Structure and spectroscopy of the carbon monoxide dimer: a theoretical approach

Gé W.M. Vissers, Paul E. S. Wormer, and Ad van der Avoird

Institute of Theoretical Chemistry, Nijmegen, The Netherlands

Andreas Heßelmann and Georg Jansen

Institut für Organische Chemie, Essen, Germany

CO dimer

Notoriously difficult system:

- Experimentally: hard to obtain reliable spectra. Highly non-rigid, so hard to assign
- Theoretically: CO has very small dipole moment, very high level calculation in a large basis are needed to obtain correct long-range behavior

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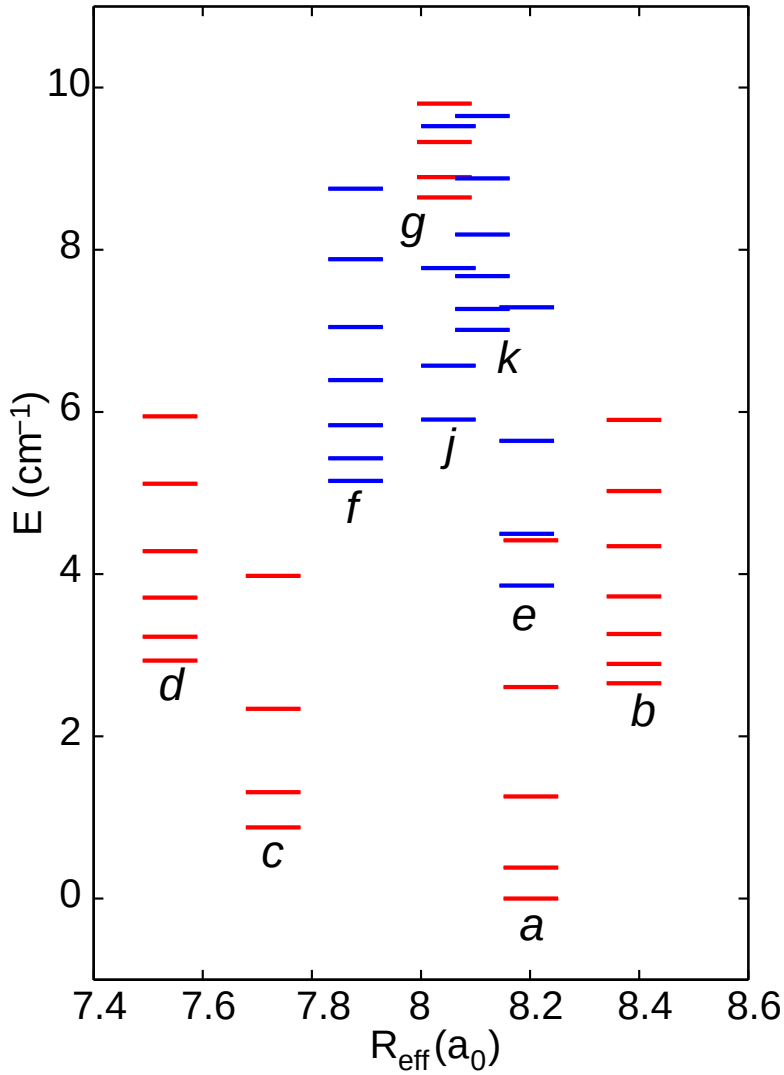
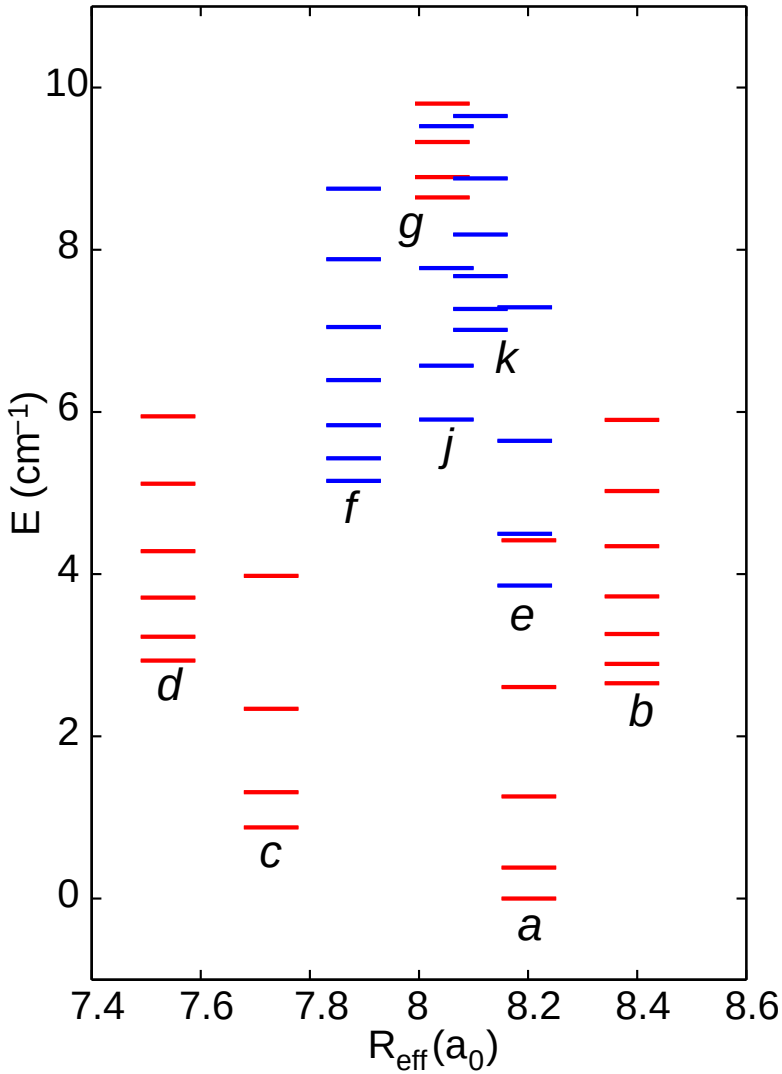
Test the potential by calculation of rovibrational energy levels

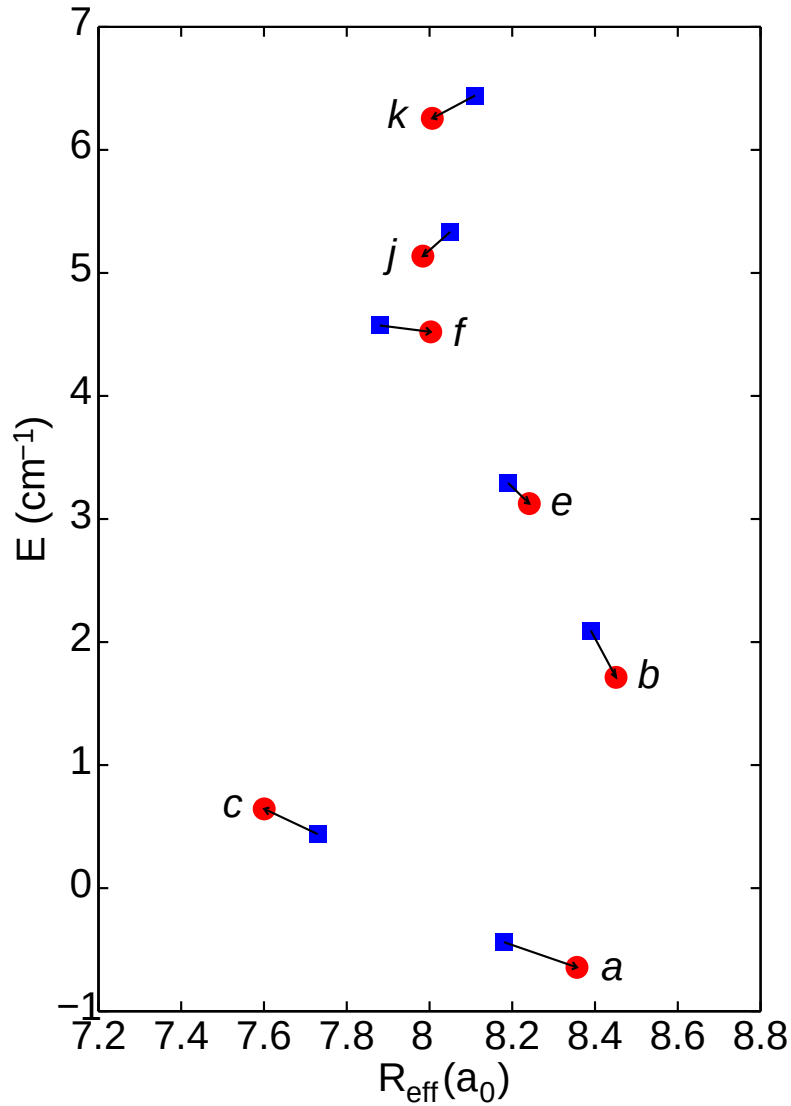
Experiment



Tang *et al*, J. Mol. Spect. 214, 87 (2002)

Experiment

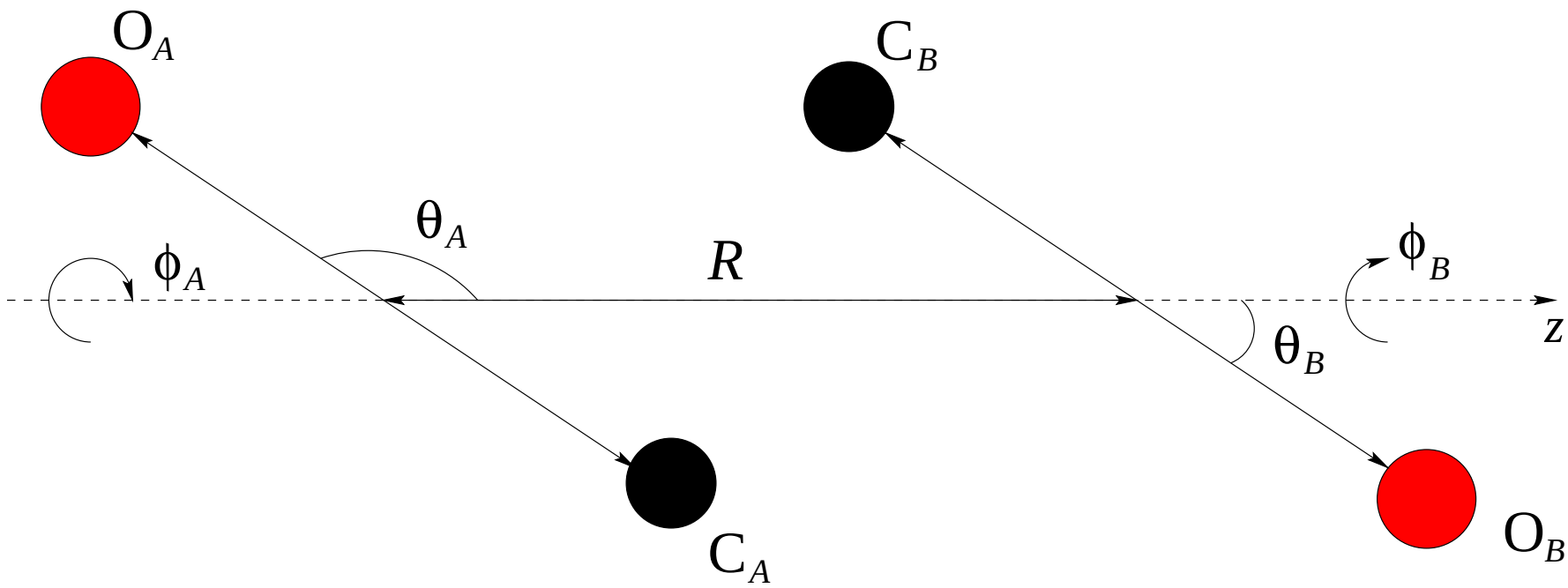




Tang *et al*, J. Mol. Spect. 214, 87 (2002)

Surin *et al*, J. Mol. Spect. 223, 132 (2004)

Coordinates



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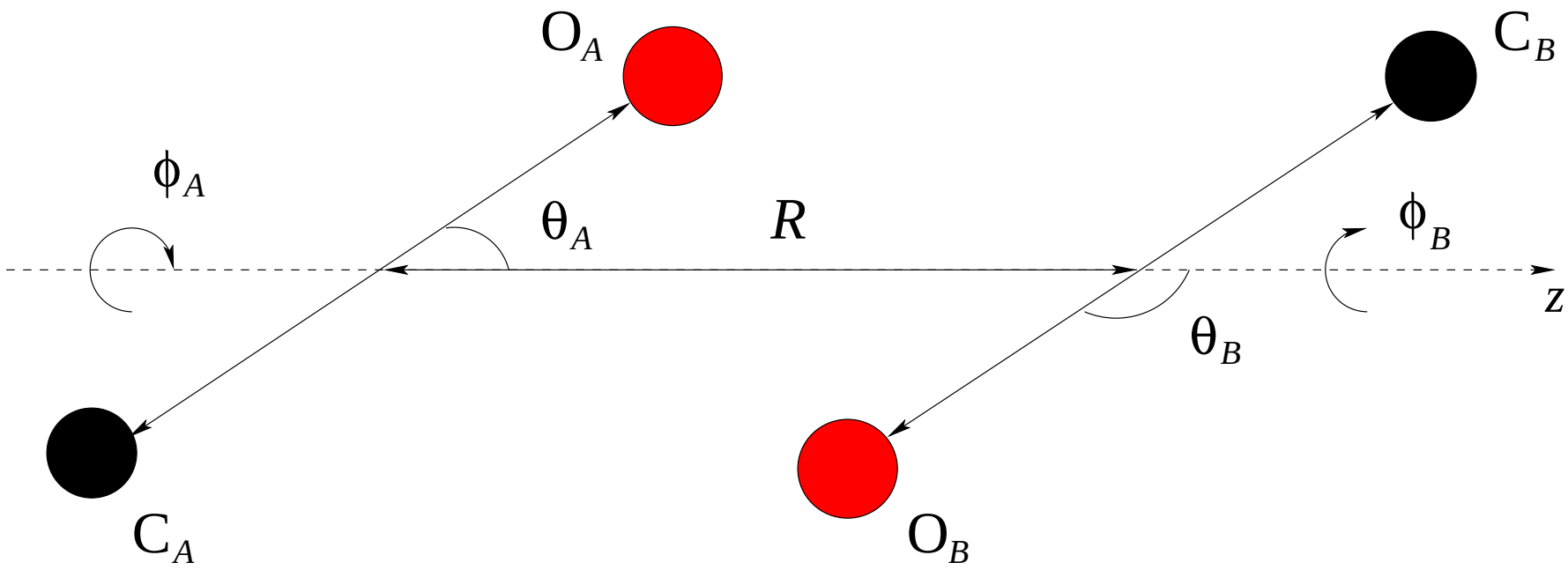

Potential energy surfaces

Two surfaces:

- CCSD(T) surface
  - CCSD(T) method, using MOLPRO
  - aug-cc-pVTZ basis on the atoms, 3s3p2d1f basis halfway CO–CO bond
  - CO bond length fixed at 2.132 a_0
  - 1512 geometries

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  - aug-cc-pVTZ basis on the atoms, 3s3p2d1f basis halfway CO–CO bond
  - CO bond length fixed at 2.132 a_0
  - 1512 geometries
- DFT-SAPT surface
  - combination of DFT for the monomers and SAPT for the intermolecular interaction
  - PBE0AC xc-potential
  - same basis as in CCSD(T) calculations
  - same points as CCSD(T) + 936 new geometries

Rovibrational calculations (1)

Hamiltonian

$$H = B_{\mathrm{CO}}(j_A^2 + j_B^2) - \frac{1}{2\mu_{AB}R}\frac{\partial^2}{\partial R^2}R + \frac{J^2 + j_{AB}^2 - 2\boldsymbol{j}_{AB}\cdot\boldsymbol{J}}{2\mu_{AB}R^2} + V$$

is expanded in basis $|n\rangle|(j_A j_B)j_{AB}K; JM\rangle$, with angular functions

$$\begin{aligned}|(j_A j_B)j_{AB}K; JM\rangle =& \sqrt{\frac{2J+1}{4\pi}} D^{(J)}_{MK}(\alpha,\beta,0)^* \\ & \times \sum_{m_A m_B} Y^{j_A}_{m_A}(\theta_A,\phi_A) Y^{j_B}_{m_B}(\theta_B,\phi_B) \\ & \times \langle j_A m_A j_B m_B | j_{AB} K\rangle\end{aligned}$$

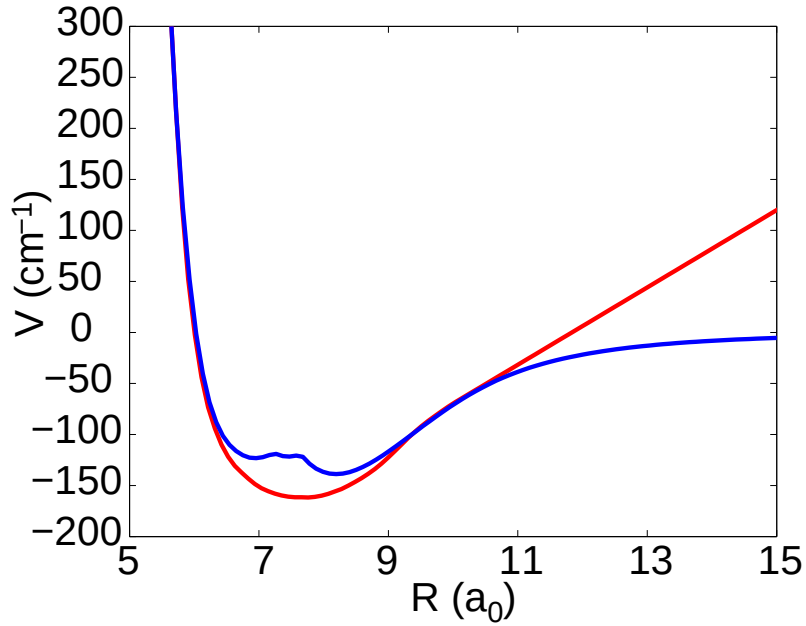
Rovibrational calculations (2)

Radial basis $|n\rangle \equiv \chi_n(R)/R$, with χ_n eigenfunctions of reference Hamiltonian

$$H^{\text{ref}} = -\frac{1}{2\mu_{AB}}\frac{\partial^2}{\partial R^2} + V^{\text{ref}}$$

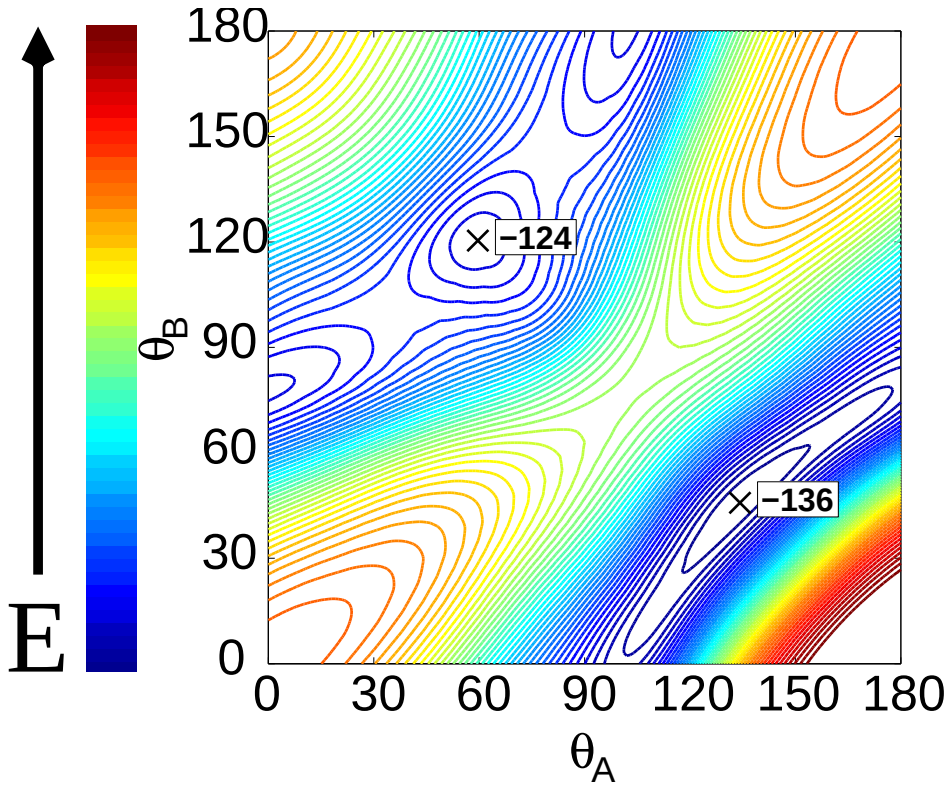
V^{ref} obtained in three-step procedure:

- minimize potential in angles
- fit Morse potential through result
- extrapolate linearly after 10.05a_0

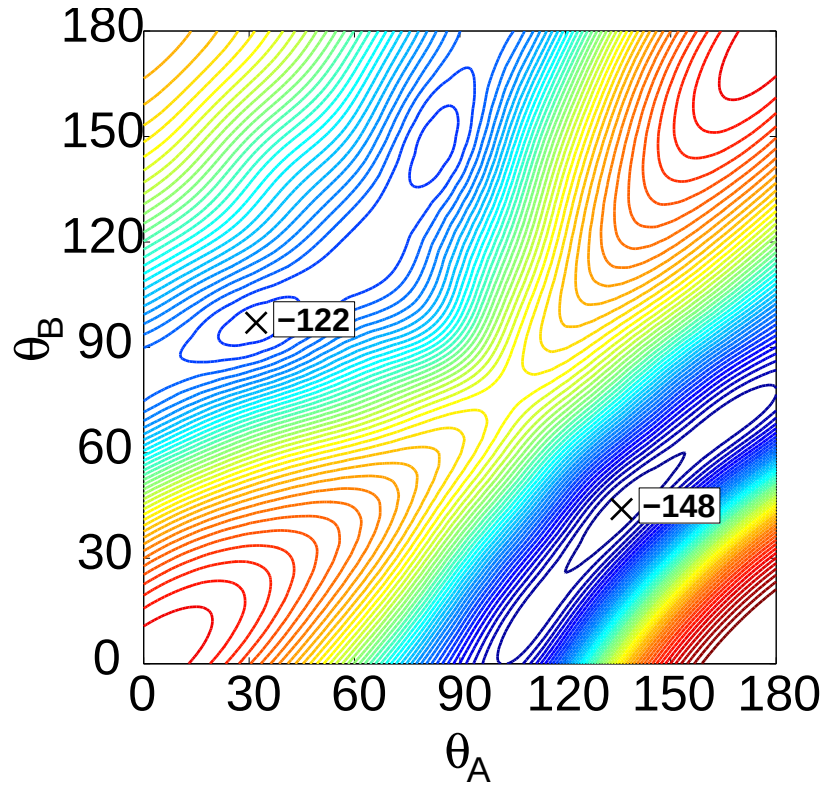


$\chi_n(R)$ calculated with sinc-DVR

The surfaces (1)

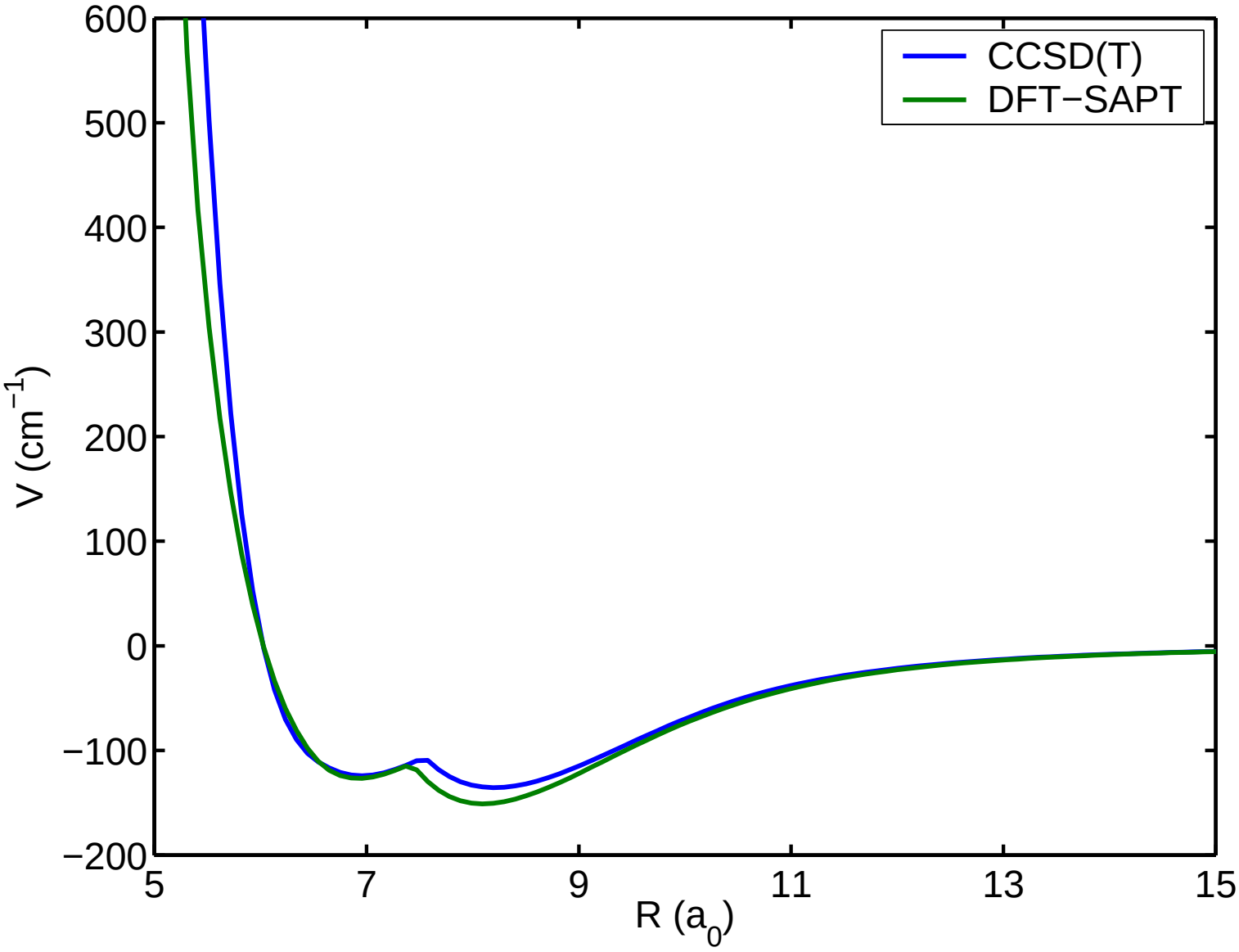


CCSD(T)

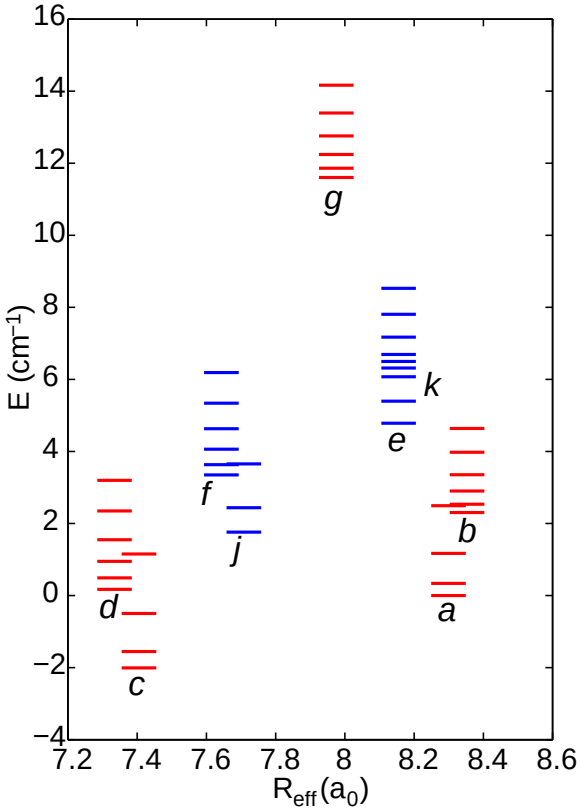


DFT-SAPT

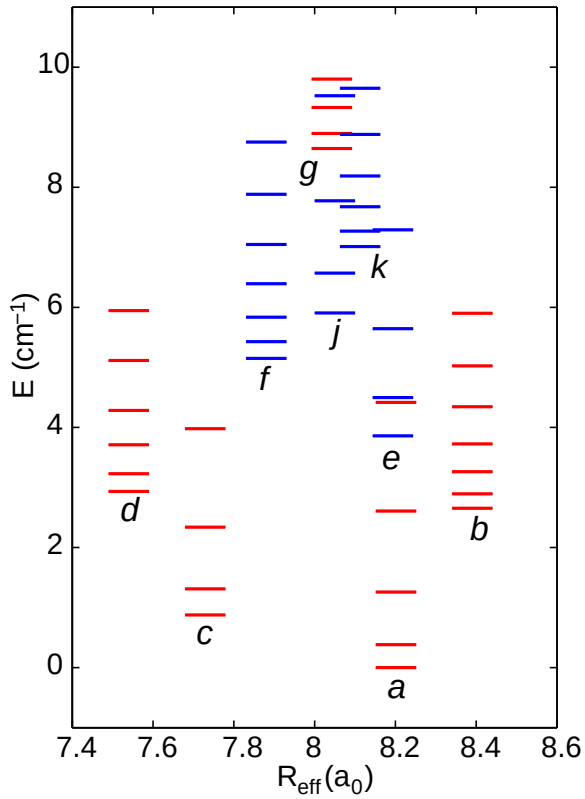
The surfaces (2)



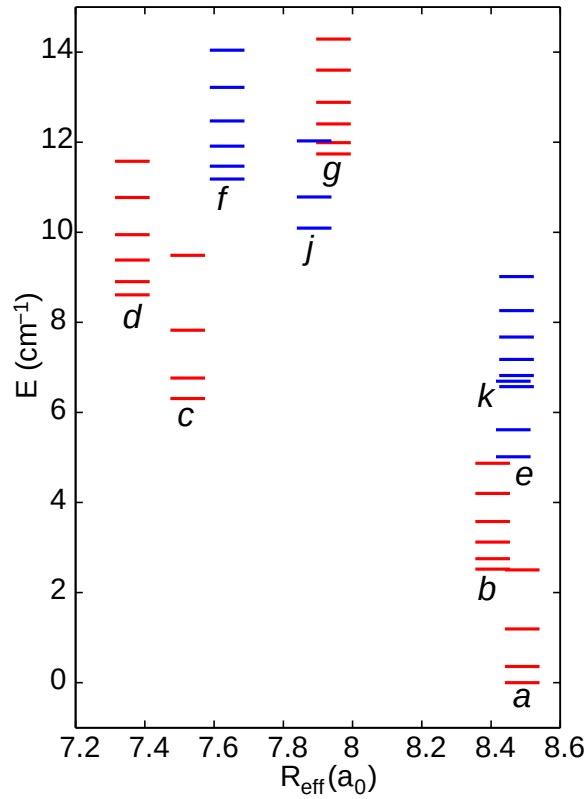
Rovibrational levels



CCSD(T)

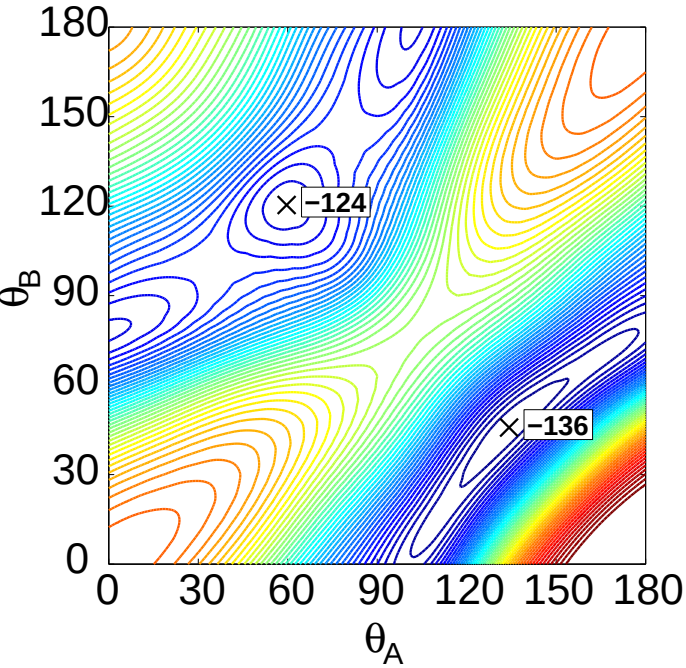


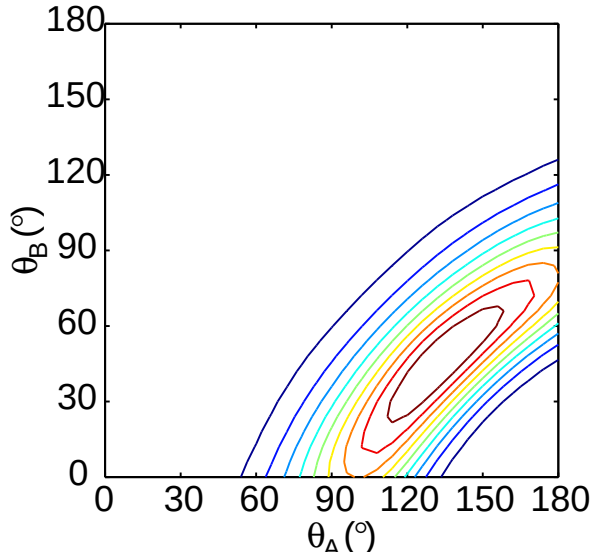
Experiment

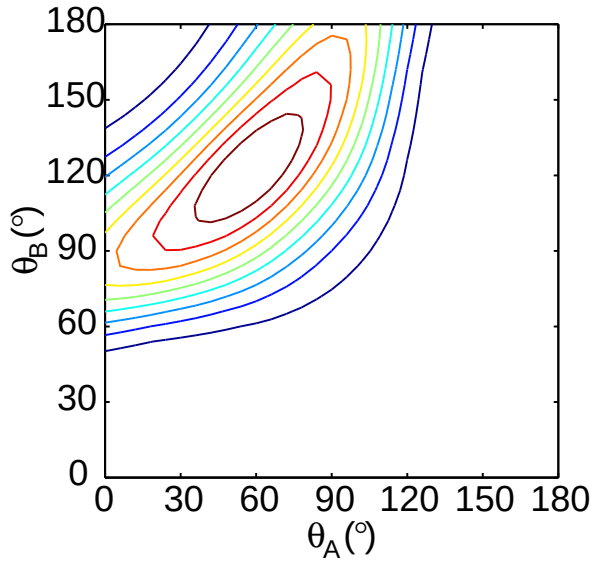


DFT-SAPT

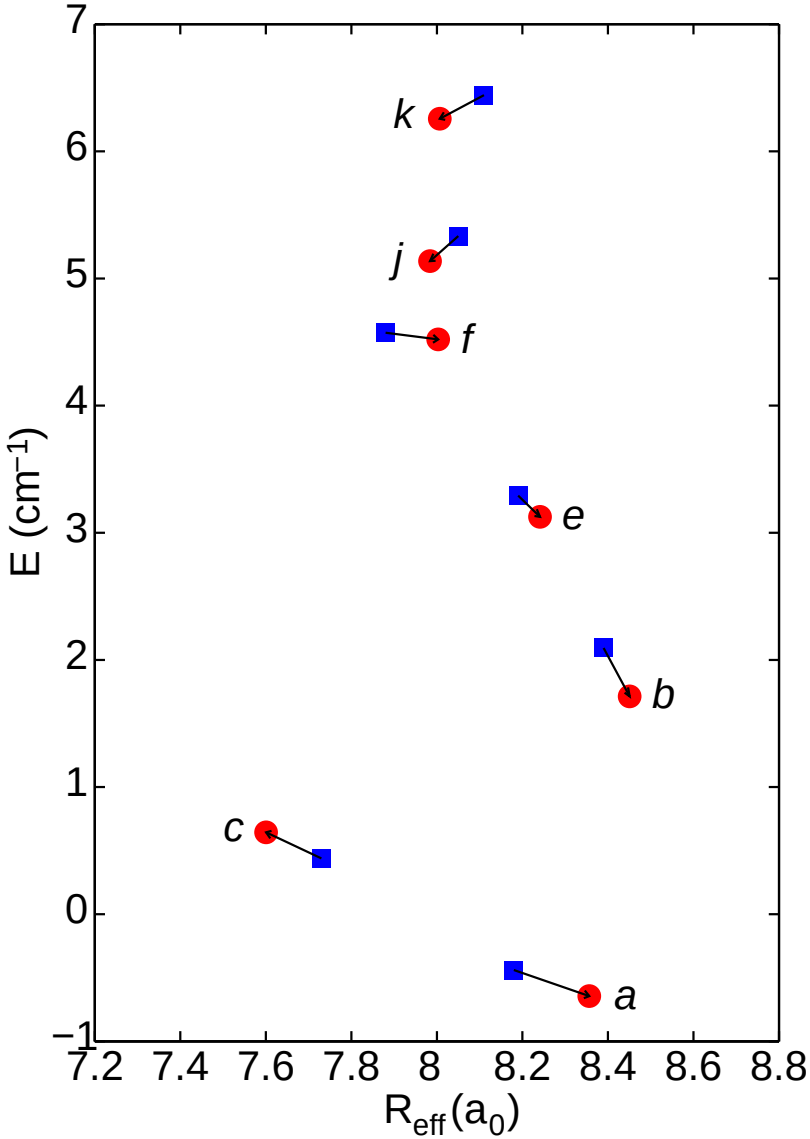
Wave functions

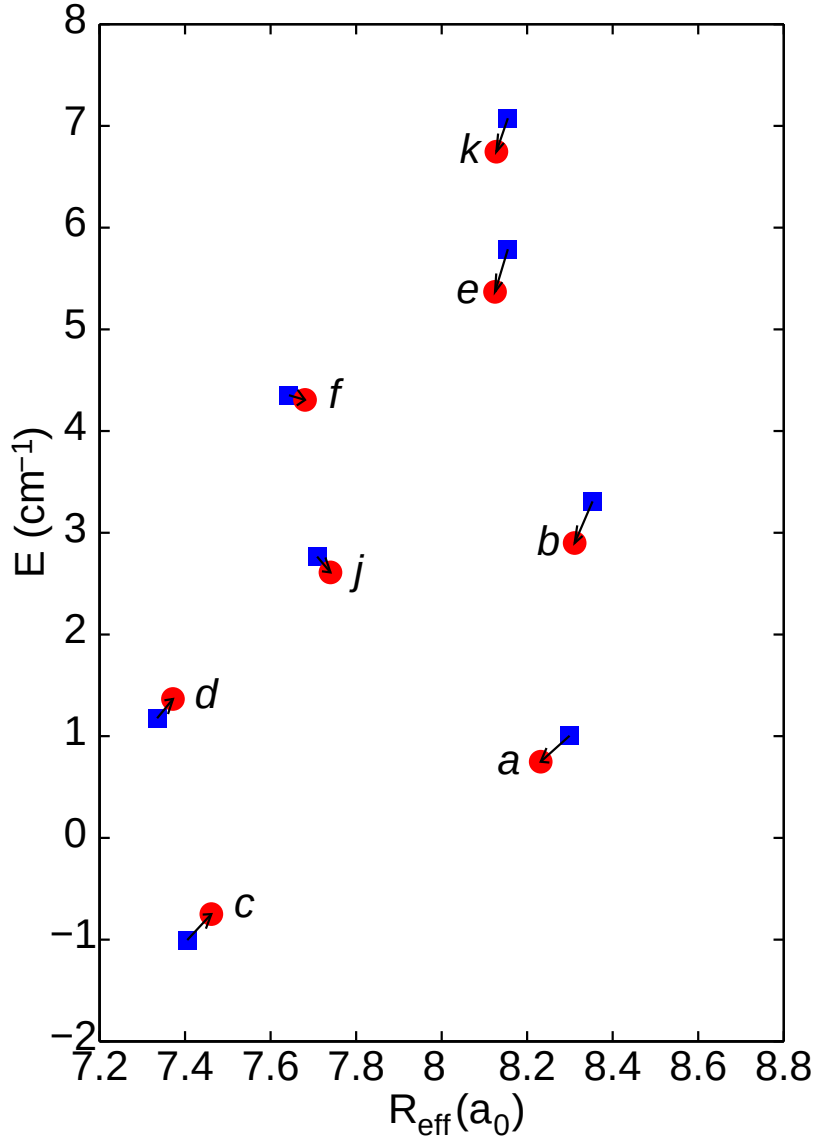






Isotope effect: $(^{12}CO)_2 \rightarrow (^{13}CO)_2$

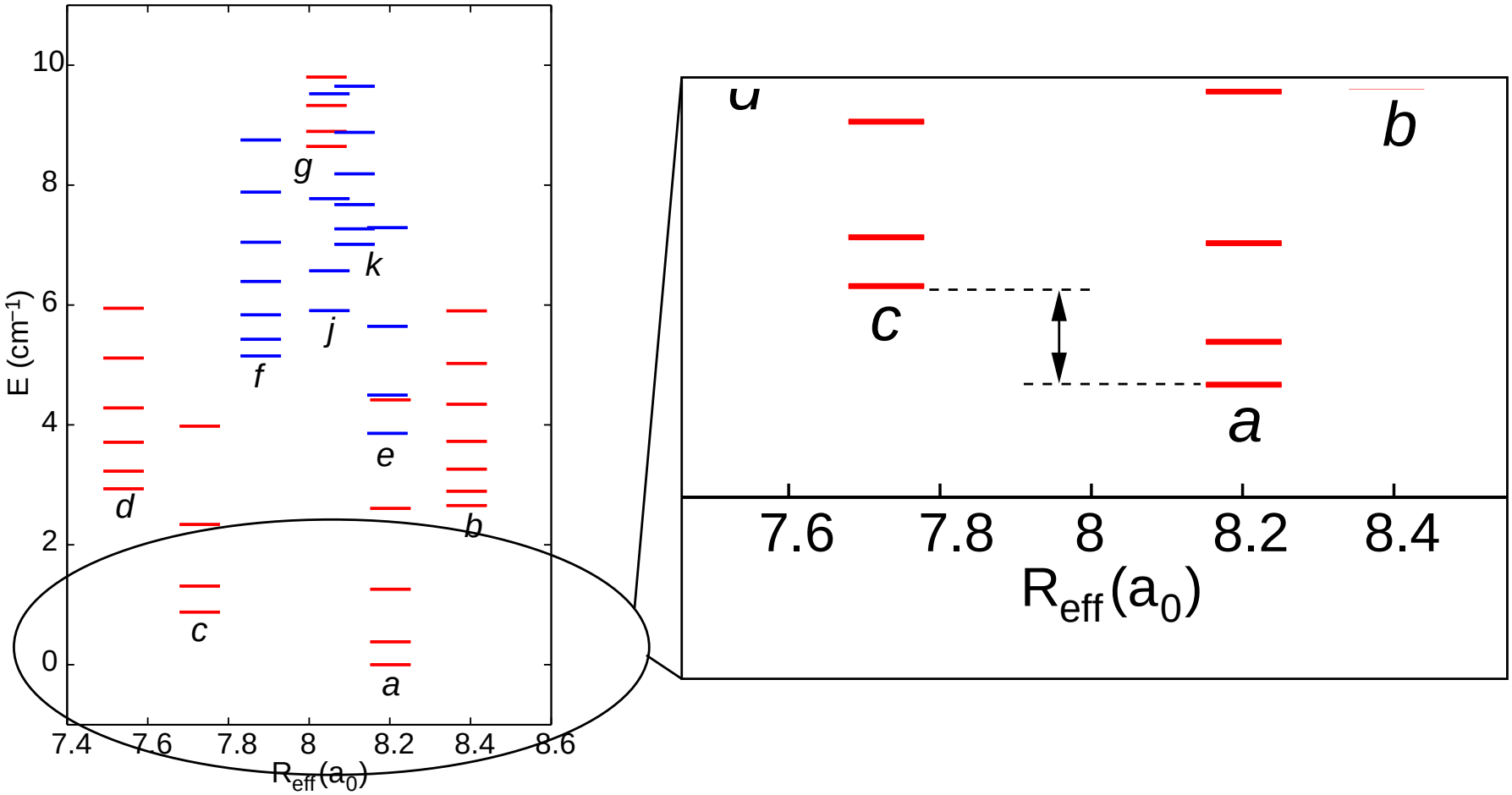




Experiment

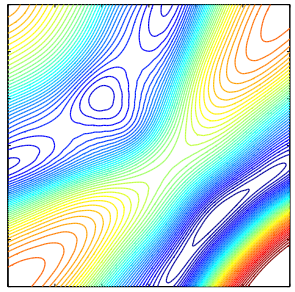
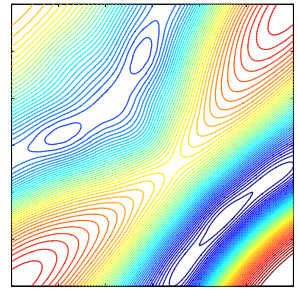
CCSD(T)

Tuning


E (cm⁻¹)
10
8
6
4
2
0
7.4
7.6
7.8
8
8.2
8.4
8.6
R_eff(a_0)
g
k
j
f
e
d
b
c
a
7.6
7.8
8
8.2
8.4
R_eff(a_0)
c
a
b

Tuning

Energy between two wells too small for CCSD(T), too large for DFT-SAPT $\Rightarrow$

0.7  + 0.3 

CCSD(T) DFT-SAPT

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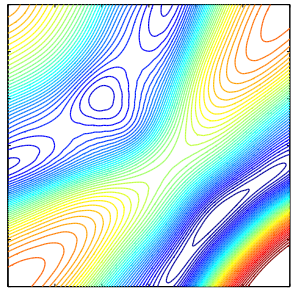
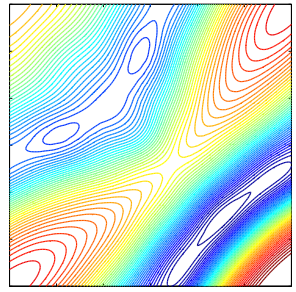
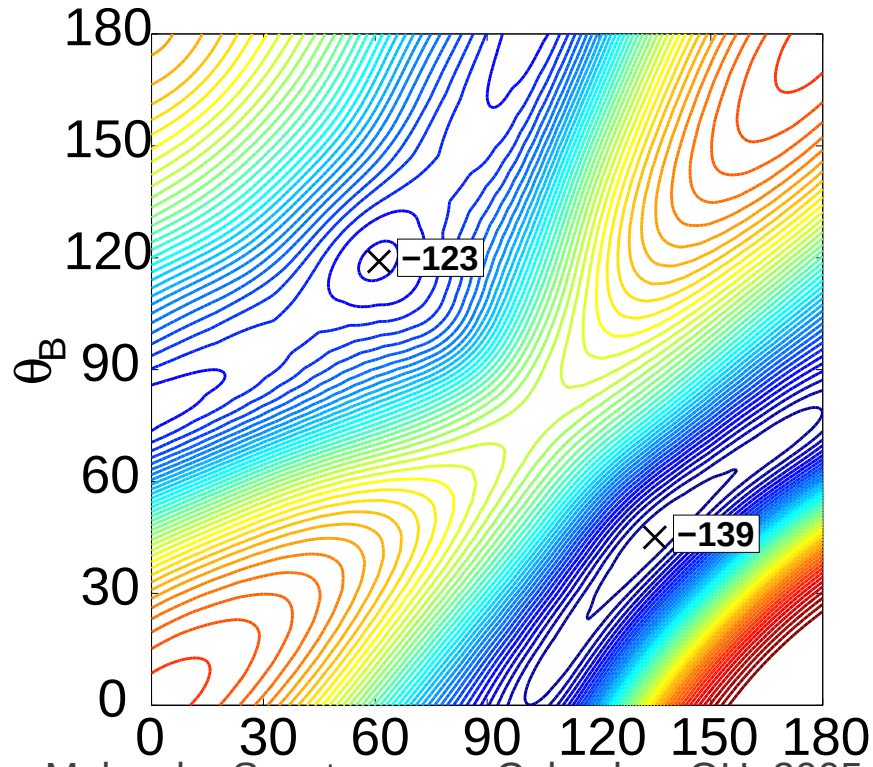
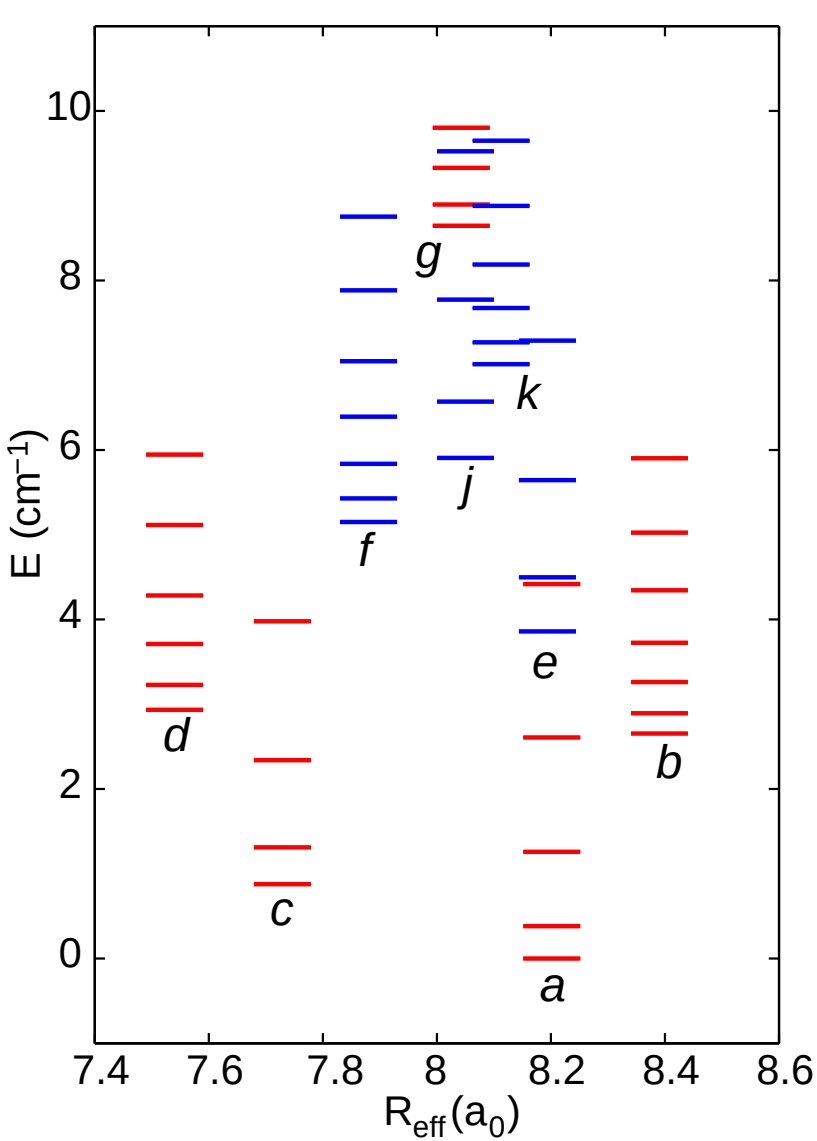
0.7  + 0.3  =

CCSD(T) DFT-SAPT

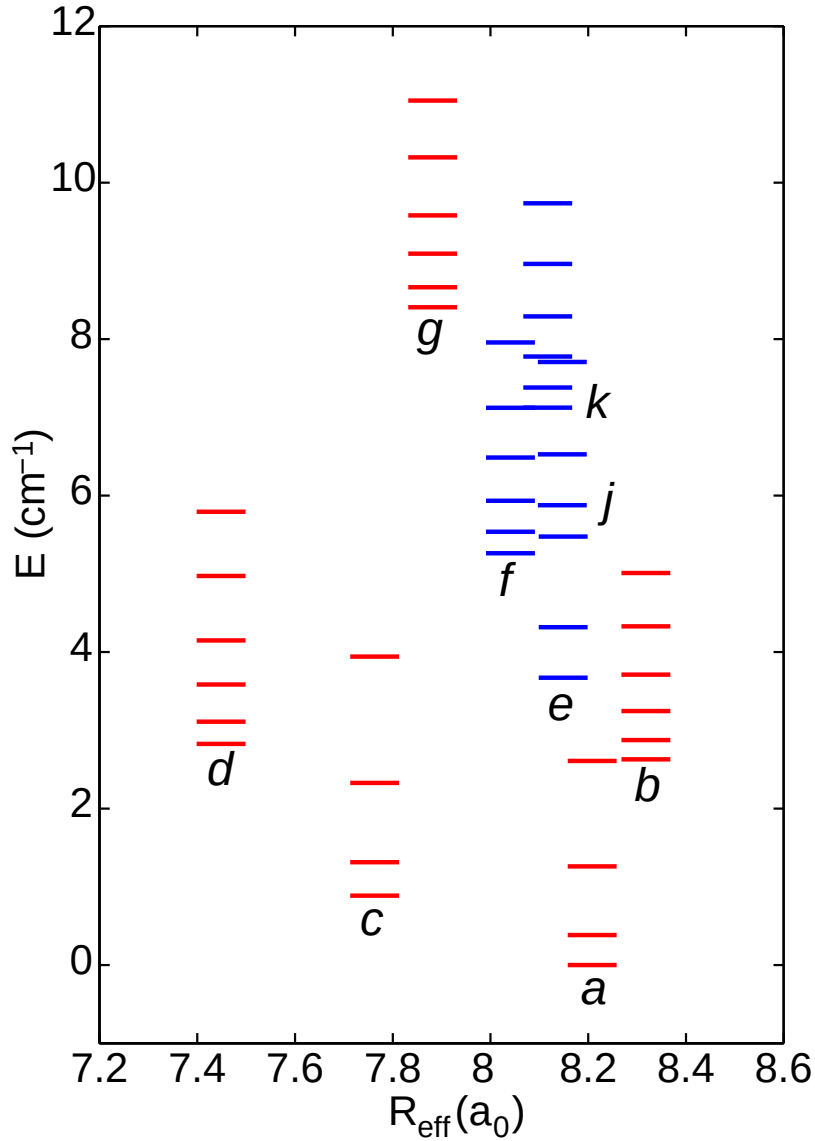
Hybrid



Rotational stacks after tuning

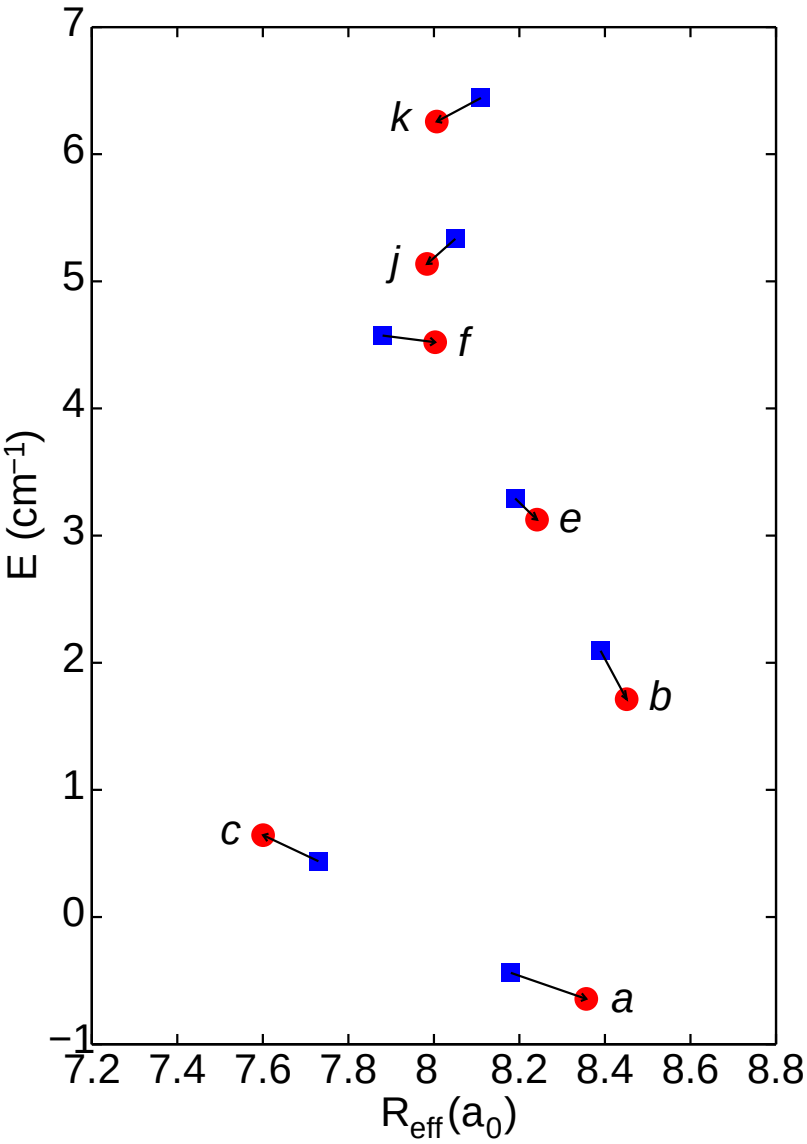


Experiment

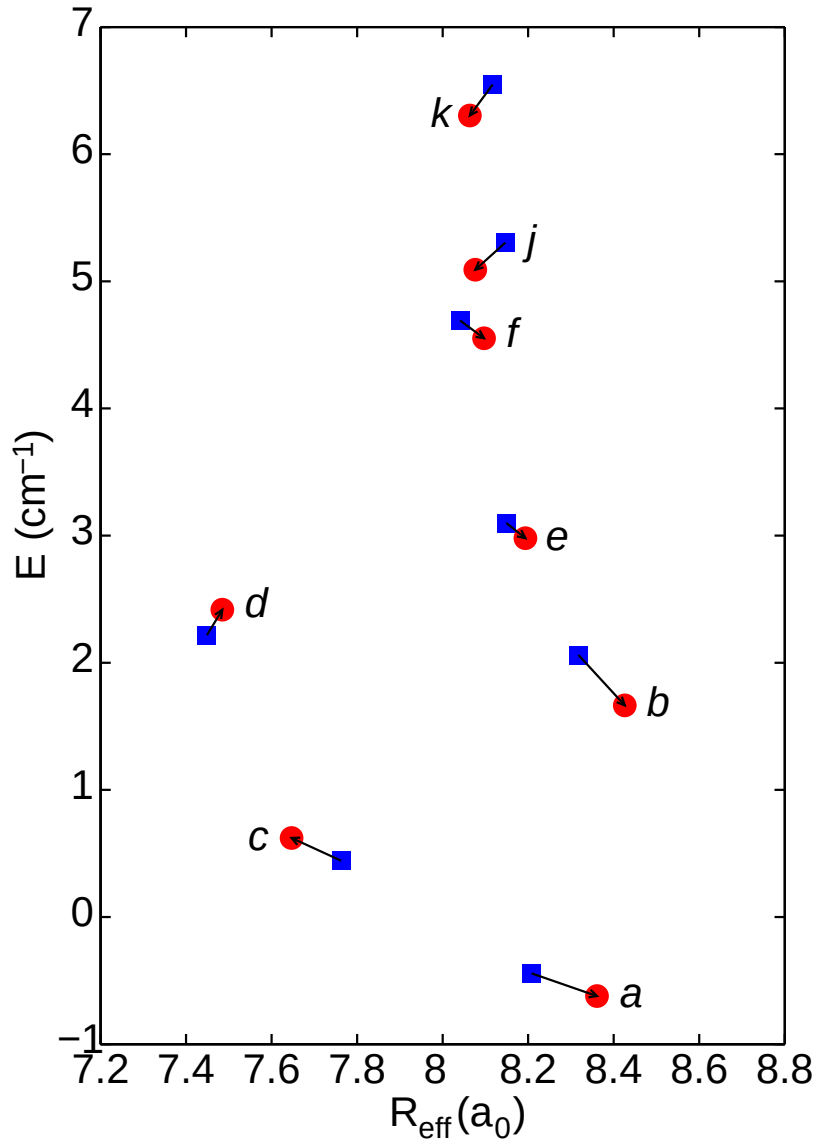


Hybrid

Isotope effect after tuning

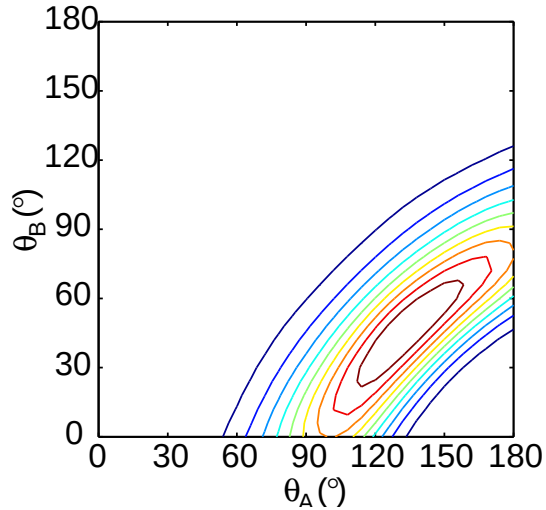


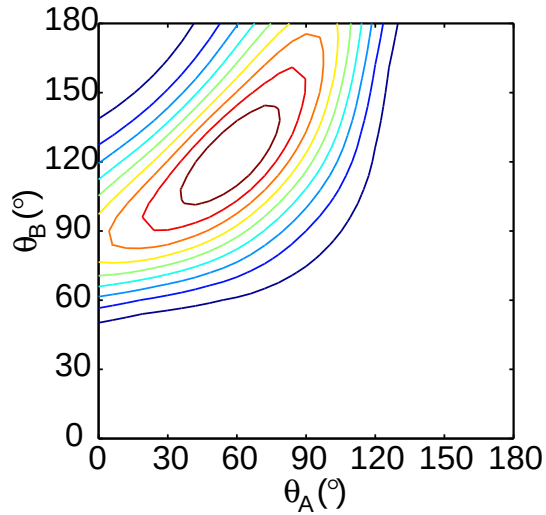
Experiment



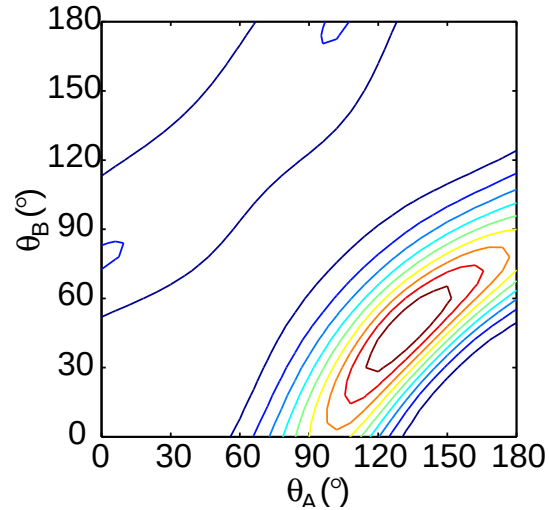
Hybrid

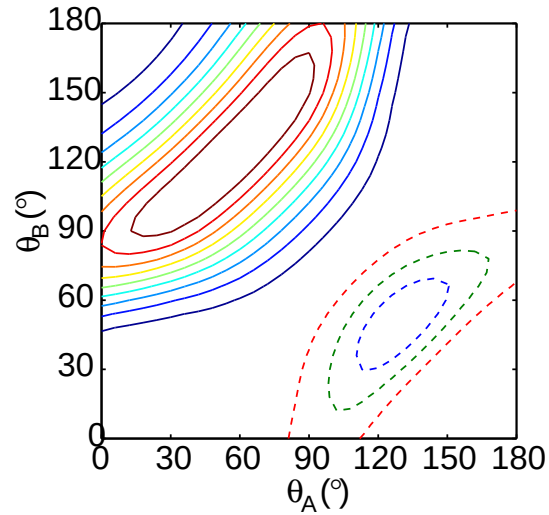
Comparison of wave functions





CCSD(T)





Hybrid

Conclusions

- Both the CCSD(T) and the DFT-SAPT surface give a qualitatively correct description of the dynamics of CO–CO
- Equilibrium geometry of the CO dimer is a slipped anti-parallel structure
- Experimentally observed isotope shift cannot be explained by the original potentials
- Hybrid potential gives quantitative results, both for ^{12}CO dimer and ^{13}CO dimer
- Dynamical effects are very important, and very sensitive to the potential

Acknowledgements

- NWO-CW
- Gerrit Groenenboom