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Density Functional Theory (DFT) simulations of CO_2 under shock compression and design of liquid CO_2 experiments on Z

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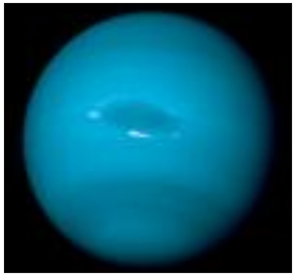
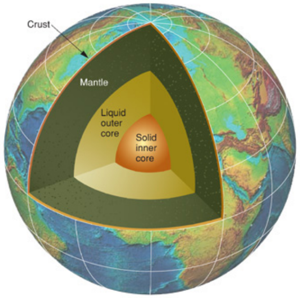
Properties of light elements in the Mbar regime are important for several reasons

- **Planetary science – Uranus & Neptune and exo ice-giants**
  - High-pressure mixtures of C, H, O, N:
- **Planetary science – earths and super-earths**
  - Equation of state of Fe and subducted CO_2
  - Mbar, 1000 – 4000 K
- **Inertial confinement fusion (ICF) materials**
  - Fundamental behavior of carbon and carbon compounds
  - Mbar, +10 000 K
- **Chemistry at high pressure and temperature**
  - Different phases
  - Dissociation by pressure and temperature

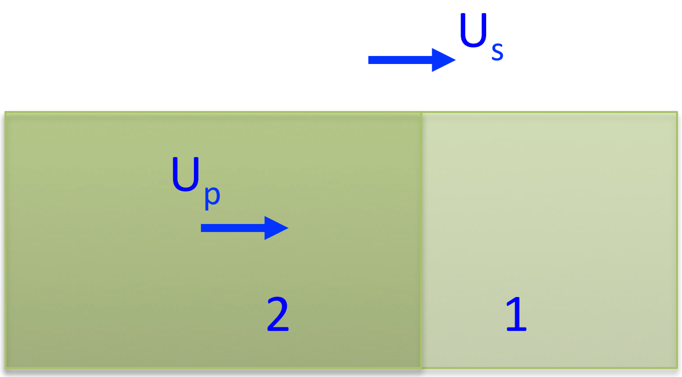


Ice giants: C-H-N-O mixtures at Mbar



Deep carbon cycle, CO_2 in the mantle

Shock compression is a way to investigate thermo-physical properties of matter at extreme pressures



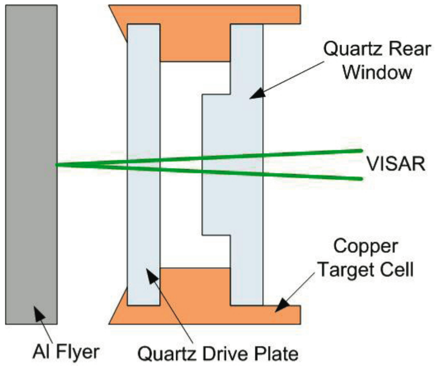
- *Conservation of mass, energy, and momentum* lead to the **Rankine-Hugoniot condition** for the initial (1) and final state (2)

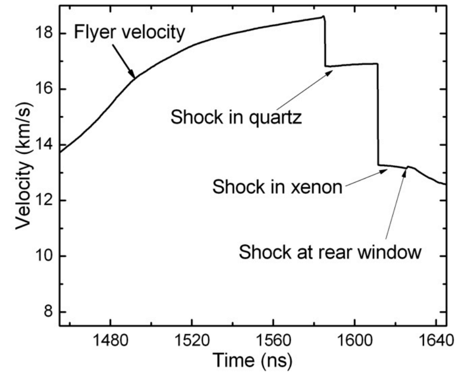
  - E - internal energy
  - P - pressure
  - v – specific volume

$$2\left(E_2 - E_1\right) = \left(P_2 + P_1\right)\left(v_1 - v_2\right)$$

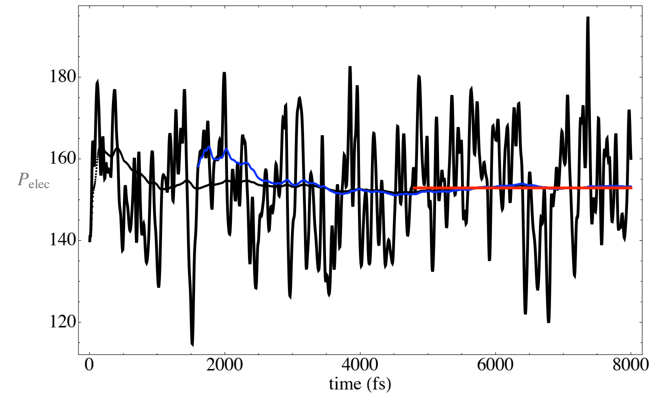
- *With high accuracy measure and/ or calculate thermo-physical properties*

Experiments on Z and density functional theory (DFT) calculations give independent information



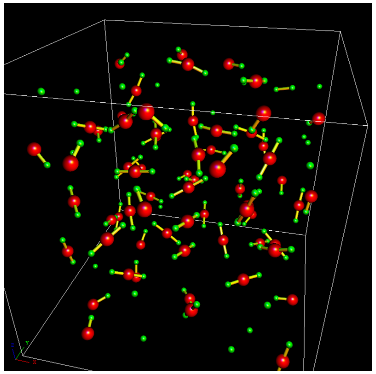


Large samples give long steady shocks,



- **Z – Mbar measurements to high accuracy**
  - **Magnetically launched flyers + VISAR**
  - **Well-defined plate-impact experiments**
    - *M.D. Knudson and M.P. Desjarlais, Phys. Rev. Lett.* ***103****, 225501 (2008)*
    - *S. Root et. al. Phys. Rev. Lett.* ***105****, 085501 (2010)*

Molecular dynamics (MD) simulations give thermo-physical properties

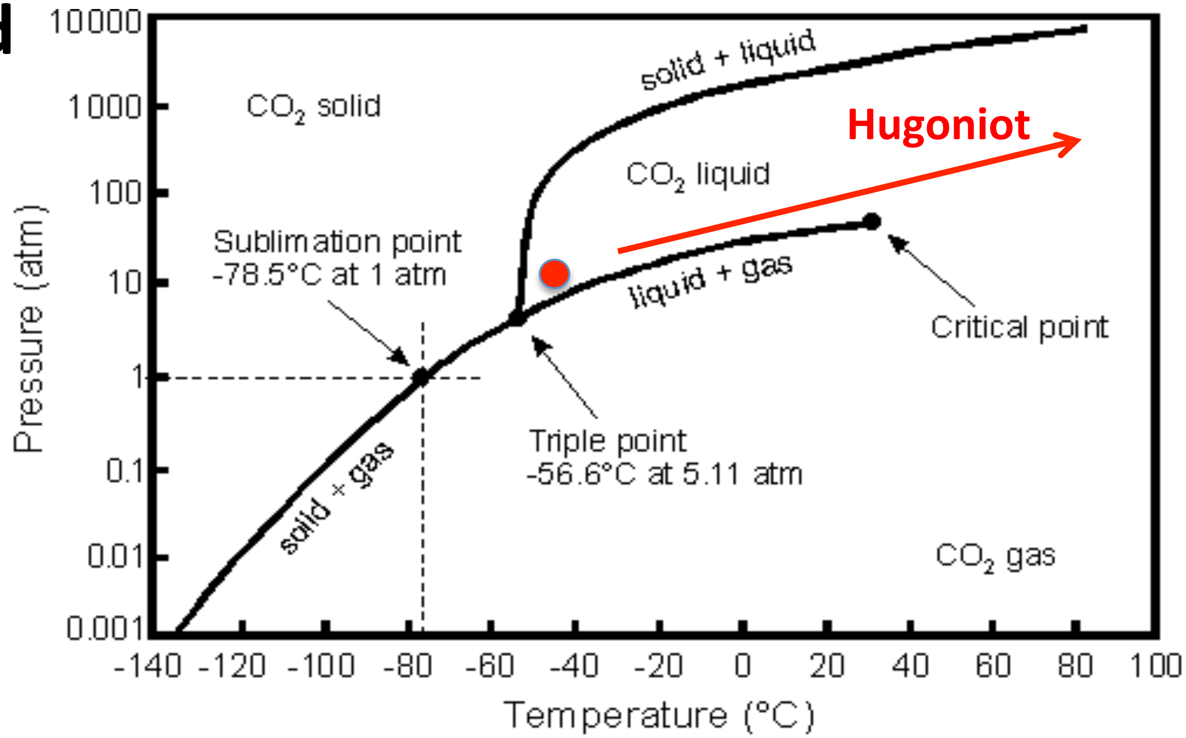


- **First-principles simulations DFT**
  - **VASP – plane-wave code w PAW core-functions**
  - **Great care in convergence**
    - *A. E. Mattsson et. al. Modelling and Simulation in Material Science and Engineering* ***13****, R1 (2005)*
  - **Importance of exchange-correlation functionals**
    - *A. E. Mattsson et al. JCP* ***128****, 084714 (2008)*

Liquid CO2 requires an experimental cell under pressure

- **Advantages of liquid**
  - Uniform sample
  - Initial state EOS well-defined
- **Phase-diagram of CO2**
  - Sublimation at 1 atm
- **Initial state in liquid**
  - 7 bar/ 700 kPa
  - 1.173 g/cm^3
  - 218 K

Phase-diagram of CO2



The initial state for upcoming experiments on Z will be liquid close to the triple points

Liquid CO_2 requires an experimental cell under pressure

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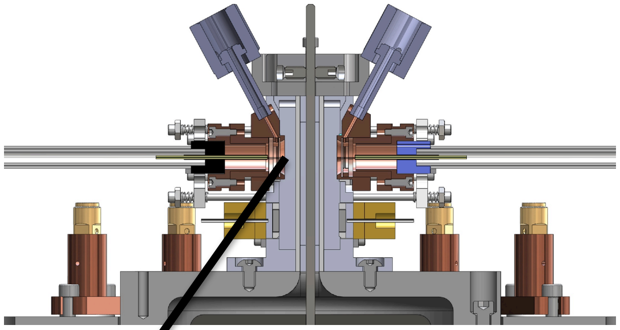
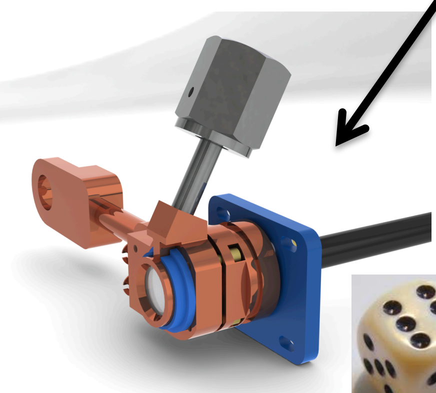


New experimental setup allows for dual cryogenic experiments



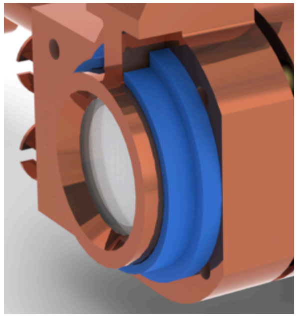
The pressure cell is the size of a die

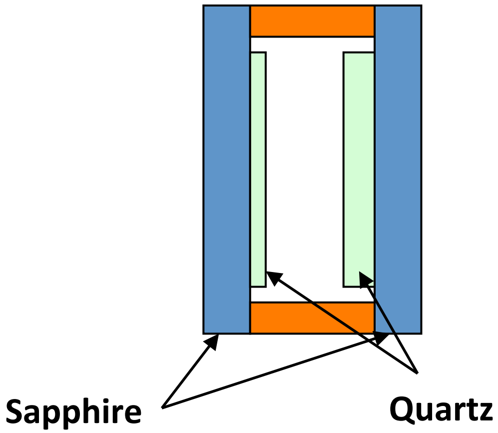
Liquid CO_2 target design and projected resulting pressure range

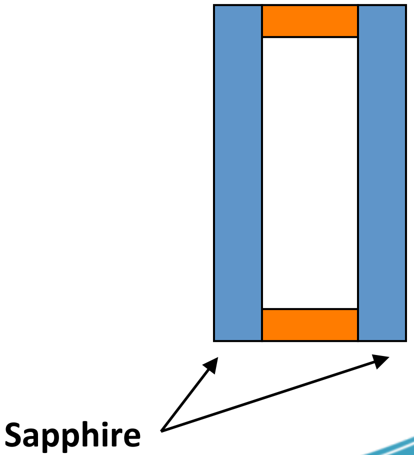
- **Al Flyer Velocity Range: 18 – 30 km/s**
- **Designed the window thickness with margin for break**
- **Sapphire Reflective above 600 GPa**
- **Will use quartz plates to measure shock speeds at pressures lower than 600 Gpa.**

- **Expected CO_2 pressure range: 150 GPa – 600 GPa**

Different target designs depending on sought pressure



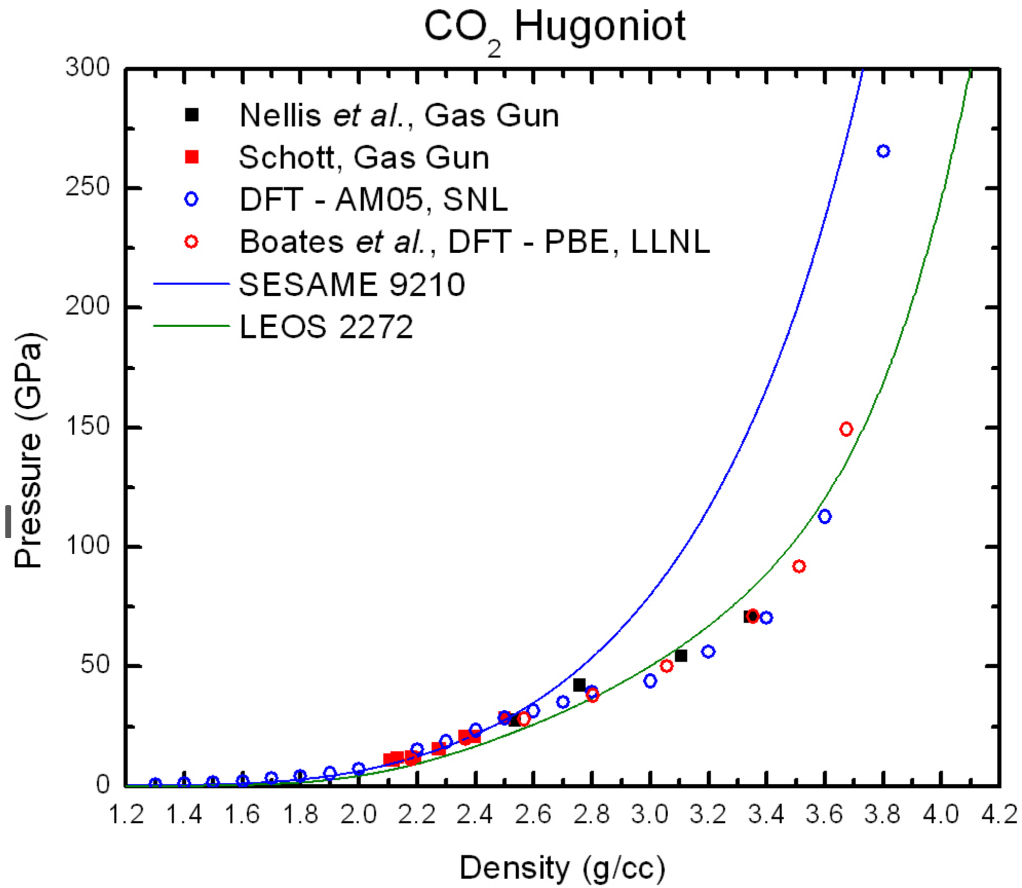




DFT calculations in agreement with available experimental data and predictions above 100 GPa

- **DFT simulations**
  - Quantitative and qualitative agreement with Schott (High Press. Res. 6, 187 (1991)) and Nellis et al (J. Chem. Phys. 95, 5268 (1991)).
  - Minor difference between PBE and AM05 exchange-correlation functionals
  - Existing EOSs do not capture the full behavior

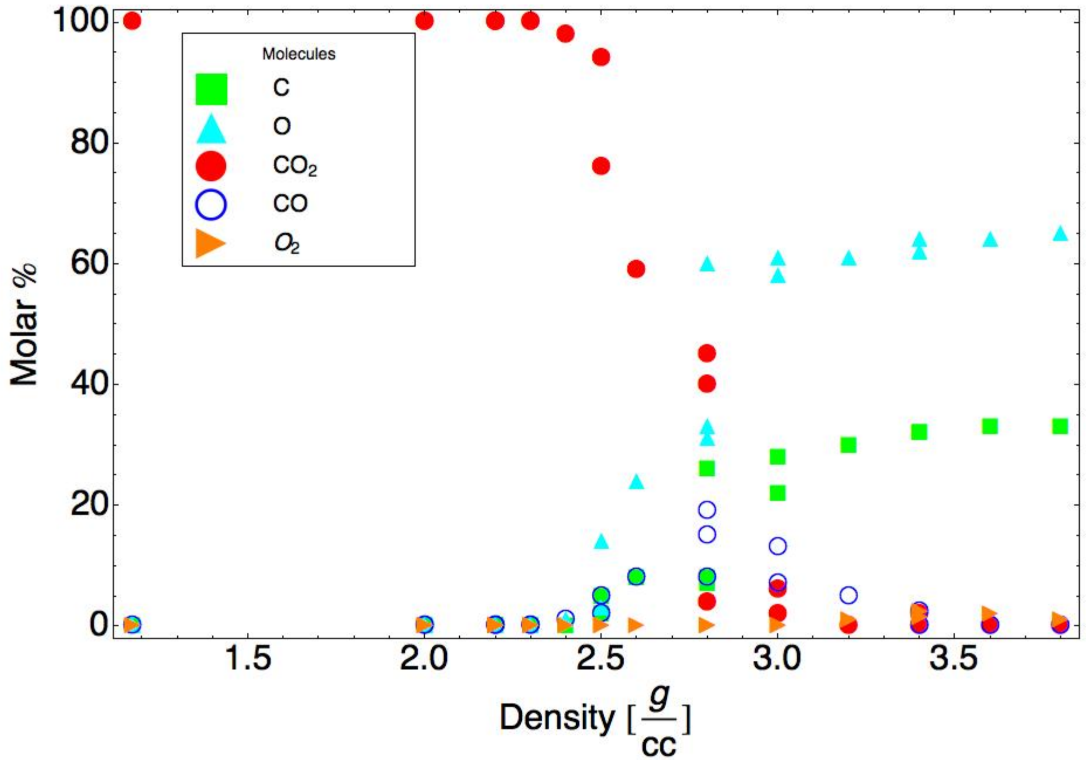
- **Behavior above 100 GPa**
  - Relatively steep raise in pressure beyond 3-fold compression
  - We confirm very recent DFT results by Boates et al. (J. Chem. Phys. 134, 064504 (2011))



We expect a steep rise in shock pressure towards four-fold compression

DFT simulations contributes to understanding the physical behavior of the system

- **Shoulder in shock pressure**
  - Nellis et al attributed it to dissociation
- **We analyze the simulations along the Hugoniot**
  - Dissociation begins at 2.5 g/cm3 and is completed above 3.0 g/cm^3
  - Confirm dissociation as the cause for a shoulder in the Hugoniot pressure
- **After completed dissociation, we expect a strong increase in shock pressure**



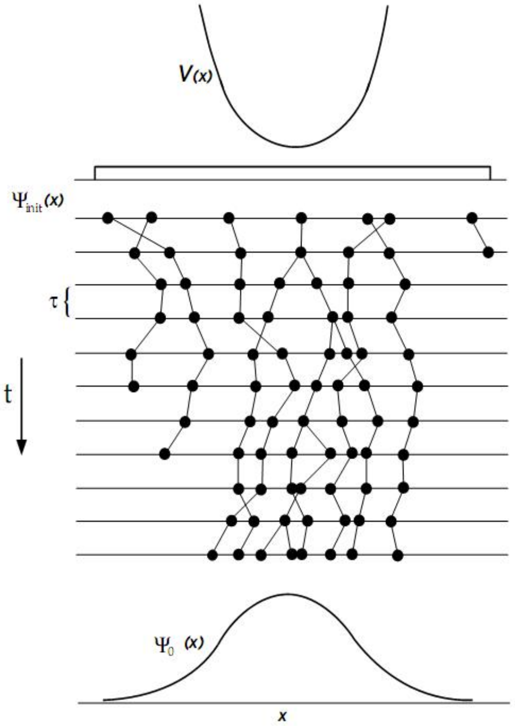
Mole % of CO, CO2, O, C, and O2 as a function of density along the Hugoniot

Going deeper – assessing the initial state with Quantum Monte Carlo

$$2(E_2 - E_1) = (P_2 + P_1)(\upsilon_1 - \upsilon_2)$$

- **Which errors are present in DFT calculations of CO_2?**
  - At low T and P, intermolecular forces are influenced by van der Waals
  - At high T and P, orbital overlap and hybridization dominates
  - Widely used DFT approximations do not treat van der Waals correctly
    - *Local approximations v.s. nonlocal interactions*
- **What can we do?**
  - Quantum Monte Carlo
    - *Use stochastic projection to solve Schrodinger equation exactly*
    - *Main approximation (fix node) does not involve the interactions*
    - *Limitations*
      - Significantly more expensive than DFT
      - Limited norm-conserving pseudo potentials

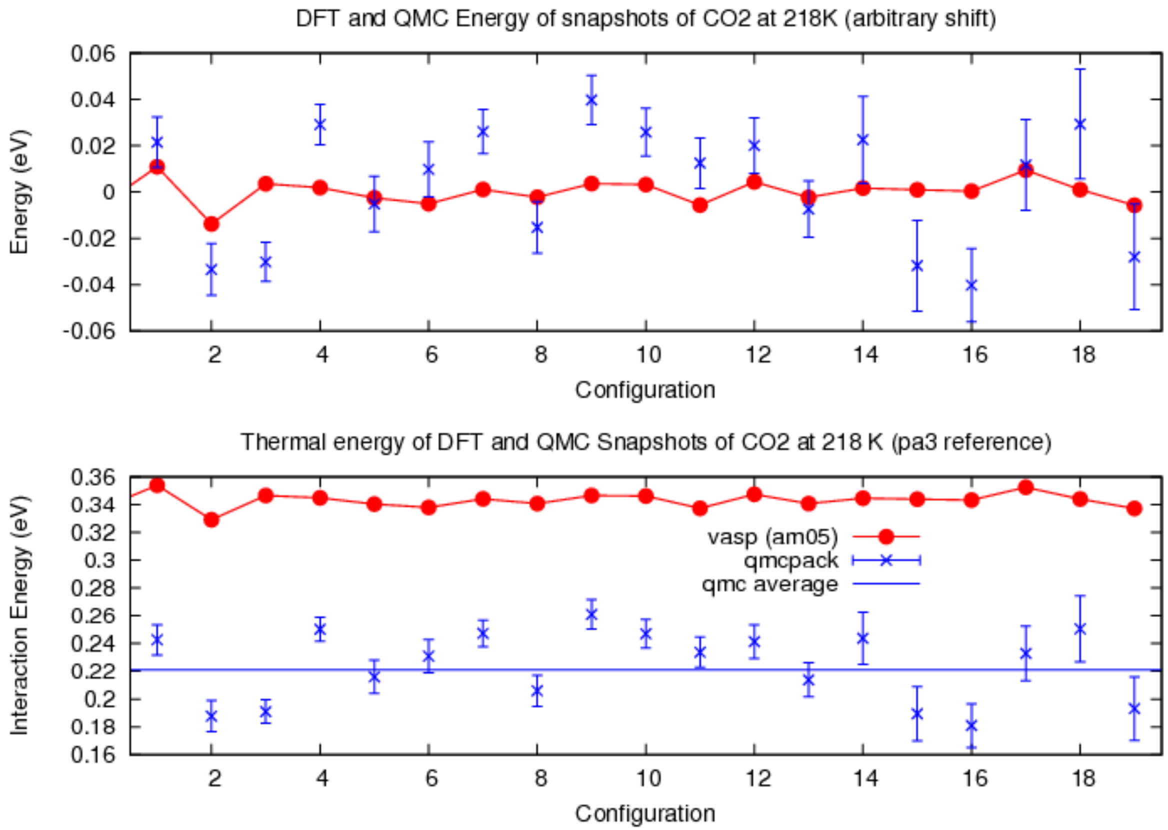
The many-body wave-function is sampled by walkers in the potential



J. Needs, M. D. Towler, N. D. Drummond, and P. Lopez-Rios, Casino Version 2.2 User Manual, University of Cambridge, Cambridge (2008)

Going deeper – assessing the initial state with Quantum Monte Carlo

- **Assess energy landscape of CO_2 at initial conditions of the experiment**
  - **Assume DFT molecular dynamics sample configuration space correctly**
  - **Calculate energies of snapshots along the MD run to validate internal energy**
    - *Lack of significant uncorrelated discrepancies suggest sampling is reasonable*
    - *Constant offset with respect to reference systems to make correction of Hugoniot*



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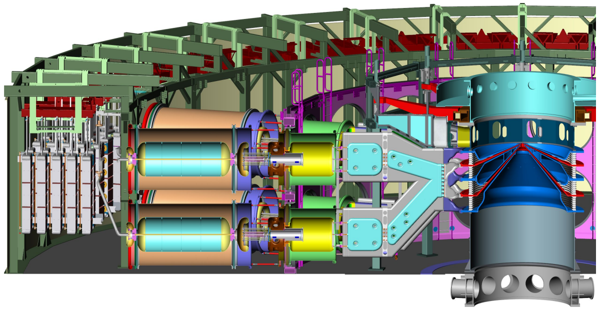
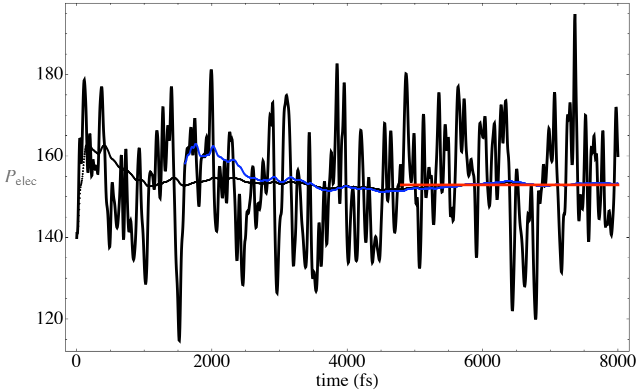
Summary and conclusions

- **Employed DFT based MD simulations to model shock compression of CO2**
  - Agreement with existing data < 100 GPa
  - Confirm a dissociation plateau at 60 GPa
  - Predictions for shock compression to 500 GPa
  - Steep rise in shock pressure following the dissociation region
- **Designed and planned experiments on Z to measure the shock Hugoniot of CO_2 to 500 GPa**
- **Inititial experiments are planned for this spring, we will present results at the SCCM meeting in Chicago, June 26 – July 1, 2011**



Shock experiments on Sandia's Z machine



Density Functional Theory simulations

Acknowledgments

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- The cryogenic team – D. L. Hanson
- Sandia High-Performing Computing (HPC) – S. Corwell
- Dawn Flicker

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