

A Protocol for the Calculation of Vibrationally Averaged Long Range Forces



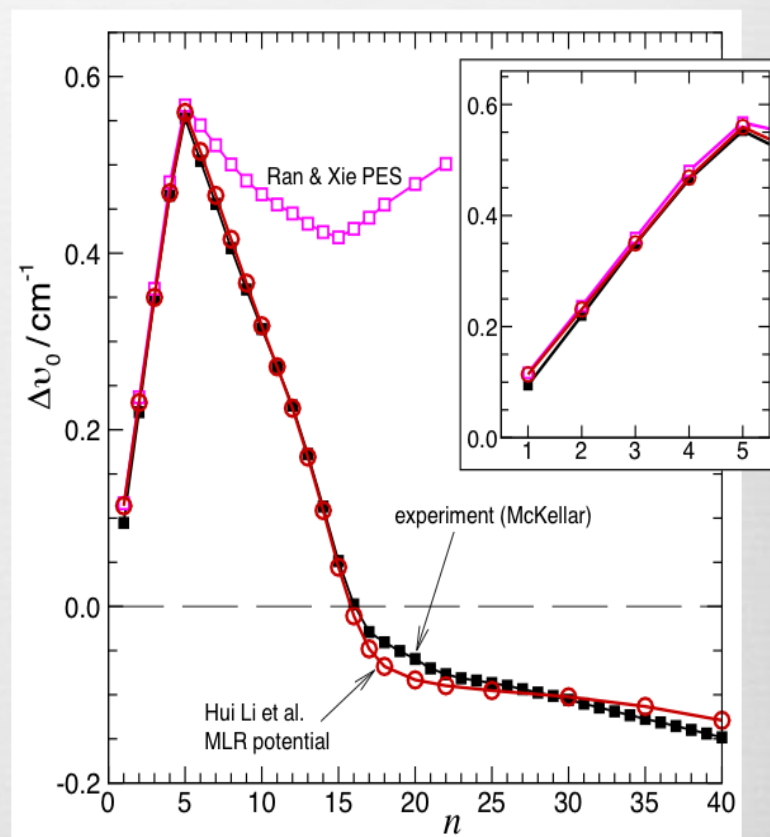
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Under Supervision of:
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Motivation

He-CO₂ Vibrational Frequency Shifts With Increasing No. Helium Atoms

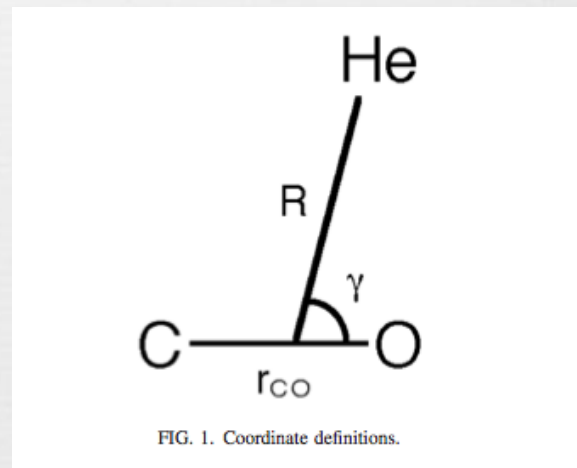
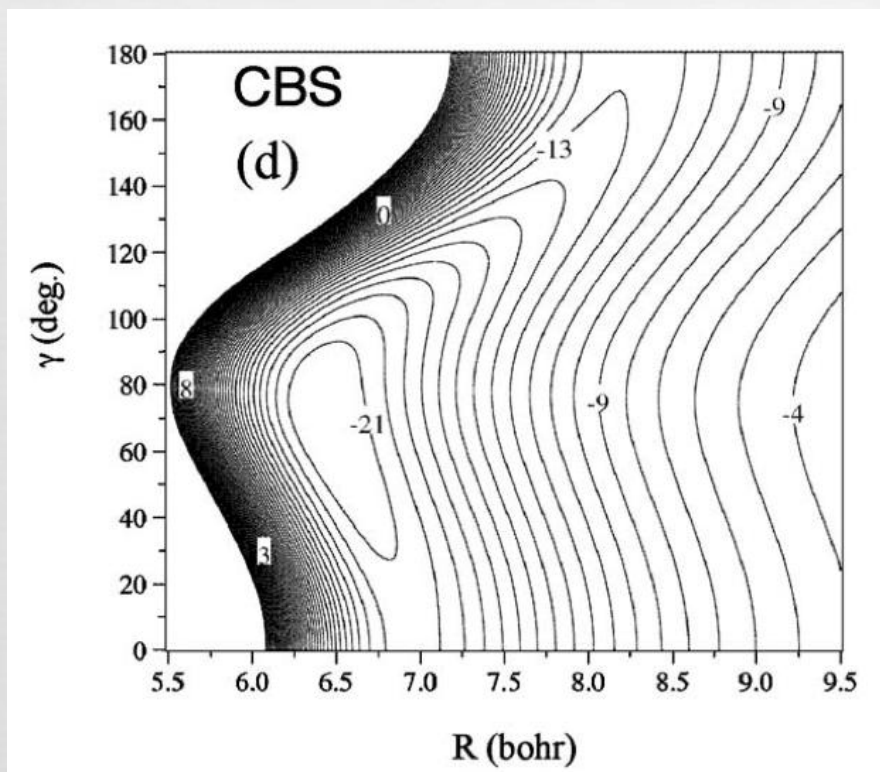
- Observe vibrational frequency shift of CO₂ in (He)_n cluster
- Two groups generated approx equal quality PES's and used PIMC simulations to predict shifts
- Hui Li PES incorporated “true” long-range dispersion coefficients
- Ran + Xie's PES did not



Experimental $v_0 = 2349.143 \text{ cm}^{-1}$

Li H., Blinov N., Roy P.-N., LeRoy R., J. Chem. Phys. **130**, 144305 (2009)

How CO-He Potential Changes with Structure



$$V(R, \gamma) = -\frac{C_6(\gamma)}{R^6} - \frac{C_8(\gamma)}{R^8} - \frac{C_{10}(\gamma)}{R^{10}} - \dots$$

Potential Energy Surfaces



- ❧ 'Short-Range' Portion

- ❧ From *Ab Initio* electronic structure calculations
- ❧ Very accurate in 'bound region'

- ❧ Our focus is the 'Long-Range' Portion

$$V(r, \gamma) = -\frac{C_6(\gamma)}{r^6} - \frac{C_8(\gamma)}{r^8} - \frac{C_{10}(\gamma)}{r^{10}} - \dots$$

- ❧ Need to calculate accurate long range coefficients
 - ❧ Including angular dependence
 - ❧ Including vibrational averaging for each monomer

The Goal



- ❧ To compute molecule – molecule (atom) dispersion energy coefficients $C_6(r)$, $C_8(r)$, $C_{10}(r)$
- ❧ Use vibrational averaging to get differential dispersion coefficients for each individual vibrational state
- ❧ Develop protocol for a generic chromophore with He (or H₂)
- ❧ For example CO chromophore with He (solvent)
 - ❧ 3 co-ordinates needed to specify interaction
 - ❧ Also need He + He interactions
- ❧ Construct potentials for simple 2-body systems (CO-He, He-He)
- ❧ Assume potential for complex n-body system is sum of pairwise interactions

Calculate Frequency Shift



∞ Perturbation Theory Method

∞ Solve for ψ_v for CO

∞ Evaluate : $\langle \psi_v^{CO} | H^{He-CO} | \psi_v^{CO} \rangle$

$$= \langle \psi_v^{CO} | (T + V^{CO}) + (V^{He-CO} - V^{CO}) | \psi_v^{CO} \rangle$$

$$= E_{v,CO} + \langle \psi_v^{CO} | (V^{He-CO} - V^{CO}) | \psi_v^{CO} \rangle$$



This term allows us to find change in vibrational frequency!

∞ Can evaluate this by numerical integration over n orientations

$$\sum_{i=1}^n w_i [V^{He-CO}(\vec{R}_i) - V^{CO}(\vec{R}_i)] \quad V^{He-CO}(\vec{R}) = \int V_{2-body}^{He-CO}(\vec{R}, \vec{r}) \rho^{He}(\vec{r}) d^3\vec{r}$$

Protocol



- ∞ For Each Monomer A and B
 - ∞ Calculate harmonic vibrational frequencies
 - ∞ Calculate quartic 2D potential for \geq triatomics
 - ∞ Solve for vibrational wavefunctions
(using quartic Potential)
 - ∞ Calculate weights and points for vibrational averaging
 - ∞ Calculate static multipoles and dynamic polarizabilities
(at selected geometries)
- ∞ Accumulate A + B
 - ∞ Calculate vibrationally averaged, orientationally dependent long range coefficients
 - ∞ Merge with short range portion of intermolecular potential

Long Range Forces



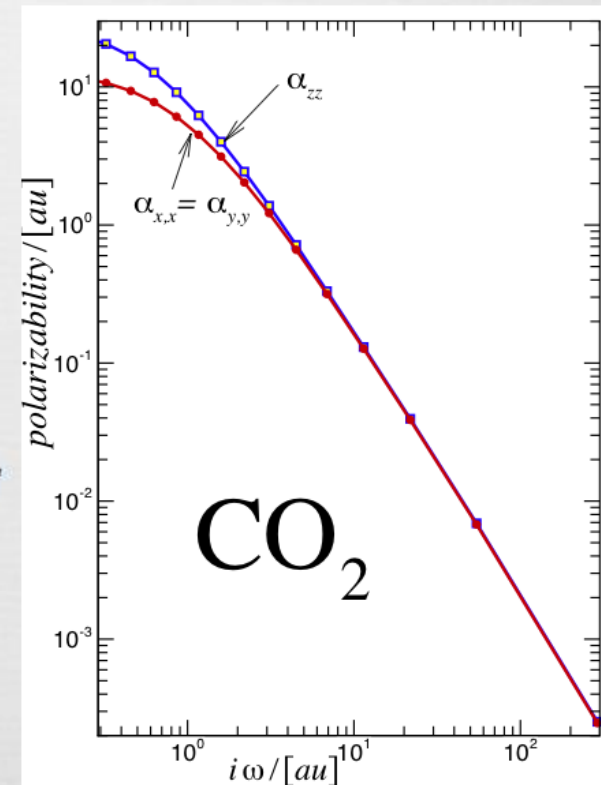
- ∞ Calculate Static + Dynamic Multipole Moments
 - ∞ Calculation : EOM-CC
 - ∞ Method : CCSD(T)

$$C_6(A,B) = \frac{3}{\pi} \int_0^{\infty} d\omega \alpha_A(i\omega) \alpha_B(i\omega)$$

$$\alpha_{a,b}(i\omega) = \frac{\sum_n \langle \psi_0 | \mu_a | \psi_n \rangle \langle \psi_n | \mu_b | \psi_0 \rangle}{E_n - E_0 + i\omega} + \text{permutations}$$

Sum over all electronic excited states

Implicitly solved as a linear equation



Why EOM-CCSD/CCSD(T)?



∞ CCSD(T)

- ∞ Very accurate for good “Hartree Fock molecules”
- ∞ Requires a large basis set
 - ∞ Ex. AUG-CC-PVQZ
- ∞ Potential Energy Surface calculated using CCSD(T)
- ∞ Static Multipole moments calculated using CCSD(T)

∞ EOM-CCSD

- ∞ Dynamic Polarizabilities at imaginary frequencies
- ∞ Good accuracy for electronic excited states
- ∞ Computationally feasible for many perturbations (up to octupole moments)

Results



- ❧ Vibrational Averaging in 1 or 2 Dimensions using quartic potentials
- ❧ Calculate quartic potential at CCSD(T) / AUG-CC-PVQZ
 - ❧ Solve for vibrational wavefunctions
 - ❧ Yields points and weights used for vibrational averaging
- ❧ Dynamic Polarizability calculations using EOM-CCSD and Static Multipole Moments using CCSD(T)
- ❧ Monomers under consideration:
 - ❧ CO₂, N₂O, OCS, CO, He, H₂

Dynamic Polarizability Calculation



C02 Dynamic Polarizability

X

C 1 XX

O 2 R1 1 A1

O 2 R2 1 A2 3 D180

XX= 1.88972599

R1= 2.20529112

A1= 90.00000000

R2= 2.20529112

A2= 90.00000000

D180= 180.00000000

*ACES2(UNITS=BOHR, BASIS=AUG-CC-PVQZ, CALC=CCSD

PROP=EOM_NLO, EOMPROP=QUADRATIC, ORDER_ALPHA=OCTUPOLE, ESTATE_MAXC=40

PRINT=0, MEM=1GB)

Numerical Frequencies: 21

0.0000000000 0

290.0614667772 1

54.5122672097 1

21.7879789324 1

11.4313920657 1

6.8843183314 1

4.4953159136 1

3.0888674614 1

2.1933888610 1

1.5899551348 1

1.1657362618 1

0.8578269655 1

0.6289485647 1

0.4559155095 1

0.3237432530 1

0.2224537762 1

0.1452576641 1

0.0874784098 1

0.0458968683 1

0.0183444948 1

0.0034475451 1

Dynamic Polarizability Calculation

Multipole polarizabilities up to order: 3

```
1 1 << X; X>>
0.12850943E+02 0.24710000E-03 0.67726200E-02 0.38733610E-01 0.12696991E+00 0.31623067E+00 0.66151630E+00\
0.12188389E+01 0.20345622E+01 0.31343031E+01 0.45104136E+01 0.61043495E+01 0.77924462E+01 0.93979103E+01\
0.10743344E+02 0.11721539E+02 0.12332049E+02 0.12655391E+02 0.12796215E+02 0.12842148E+02 0.12850626E+02
```

```
3 3 << Z; Z>>
0.27759589E+02 0.25235000E-03 0.69044700E-02 0.39488150E-01 0.13060091E+00 0.33182186E+00 0.71667170E+00\
0.13802304E+01 0.24369824E+01 0.40146615E+01 0.62375152E+01 0.91828998E+01 0.12796982E+02 0.16793045E+02\
0.20639541E+02 0.23764538E+02 0.25869898E+02 0.27036308E+02 0.27555806E+02 0.27726784E+02 0.27758425E+02
```

```
4 4 << XX; XX>>
0.97645606E+02 0.17233800E-02 0.47743700E-01 0.28296065E+00 0.96914727E+00 0.25022177E+01 0.53816467E+01\
0.10128747E+02 0.17145275E+02 0.26536155E+02 0.37974011E+02 0.50663714E+02 0.63428380E+02 0.74945831E+02\
0.84137271E+02 0.90548023E+02 0.94426790E+02 0.96441195E+02 0.97309623E+02 0.97591695E+02 0.97643693E+02
```

```
5 4 << YY; XX>>
0.24198820E+02 0.52222000E-03 0.13849020E-01 0.73507900E-01 0.22861458E+00 0.55434185E+00 0.11450427E+01\
0.21136129E+01 0.35932328E+01 0.57155935E+01 0.85354511E+01 0.11908820E+02 0.15435681E+02 0.18594270E+02\
0.21003890E+02 0.22583296E+02 0.23485679E+02 0.23936015E+02 0.24126003E+02 0.24187156E+02 0.24198399E+02
```

```
9 9 << YZ; YZ>>
0.15814885E+03 0.26509600E-02 0.72942910E-01 0.42434305E+00 0.14281215E+01 0.36356419E+01 0.77175968E+01\
0.14354589E+02 0.24091752E+02 0.37178712E+02 0.53434139E+02 0.72118358E+02 0.91902780E+02 0.11107597E+03\
0.12791595E+03 0.14107712E+03 0.14996727E+03 0.15498346E+03 0.15725189E+03 0.15800434E+03 0.15814387E+03
```

```
10 10 <<XXX;XXX>>
0.13336603E+04 0.23614530E-01 0.65725870E+00 0.39325402E+01 0.13532324E+02 0.34847858E+02 0.74294186E+02\
0.13805977E+03 0.23056949E+03 0.35307982E+03 0.50263309E+03 0.67089769E+03 0.84368889E+03 0.10032657E+04\
0.11337992E+04 0.12271421E+04 0.12848585E+04 0.13152923E+04 0.13285227E+04 0.13328353E+04 0.13336311E+04
```

```
13 2 <<XXY; Y>>
-0.22834494E+02 -0.45743000E-03 -0.12492470E-01 -0.71282530E-01 -0.23564506E+00 -0.59169827E+00 -0.12407271E+01\
-0.22806825E+01 -0.37853158E+01 -0.57853883E+01 -0.82540522E+01 -0.11079917E+02 -0.14041360E+02 -0.16833753E+02\
-0.19164252E+02 -0.20861037E+02 -0.21924971E+02 -0.22491042E+02 -0.22738290E+02 -0.22819038E+02 -0.22833947E+02
```

Static Multipoles Calculation



C02 Static Polarizability

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R2= 2.20529112

A2= 90.00000000

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*ACES2(UNITS=BOHR,BASIS=AUG-CC-PVQZ,CALC=CCSD(T),FFIELD=-1
ORDER_ALPHA=OCTUPOLE,SYMMETRY=ON,PROPS=FIRST_ORDER,SAVE_INTS=ON
SCF_CONV=8,CC_CONV=8,MEM=1GB)

Static Multipoles Calculation



Static Electric multipoles

n_moments

19

| | | |
|----|-----------|-----------------|
| 1 | << X >> | 0.00000000E+00 |
| 2 | << Y >> | 0.00000000E+00 |
| 3 | << Z >> | 0.10209243E-16 |
| 4 | << XX >> | 0.15802177E+01 |
| 5 | << YY >> | 0.15802177E+01 |
| 6 | << ZZ >> | -0.31604355E+01 |
| 7 | << XY >> | 0.00000000E+00 |
| 8 | << XZ >> | 0.00000000E+00 |
| 9 | << YZ >> | 0.00000000E+00 |
| 10 | << XXX >> | 0.00000000E+00 |
| 11 | << YYY >> | 0.00000000E+00 |
| 12 | << ZZZ >> | 0.91499244E-16 |
| 13 | << XXY >> | 0.00000000E+00 |
| 14 | << XXZ >> | 0.65507192E-16 |
| 15 | << XYY >> | 0.00000000E+00 |
| 16 | << YYZ >> | 0.47836346E-16 |
| 17 | << XZZ >> | 0.00000000E+00 |
| 18 | << YZZ >> | 0.00000000E+00 |
| 19 | << XYZ >> | 0.00000000E+00 |

_Static multipole polarizabilities up to order: -1

Still To Do

Longer Term



- ❧ Angular Momentum Coupling using modified SAPT code (Bukowski, Wormer, Szalewicz, et al.)
- ❧ ConstructFull Potential
 - ❧ Merging long-range with short-range seamlessly
- ❧ Perform Simulations to obtain vibrational shifts
- ❧ Compare Results with experimental data

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