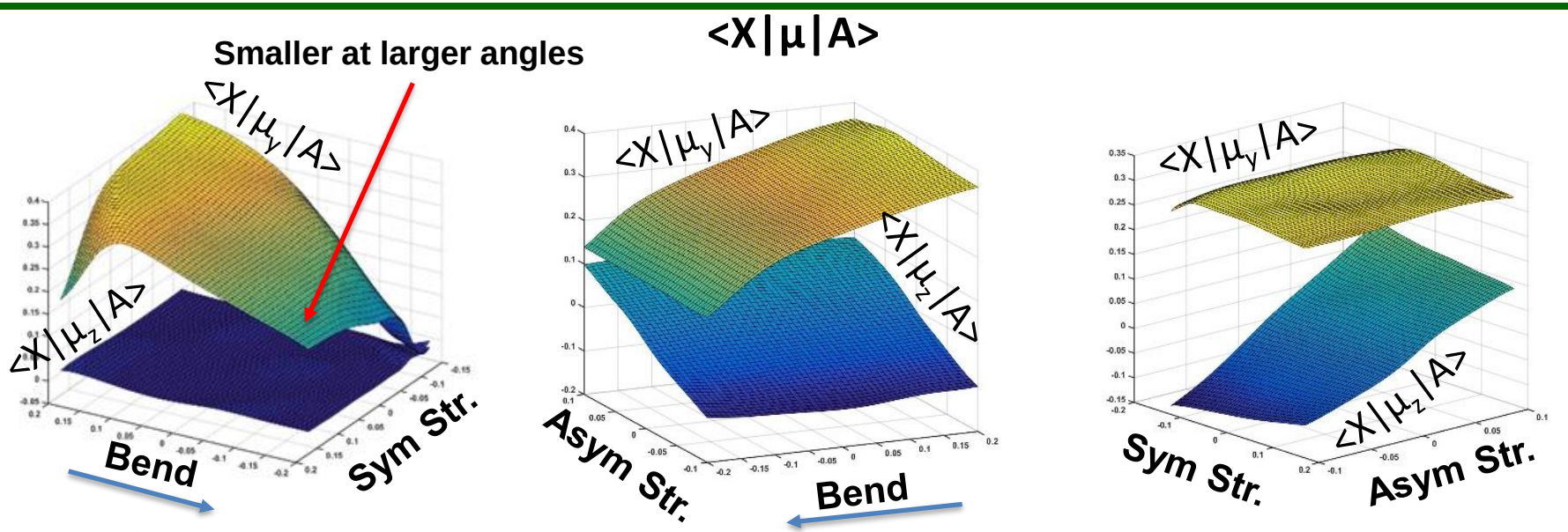


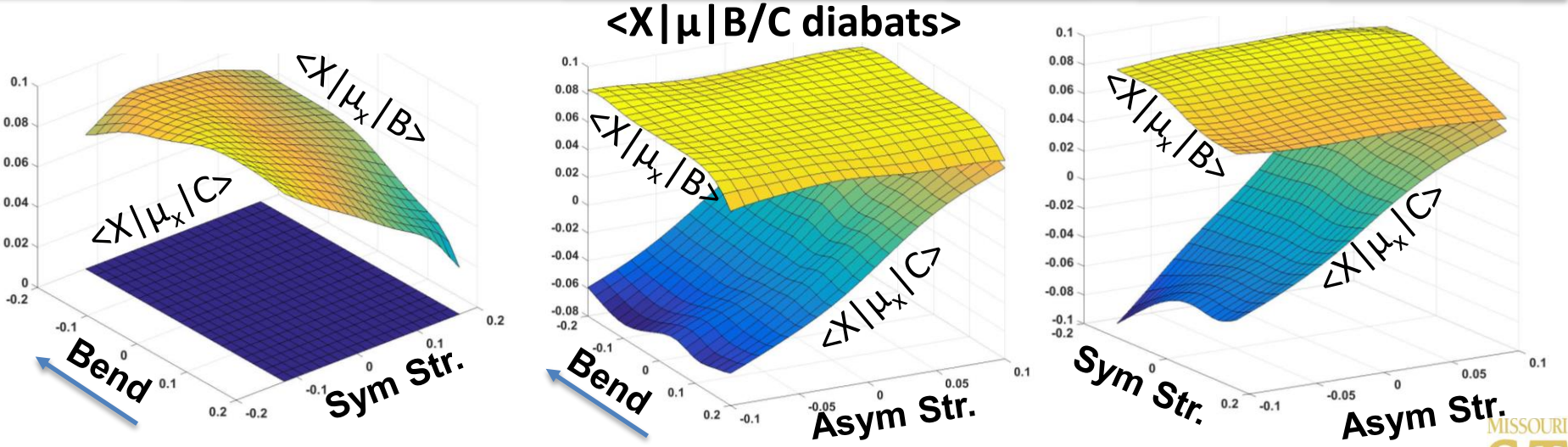




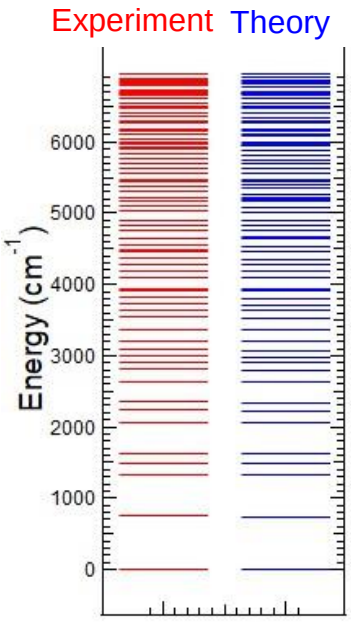


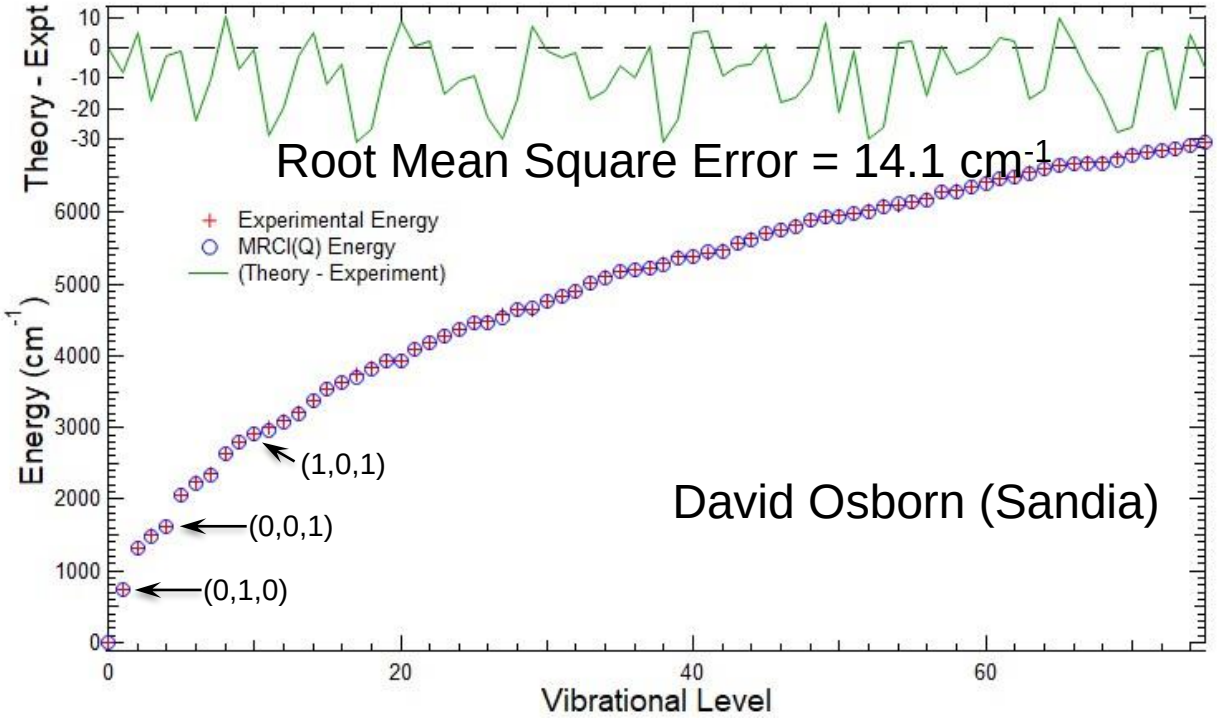
Fitted Surfaces: Transition Dipoles





Ground State Vibrational Levels





- Vibrational states computed using large DVR basis with numerically exact kinetic operator
- MCTDH method yields same energies
- Initial test of lowest 76 levels finds RMSE of 14.1 cm^{-1} confirming accuracy of PES
- Error much larger without Davidson correction (~100 cm^{-1})
- Error doesn't increase at higher energies??...

Ground State Vibrational Levels

	Modal	Calc	Calc-ZPE	EXPT*	Expt-Calc
1	0,0,0	1870.239	0.000	0.00	0.00
2	0,1,0	2611.628	741.389	749.65	8.26
3	1,0,0	3195.168	1324.929	1319.79	-5.14
4	0,2,0	3351.313	1481.074	1498.34	17.27
5	0,0,1	3484.052	1613.813	1616.85	3.04
6	1,1,0	3932.341	2062.102	2063.12	1.02
7	0,3,0	4091.960	2221.721	2246.04	24.32
8	0,1,1	4214.738	2344.499	2355.15	10.65
9	2,0,0	4507.912	2637.673	2627.34	-10.33
10	1,2,0	4668.544	2798.305	2805.60	7.30
11	1,0,1	4775.601	2905.362	2906.07	0.71
12	0,4,0	4834.125	2963.886	2993.00	29.11
13	0,2,1	4943.023	3072.784	3092.48	19.70
14	0,0,2	5069.031	3198.792	3201.44	2.65
15	2,1,0	5239.784	3369.545	3364.57	-4.97
16	1,3,0	5405.001	3534.762	3547.10	12.34
17	1,1,1	5502.523	3632.284	3637.84	5.56
18	0,5,0	5577.652	3707.413	3738.60	31.19
19	0,3,1	5672.651	3802.412	3829.34	26.93
20	0,1,2	5787.813	3917.574	3929.12	11.55
21	3,0,0	5808.052	3937.813	3922.61	-15.20
22	2,2,0	5971.248	4101.009	4100.58	-0.43
23	2,0,1	6052.372	4182.133	4179.94	-2.19
24	1,4,0	6141.782	4271.543	4286.82	15.28
25	1,2,1	6228.114	4357.875	4369.10	11.23
26	0,6,0	6321.974	4451.735	4482.57	30.84
27	1,0,2	6329.630	4459.391	4461.07	1.68
28	0,4,1	6404.246	4534.007	4564.22	30.21
29	0,2,2	6505.384	4635.145	4656.34	21.19
30	3,1,0	6533.822	4663.583	4652.00	-11.58

RMSE for lowest 76 levels = 14.1 cm^{-1}

RMSE for lowest 125 levels = 16.5 cm^{-1}

		Bend				
			E(n)-E(n-1)		E(n)-E(n-1)	
		calc		expt		Expt-calc
1	0,0,0	0.000		0.00		0.00
2	0,1,0	741.389	741.389	749.65	749.65	8.26
4	0,2,0	1481.074	739.685	1498.34	748.69	17.27
7	0,3,0	2221.721	740.647	2246.04	747.70	24.32
12	0,4,0	2963.886	742.165	2993.00	746.96	29.11
18	0,5,0	3707.413	743.527	3738.60	745.60	31.19
26	0,6,0	4451.735	744.322	4482.57	743.97	30.84
37	0,7,0	5195.909	744.174	5224.55	741.98	28.64
50	0,8,0	5938.550	742.641	5965.61	741.06	27.06
67	0,9,0	6677.777	739.227	6705.23	739.62	27.45
88	0,10,0	7411.096	733.319	7443.09	737.86	31.99

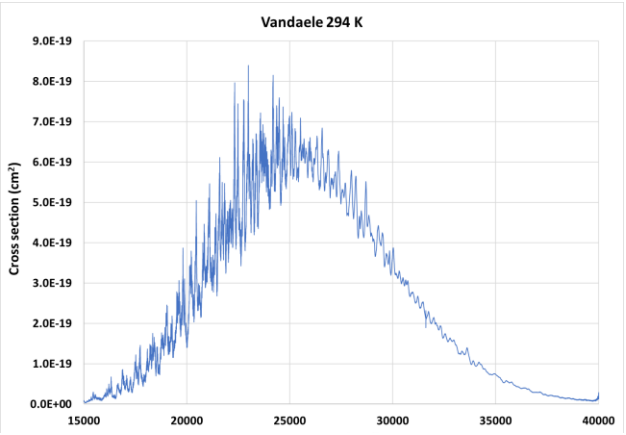
		Sym stretch						
1	0,0,0	0.000		0.00		0.00		
3	1,0,0	1324.929	1324.929	1319.79	1319.79	-5.14	calc anharm	expt anharm
9	2,0,0	2637.673	1312.744	2627.34	1307.55	-10.33	-12.185	-12.24
21	3,0,0	3937.813	1300.140	3922.61	1295.27	-15.20	-12.604	-12.28
38	4,0,0	5225.218	1287.405	5205.81	1283.20	-19.41	-12.735	-12.07
63	5,0,0	6499.670	1274.452	6475.05	1269.24	-24.62	-12.953	-13.96
98	6,0,0	7760.091	1260.421	7730.08	1255.03	-30.01	-14.031	-14.21

		asym stretch						
1	0,0,0	0.000		0.00		0.00		
5	0,0,1	1613.813	1613.813	1616.85	1616.85	3.04	calc anharm	expt anharm
14	0,0,2	3198.792	1584.979	3201.44	1584.59	2.65	-28.834	-32.26
31	0,0,3	4753.133	1554.341	4754.21	1552.77	1.08	-30.638	-31.82
58	0,0,4	6276.629	1523.496	6275.98	1521.77	-0.65	-30.845	-31.00
99	0,0,5	7767.589	1490.960	7766.28	1490.30	-1.31	-32.536	-31.47

*** Delon, A. and Jost, R., 1991. *The Journal of chemical physics*, *95*(8), pp.5686-5700.**

MISSOURI S&T

UV absorption spectrum: The reflection principle and T-dep



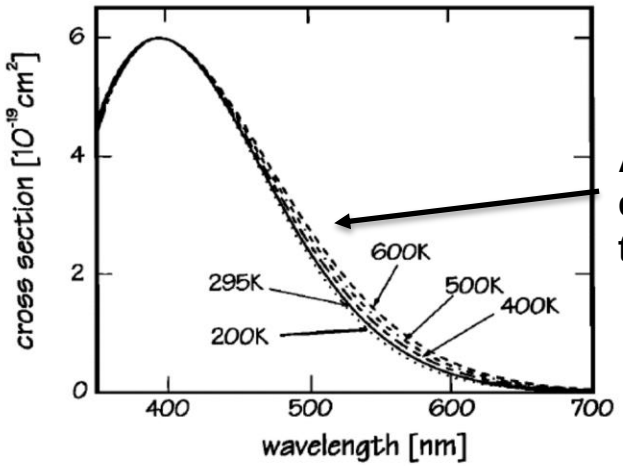


Figure 5. The evolution of the gross (envelope) cross section from 200 to 600 K. It should be noted that the temperature effect increases dramatically to the IR. The temperature dependence on the blue side, below 350 nm, is more difficult to characterize, mainly because N_2O_4 absorbs in that range. Then, it is difficult to discriminate between the temperature effect on the NO_2 absorption cross section itself and on the NO_2/N_2O_4 ratio effect.

Reflection principle estimates envelope usually with Condon approx.

Analysis of low-energy envelope as function of temperature.

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 102, NO. D13, PAGES 16,089-16,098, JULY 20, 1997

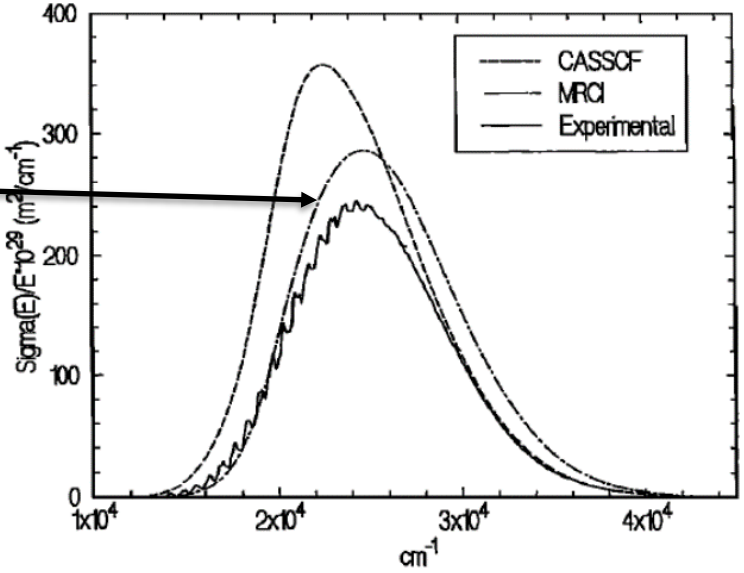
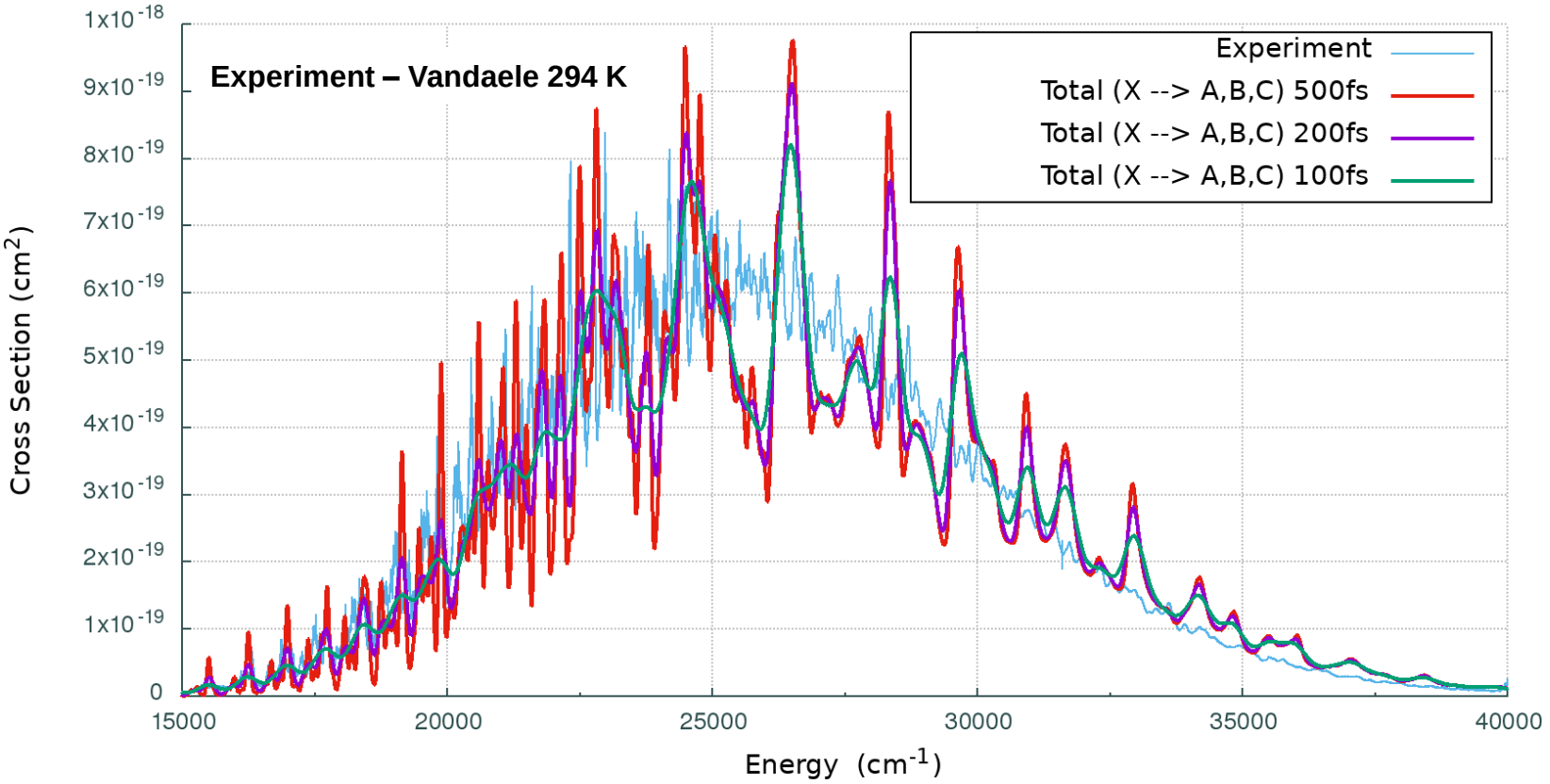


Figure 10. The comparison between the calculated absorption cross sections and the experimental absorption cross section at very low resolution. The absorption cross sections have been calculated using a two-dimensional reflection method and ab-initio PESs calculated at two levels of theory: complete active space self-consistent field (CASSCF) and internally contracted multireference configuration interaction (MRCI) (J.Lievin et al., manuscript in preparation, 1997).

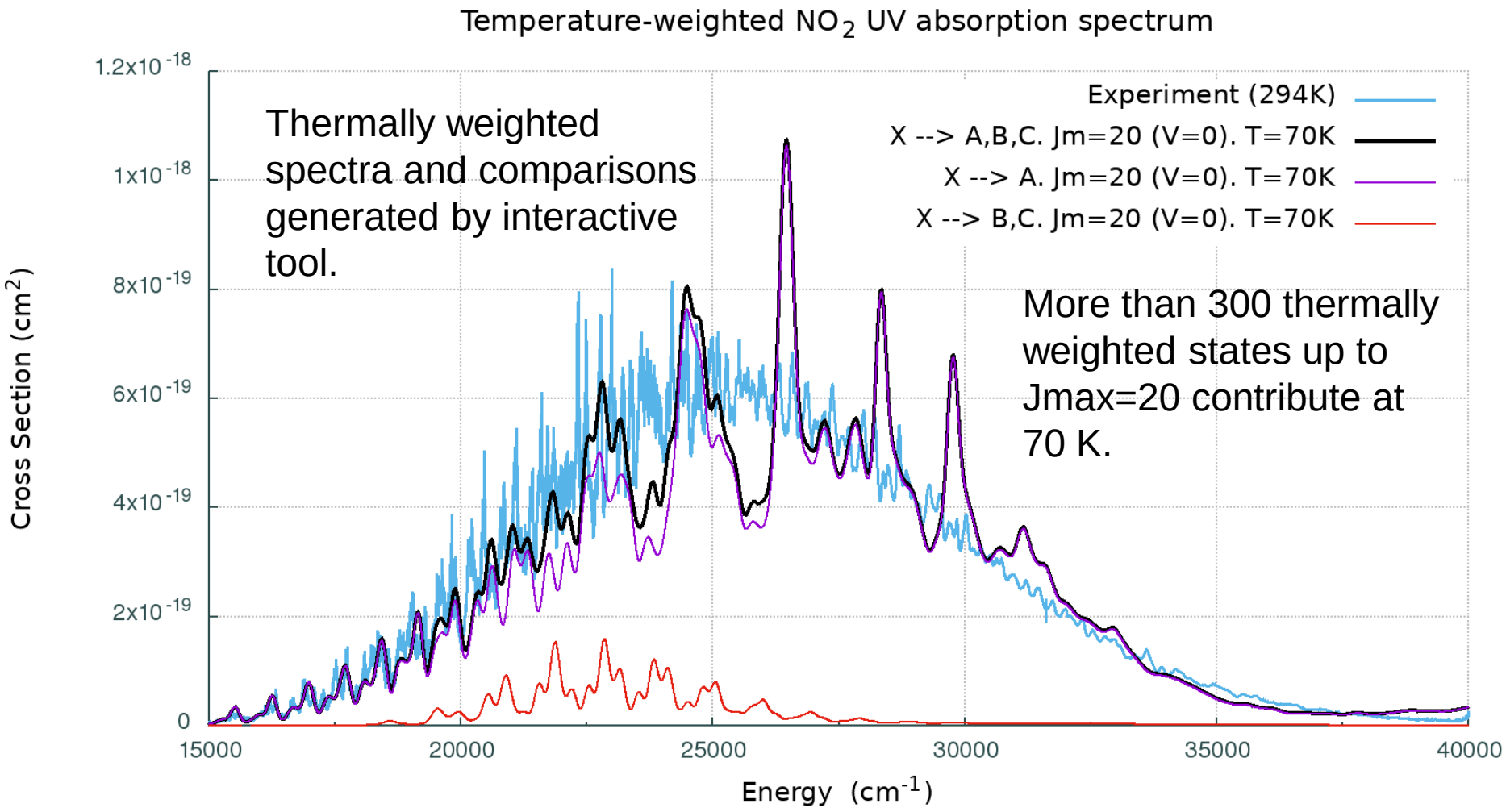
Rémy Jost studied NO_2 extensively for many years and provided a clear foundation of understanding

Calculated UV Spectrum (zero Kelvin) MCTDH 100-500 fs propagations

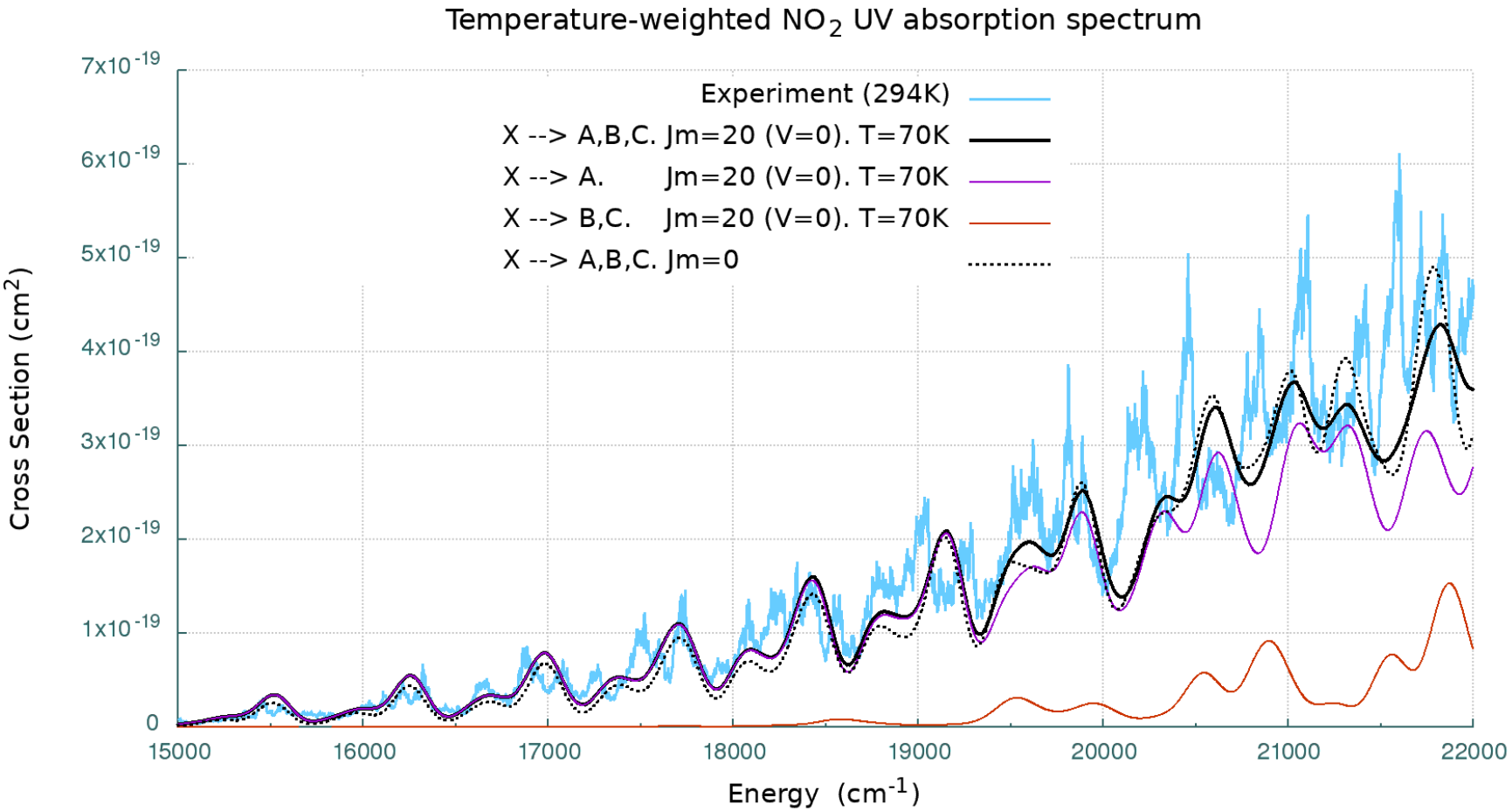


- Total integrated cross section (15,000 – 40,000) matches experiment to within 1.5%
- At 294 K, only 2.5% of population is in higher vibrational levels, but **many hundreds of rotational states** are populated

Calculated spectrum (200fs) at 70 K

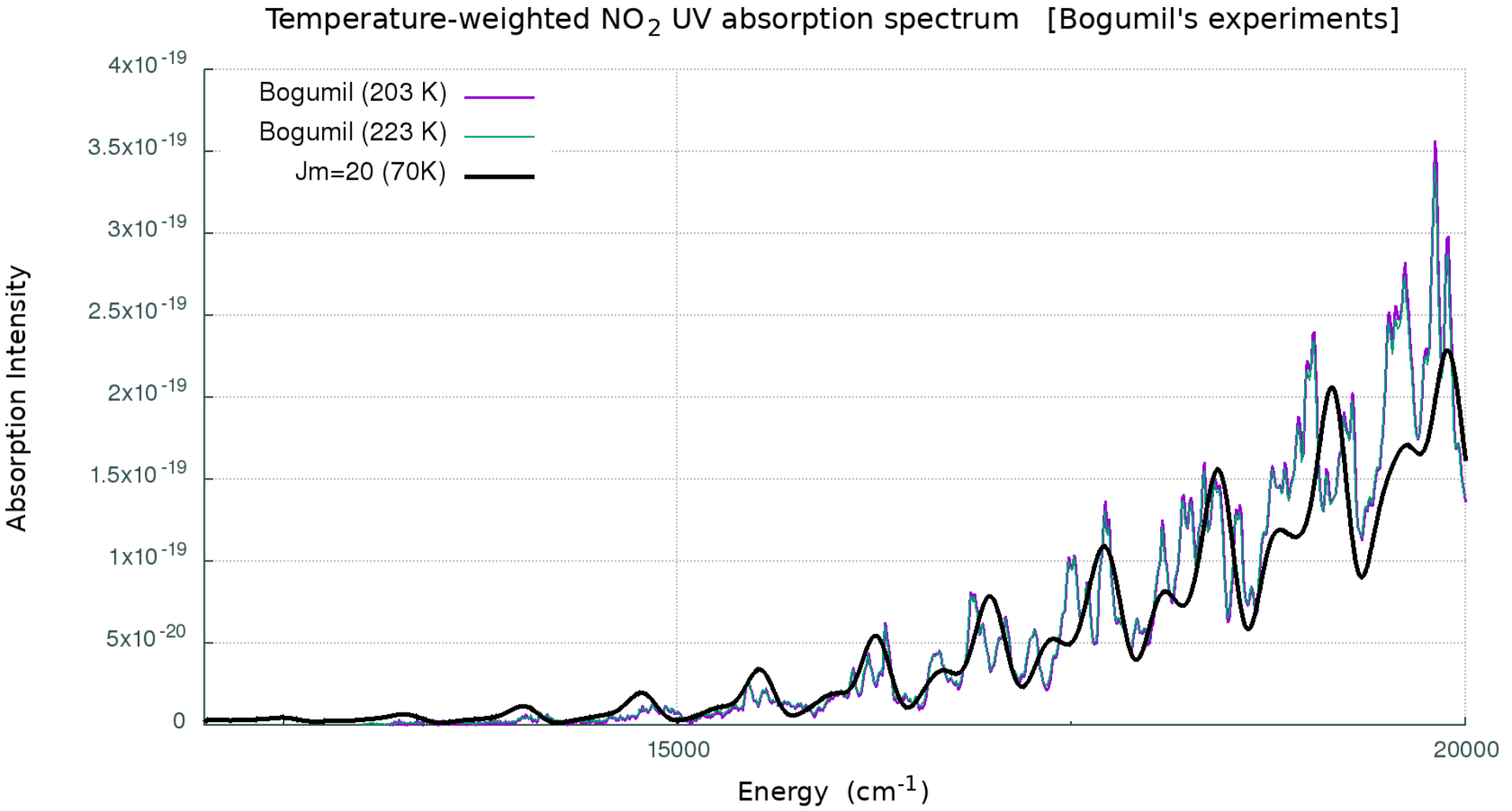


Calculated spectrum (200fs) at 70 K

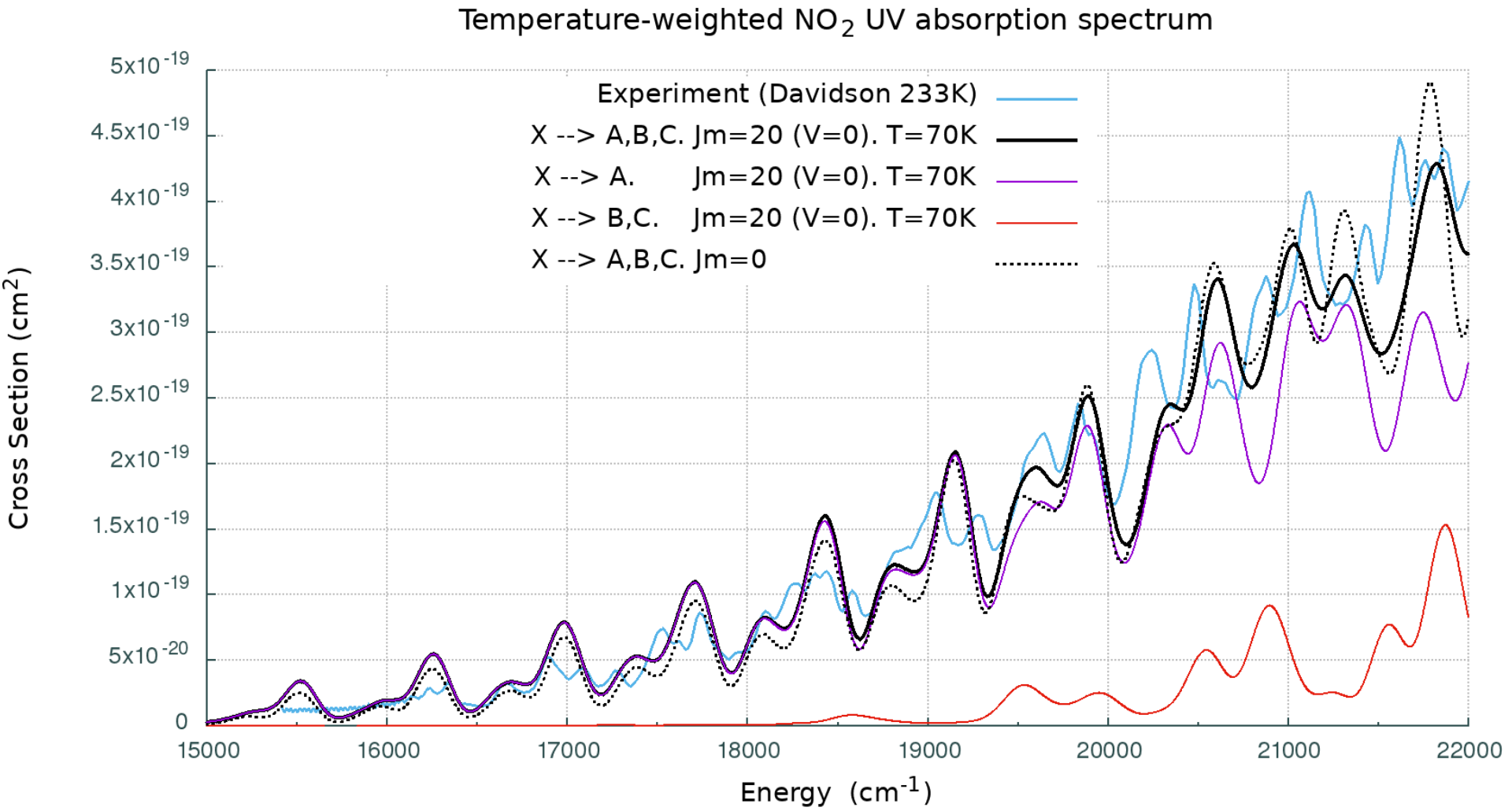


Calculation at 70 K reproduces some of the detailed structure in low-energy wing coming from both X→A and X →B/C contributions, but doesn't match expt. resolution.

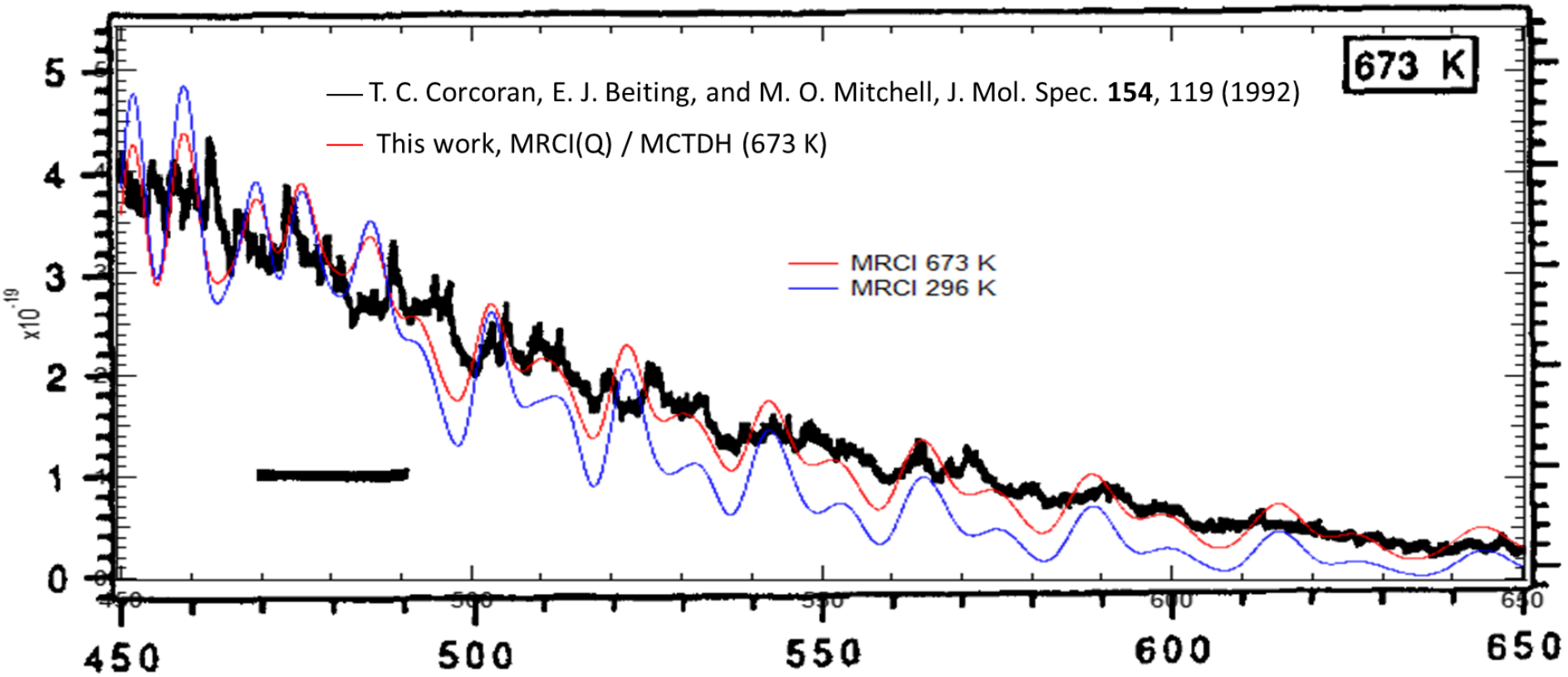
Calculated spectrum (200fs) at 70 K



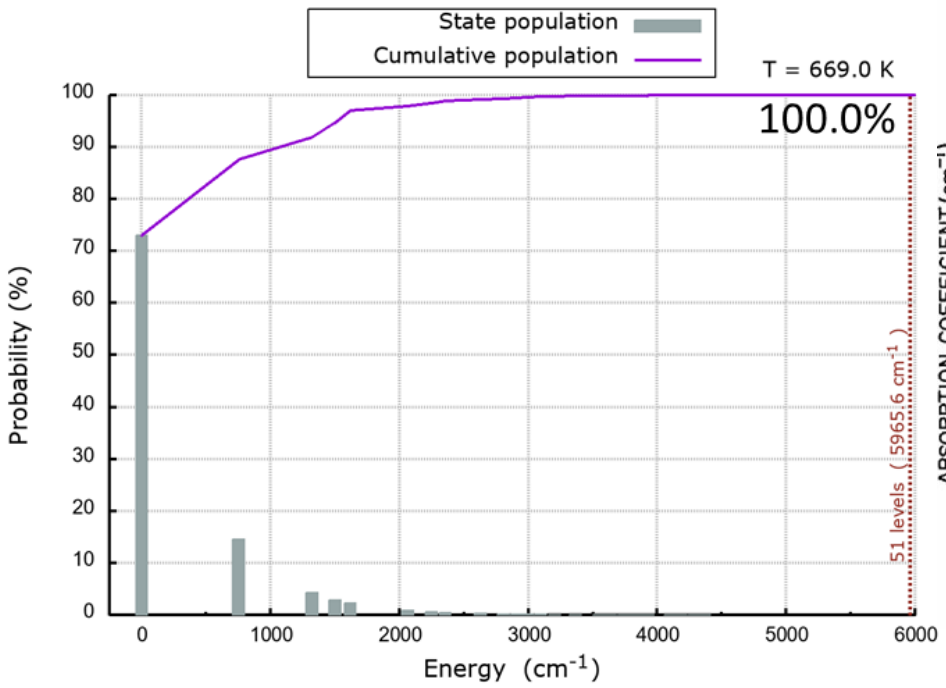
Calculated spectrum (200fs) at 70 K

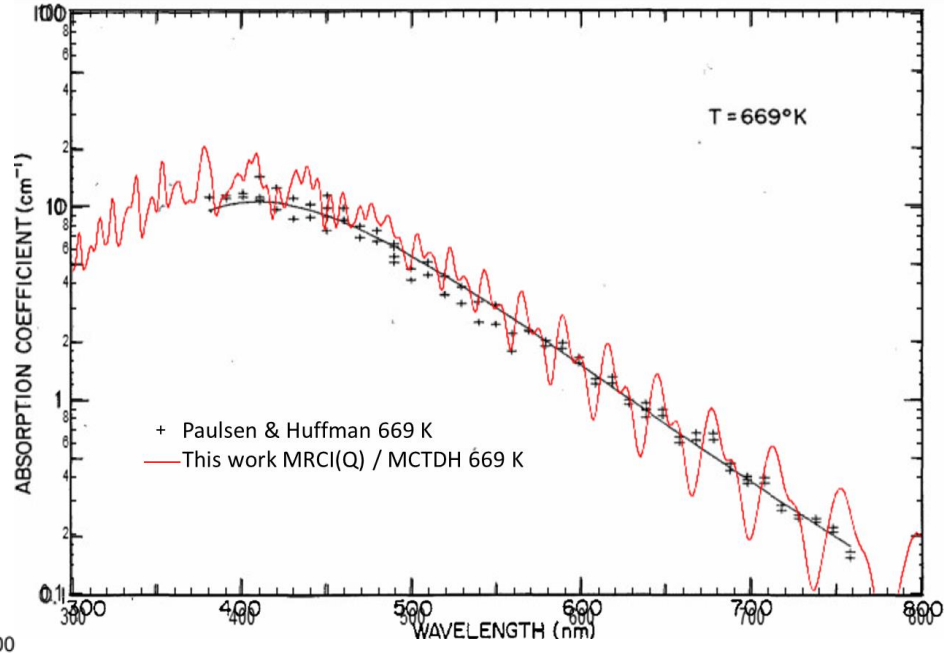


Simulations of higher temperature



Comparison to Paulsen and Huffman (669 K)

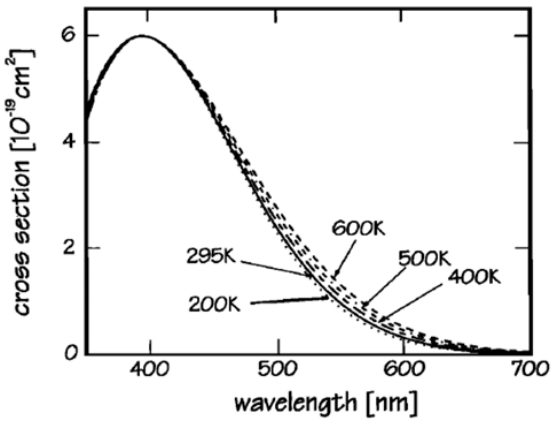


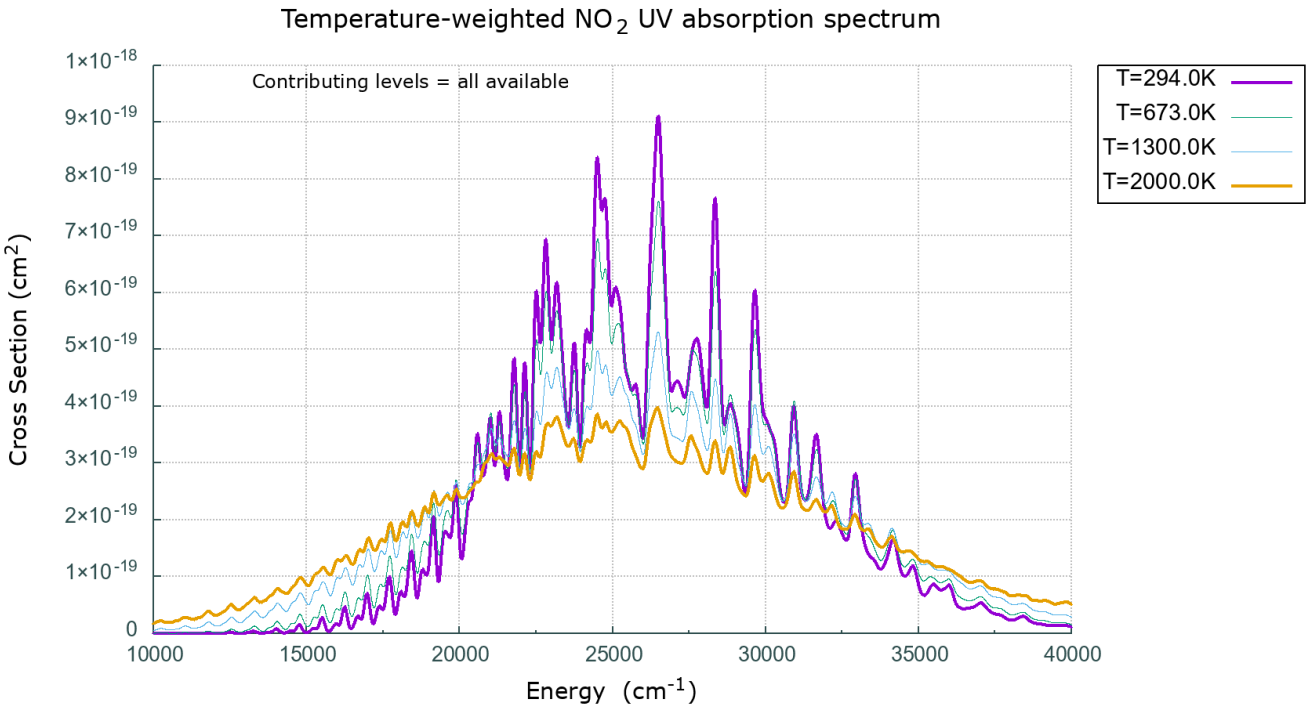


D. E. Paulsen and R. E. Huffman
Air Force Geophysics Laboratory
Hanscom AFB (1976)

Ground vibrational state remains dominant, while a rapidly increasing number of states make small contributions.

Temperature scans using the tool

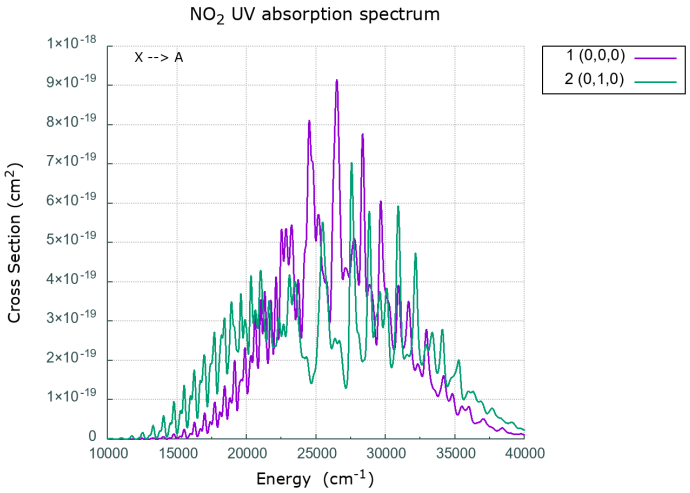


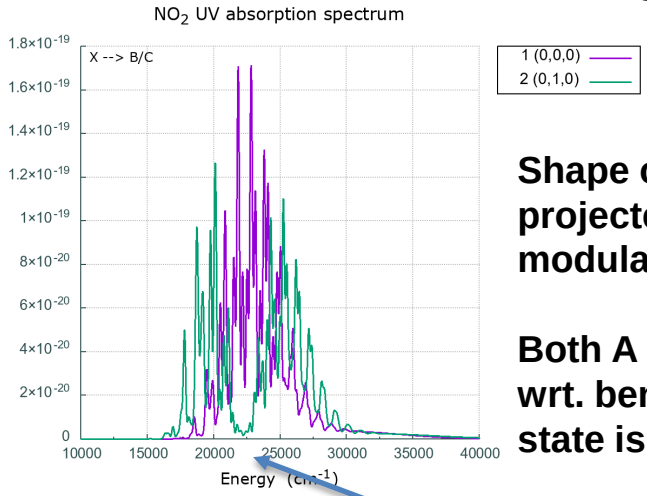


125 contributing vibrational states

Mode specific effects and contributions

Bend mode excited (0,1,0)



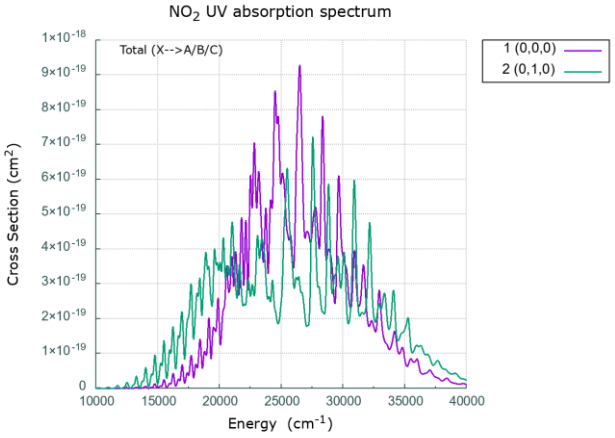


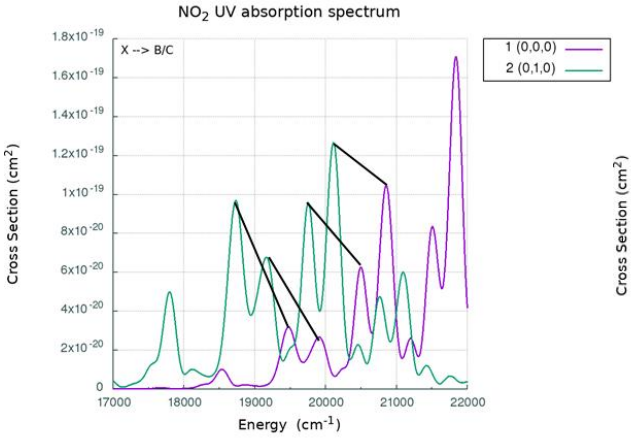
Shape of initial state prob. dens. projected onto upper state topography, modulated by TM function.

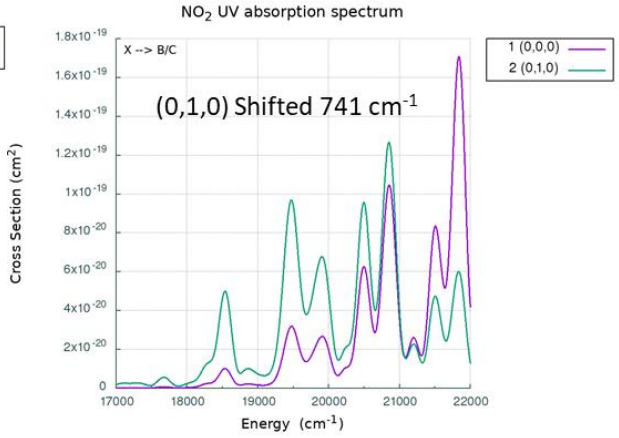
Both A and B states vary quite linearly wrt. bend in FC region, but TM for A-state is less constant.

- **More diffuse initial state spreads wings of spectrum.**
- **Peak structure shifted by mode energy.**

Result is B/C transition clearly projects prob. dens. onto energy axis.

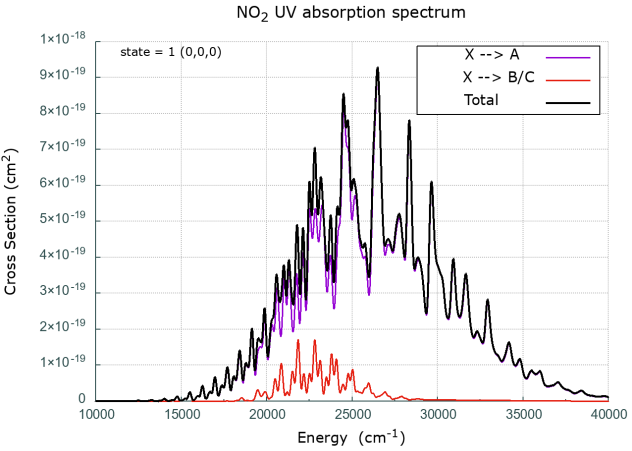




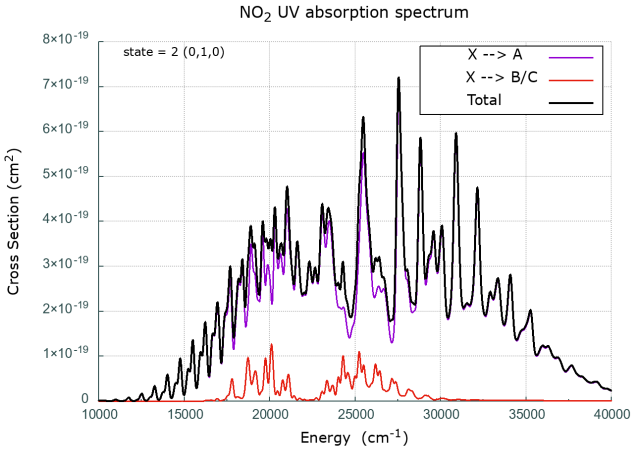


Mode specific effects and contributions
Bend progression

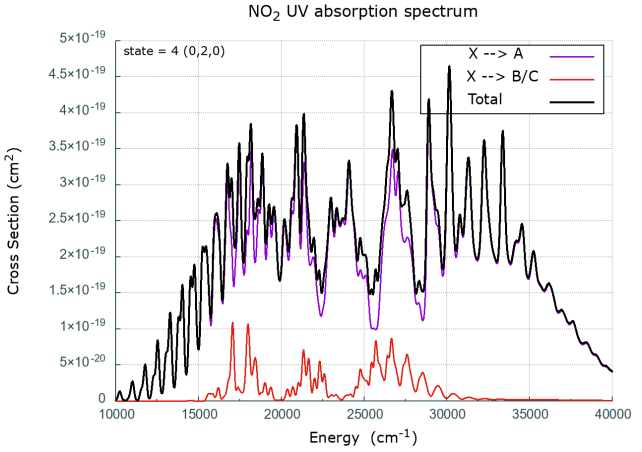
(0,0,0)



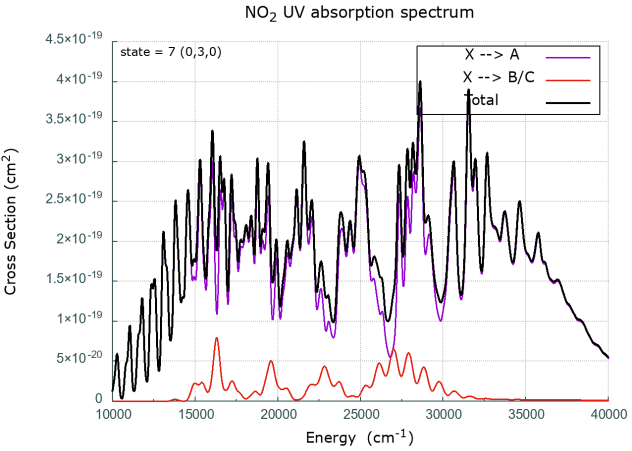
(0,1,0)



(0,2,0)



(0,3,0)



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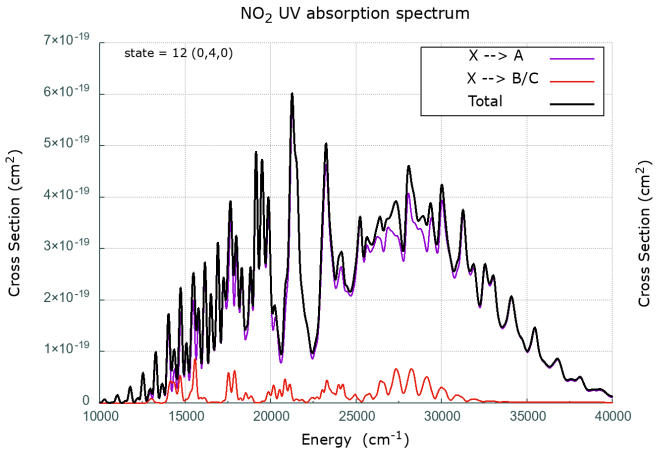
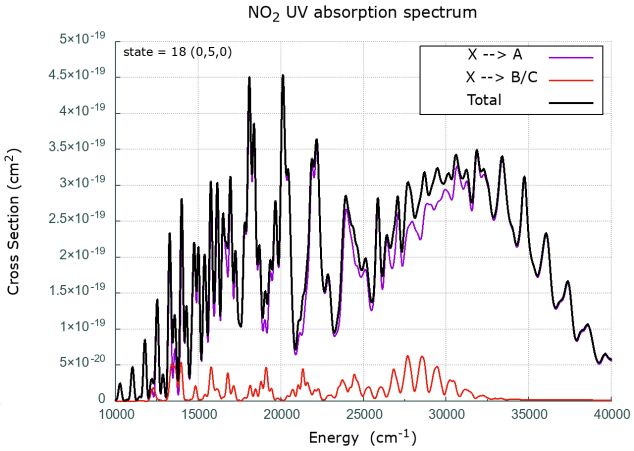
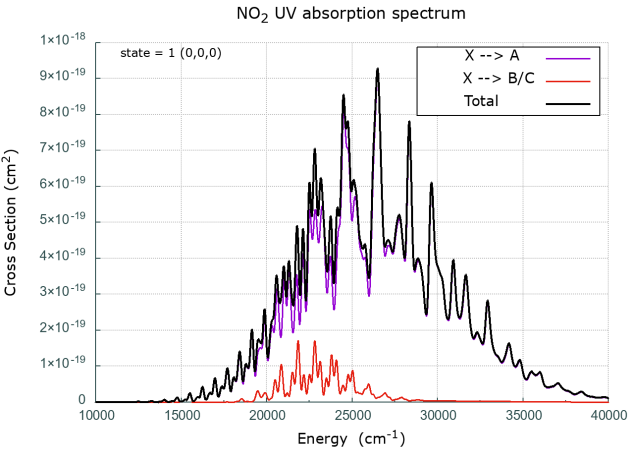


(0,5,0)

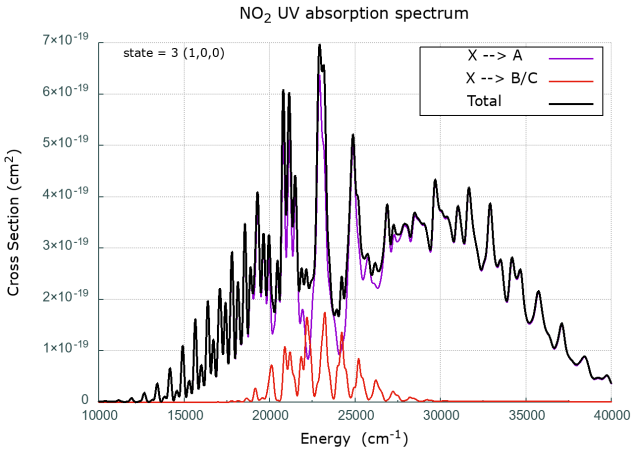


Mode specific effects and contributions

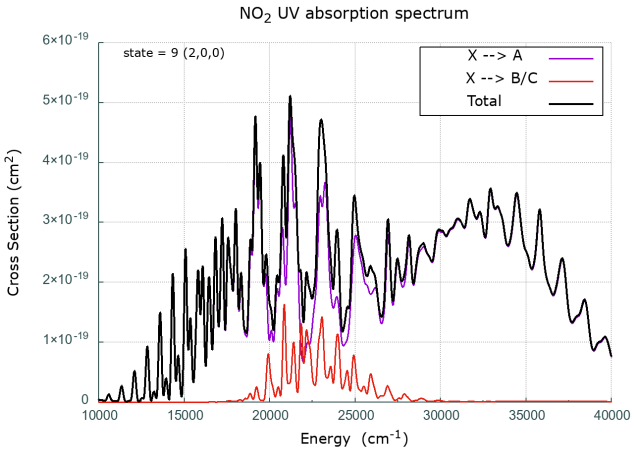
(0,0,0)



(1,0,0)



(2,0,0)



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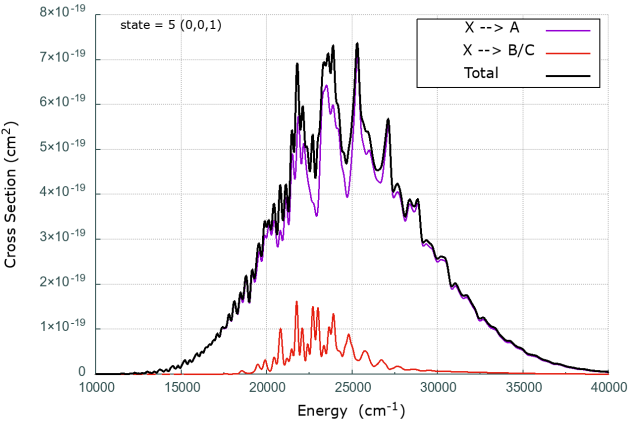

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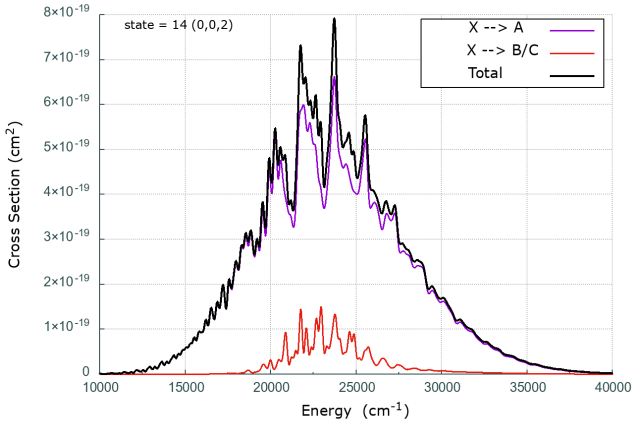

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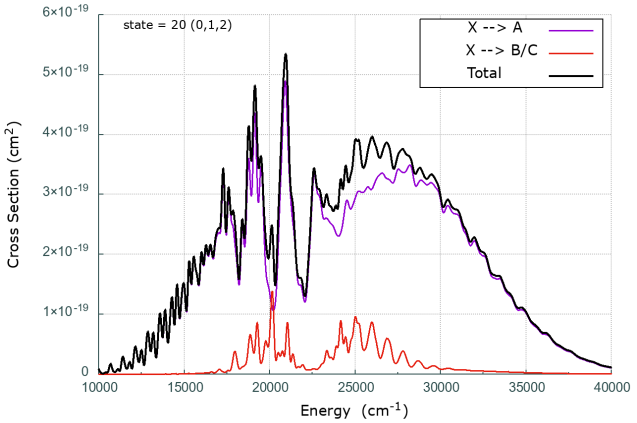
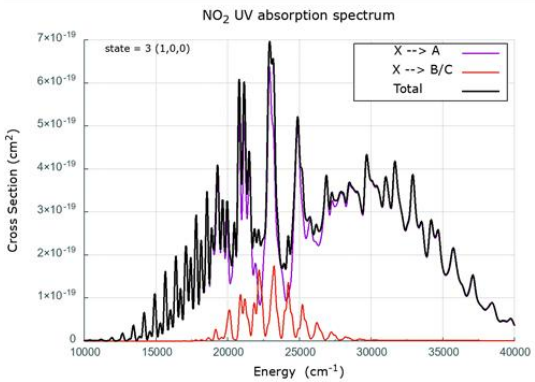


Mode specific effects and contributions
Interpretation based on energy and property surfaces

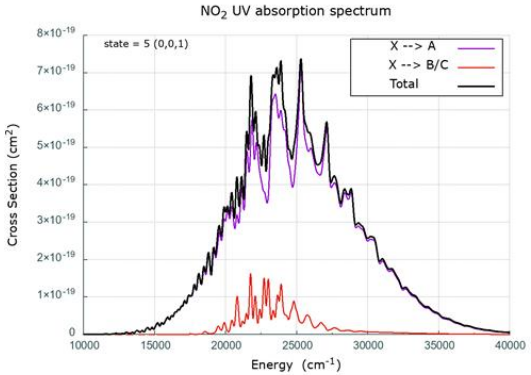
Node in A contribution, but not B/C

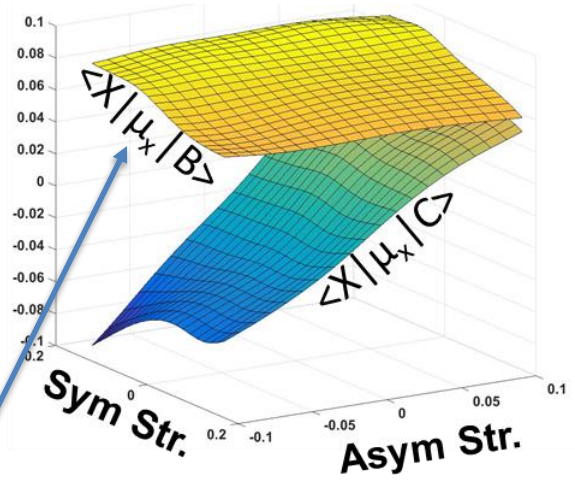
(1,0,0)



No node in either contribution

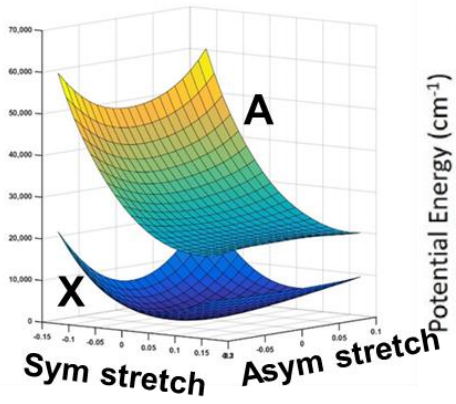
(0,0,1)

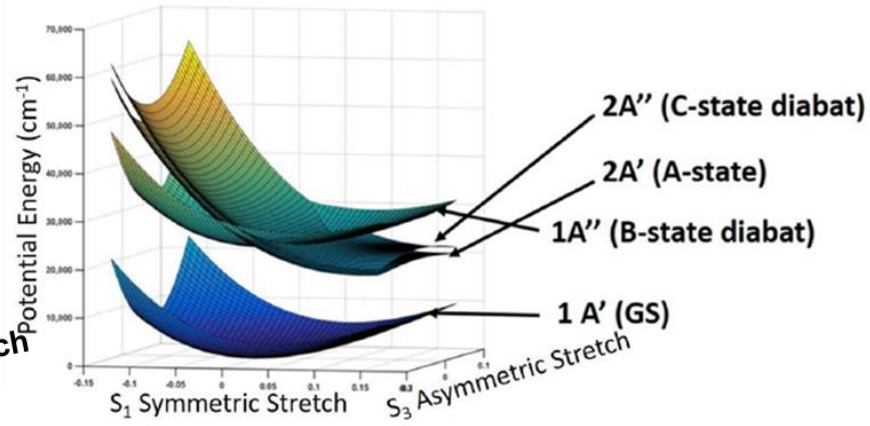


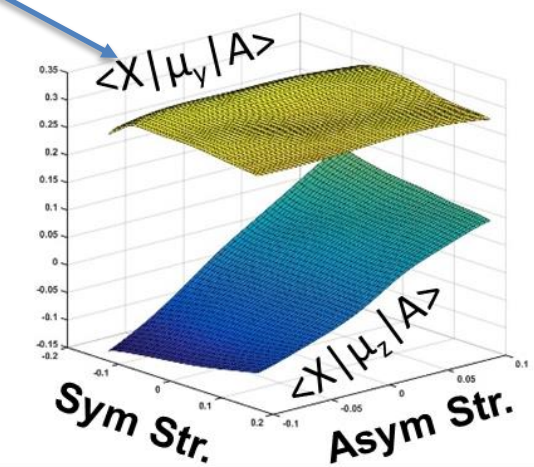


- **A-state varies with sym stretch, but much less with asym.**
- **B-state shadows ground state.**

TMs fairly constant wrt. stretches







Conclusions and Future Work

- **Fitted energy and property surfaces combined with an accurate quantum dynamics approach such as MCTDH can accurately predict spectra even in cases with complex electronic structure and dynamics**
- **Even simpler surveys using the reflection principle can benefit substantially from including the transition dipole**
- **The coupled energy and properties surfaces generated for this study provide the foundation for a variety of dynamical investigations of this remarkably complex system**

Acknowledgements

- Collaborators
  - Dynamics - Hua Guo (New Mexico), Fabien Gatti (Paris-Saclay), François Lique (Le Havre)
  - Ro-vibrational Calculations - Xiao-Gang Wang and Tucker Carrington Jr. (Queen's University)
  - Experimental Spectroscopy - Scott A. Reid (Marquette), Michael Heaven (Emory), Michael McCarthy (Harvard-Smithsonian), David Osborn (Sandia)
- Missouri S&T Graduate Students and Postdocs

Bradley Welch, Steve Ndengué, Sangeeta Sur, Richard Dawes, Andrew Powell, Ernesto Quintas Sánchez

http://web.mst.edu/~dawesr/people.html