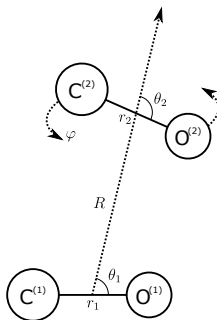


# Some notes on CO dimer

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**Figure:** Geometry of CO dimer.

$$\Delta V = V(r_1, r_2; R, \theta_1, \theta_2, \phi). \quad (1)$$

CO dimer is a flopping supramolecular so that we use permutation-inversion (PI) group  $G_4$  to describe its symmetry.

**Table:** Character table of PI group  $G_4$ .

$G_4$	$\hat{E}$	$\hat{P}$	$\hat{E}^*$	$\hat{P}^*$
$A^+$	1	1	1	1
$A^-$	1	1	-1	-1
$B^+$	1	-1	1	-1
$B^-$	1	-1	-1	1

$$\begin{aligned}\hat{E}(r_1, r_2; R, \theta_1, \theta_2, \phi) &= (r_1, r_2; R, \theta_1, \theta_2, \phi), \\ \hat{P}(r_1, r_2; R, \theta_1, \theta_2, \phi) &= (r_2, r_1; R, \pi - \theta_2, \pi - \theta_1, \phi), \\ \hat{E}^*(r_1, r_2; R, \theta_1, \theta_2, \phi) &= (r_1, r_2; R, \theta_1, \theta_2, -\phi), \\ \hat{P}^*(r_1, r_2; R, \theta_1, \theta_2, \phi) &= (r_2, r_1; R, \pi - \theta_2, \pi - \theta_1, -\phi).\end{aligned}\tag{2}$$

# *Ab initio* calculation test

Core electronic correlation<sup>1</sup>

Dawes et al. built an intermolecular PES with all electrons correlated (AE). Compared to the case where only valence orbitals are correlated (Val.), the intermolecular PES is...?

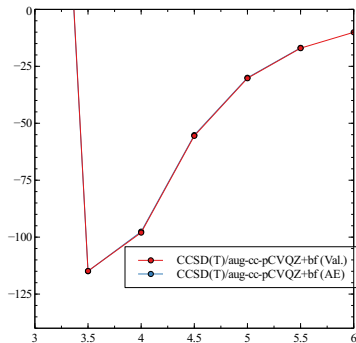
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<sup>1</sup>*J. Phys. Chem. A*, **117**, 7612 (2013) doi:10.1021/jp404888d

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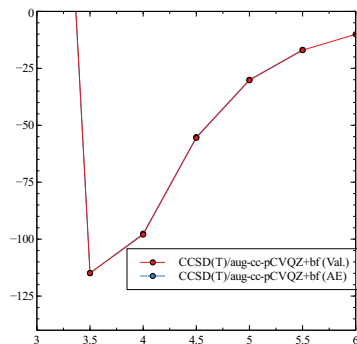
Almost the same!

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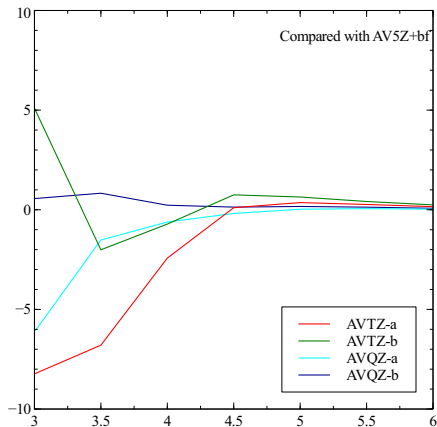


Almost the same! Unluckily they did not find that.

<sup>1</sup>*J. Phys. Chem. A*, **117**, 7612 (2013) doi:10.1021/jp404888d

# *Ab initio* calculation test

Explicit correlation method and basis sets



CCSD(T)-F12b/aug-cc-pVQZ wins.



# *Ab initio* calculation test

## Triple excitation correction

*... It follows from this analysis that the calculation of an accurate intermolecular potential for CO is a particularly difficult problem: even the CCSD(T) method is not sufficiently reliable since it lacks important fifth-order correlation contributions.*

*Rode et al., Chem. Phys. Lett., **314**, 326 (1999)*

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## Triple excitation correction

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Correction energies on ang-cc-pVDZ, in  $\text{cm}^{-1}$ .

Landmark	Correction <sup>†</sup>
Global minimum (C-in)	-4.8725
Local minimum (O-in)	3.9640

<sup>†</sup> Using MRCC2016.



Walltime ~16hr. for a geometry under  $C_1$  point group.

# Infrared spectrum: Consider the CO stretches

Based on Born-Oppenheimer Approximation, intramolecular vibration can be 'split out'. For only one chromophore, the vibrational average reads

$$\bar{V} = \int \Psi^*(r) V \Psi(r) dr. \quad (3)$$

What about CO dimer?

Two chromophores,  $C^{(1)}O^{(1)}$  and  $C^{(2)}O^{(2)}$ , or 1 and 2 for short. If the two ones are all isolated, we have

$$\begin{aligned} |00\rangle &= |0\rangle_1 |0\rangle_2, \\ |10\rangle &= |1\rangle_1 |0\rangle_2, \\ |01\rangle &= |0\rangle_1 |1\rangle_2 \\ \text{and } |11\rangle &= |1\rangle_1 |1\rangle_2, \end{aligned} \quad (4)$$

where 0 stands for the vibrational ground state and 1 for excited state.

# Infrared spectrum: Consider the CO stretches

Use only  $|10\rangle$  and  $|01\rangle$  as the bases, the problem becomes a perturbation problem with degenerate states.

The Hamiltonian reads

$$\hat{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}, \quad (5)$$

where

$$\begin{aligned} H_{11} &= \langle 10 | \hat{H}_1 + \hat{H}_2 + \Delta V(r_1, r_2) | 10 \rangle = E_v + \langle 10 | \Delta V | 10 \rangle = E_v + \Delta_1, \\ H_{22} &= \langle 01 | \hat{H}_1 + \hat{H}_2 + \Delta V(r_1, r_2) | 01 \rangle = E_v + \langle 01 | \Delta V | 01 \rangle = E_v + \Delta_2, \\ H_{12} &= \langle 10 | \hat{H}_1 + \hat{H}_2 + \Delta V(r_1, r_2) | 01 \rangle = \langle 10 | \Delta V | 01 \rangle = \varepsilon, \\ \text{and } H_{21} &= \langle 01 | \hat{H}_1 + \hat{H}_2 + \Delta V(r_1, r_2) | 10 \rangle = \langle 01 | \Delta V | 10 \rangle = \varepsilon. \end{aligned} \quad (6)$$

Here  $E_v$  can be obtained experimentally. The results read

$$E = E_v + \frac{\Delta_1 + \Delta_2 \pm \sqrt{(\Delta_1 - \Delta_2)^2 + 4\varepsilon^2}}{2}. \quad (7)$$

*Is it really necessary to include the coupling term?*

I am not sure since in *J. Phys. Chem. A*, **117**, 9612 (2013), Rezaei et al. said the splitting between symmetric and antisymmetric stretching is only  $\sim 0.2 \text{ cm}^{-1}$ . However, since we will calculate the data, it is just a simple calculation using little time. So why not? However, since the PES can be fairly inaccurate...

*Why does not you include the states  $|00\rangle$  and  $|11\rangle$ ?*

Our experience with  $\text{CO-H}_2$  tells us that high-order perturbation is NOT necessary. It means that the contribution from ground state and the higher excited state is small enough to ignore.

# Thank you for your attention!