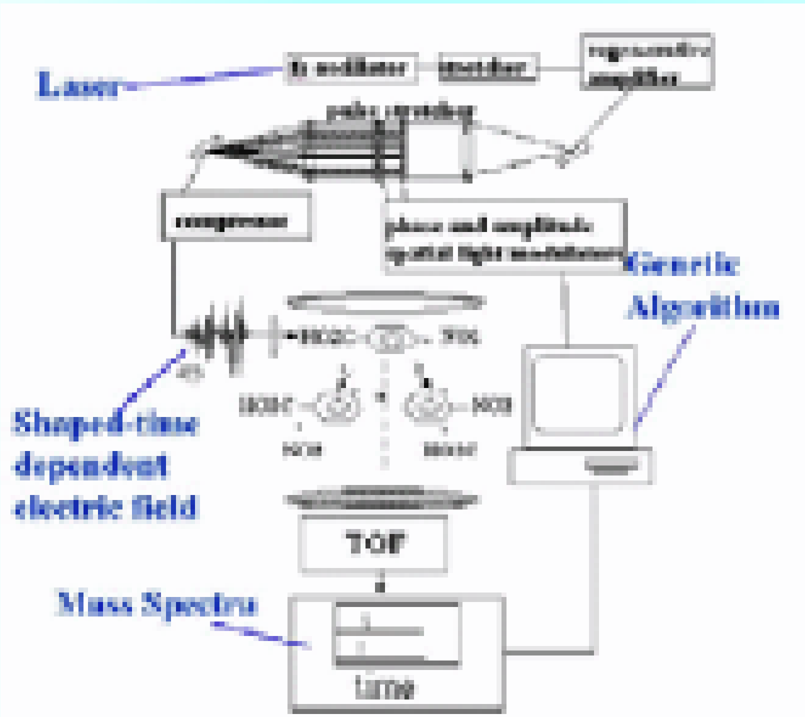
FEL Measurements on Gas Phase Samples?

Trevor Sears-Personal overview

- Workshop: Scientific Frontiers with Accelerator-Based Lasers (Oct 2000)
  - Number of distinct areas of focus-including possibilities for new fields and opportunities in gas phase chemical physics
  - Within this sub-topic:
    - Control
    - Dynamics up to the dissociation point
    - Single molecule ionization
    - Also: molecular understanding of cluster and thin-film formation
  - Also Physics Today article Jan. 2002

Chemical Control

Control of photochemistry using "shaped" pulses of light



Rob Levis, Wayne State University

- Requires tunable UV-DUV FEL
  - Large bandwidth,* high peak powers, accurate pulse to pulse phase relationship and amplitude stability.

* So that one can explore a large Fourier space- simultaneously drive many molecular modes.

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Related

Control of dynamics through to the dissociation point

- Tunable high intensity IR pulses
  - Require similar characteristics to chemical control via electronic excitation.
    - Excite molecule from fundamental vibrational mode through dissociation.
    - Require tunable high intensity pulses which can be swept in frequency during the pulse, as well as slowly varying frequency of successive pulses.
- Strong field experiments
  - Require 10^{13} W/cm^2, ps pulses

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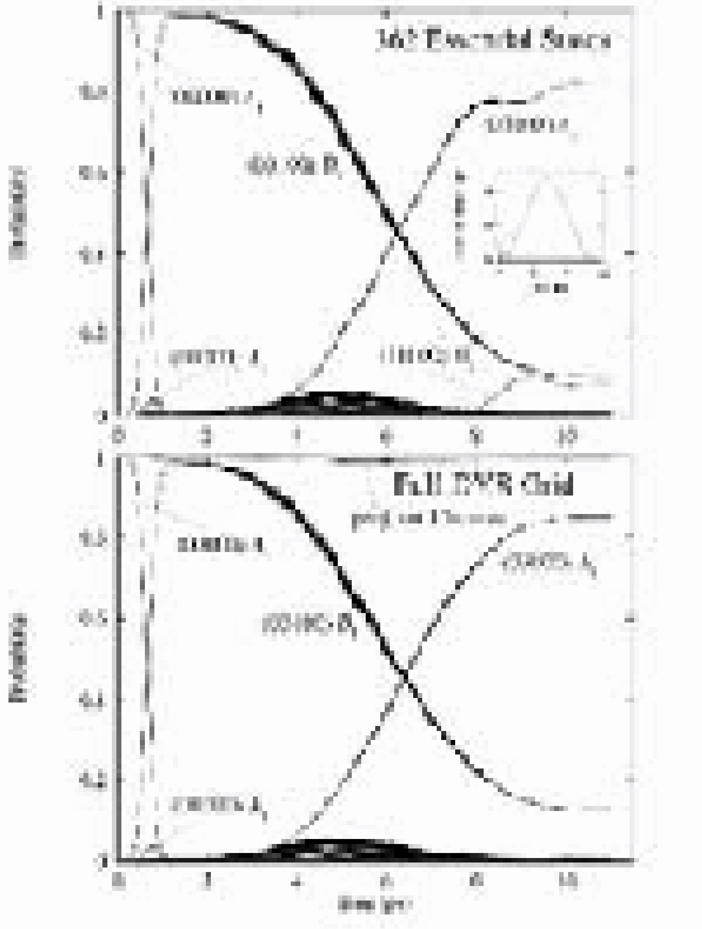
Dissociation of HCCH

Calculations: (Jim Muckerman, BNL)



- 2-pulse sequence to populate ν_2 (C-C symmetric stretch)
  - First drives ν_3 fundamental, second excites further and transfers population to desired vibration.
  - Pulses need to be chirped to maintain resonance with shifted molecular frequencies

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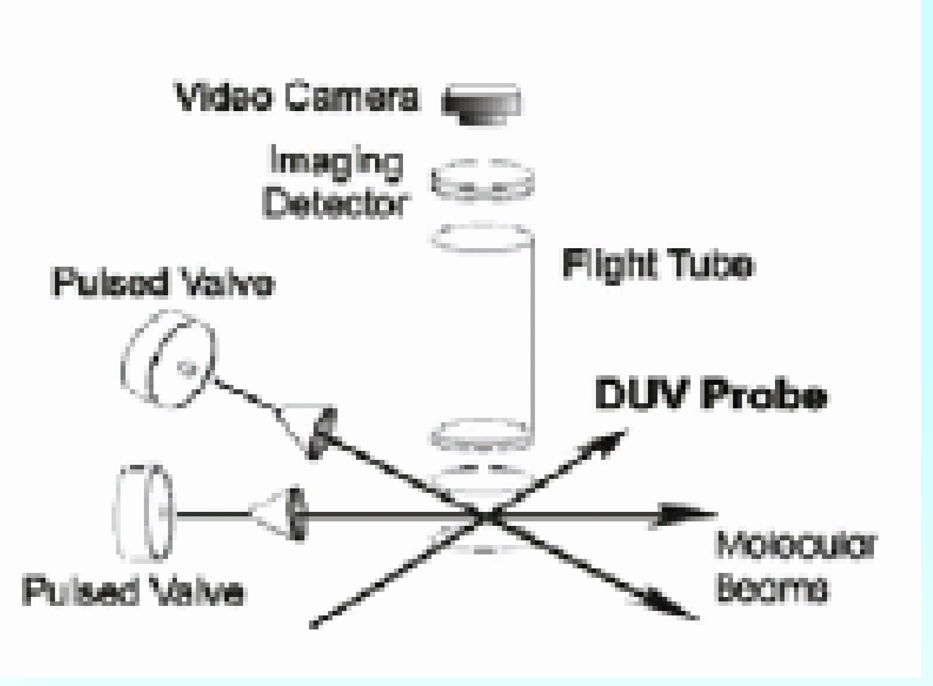
Single Molecule Ionization

Universal, but specific, detection scheme



Arthur Suits, Stony Brook/BNL

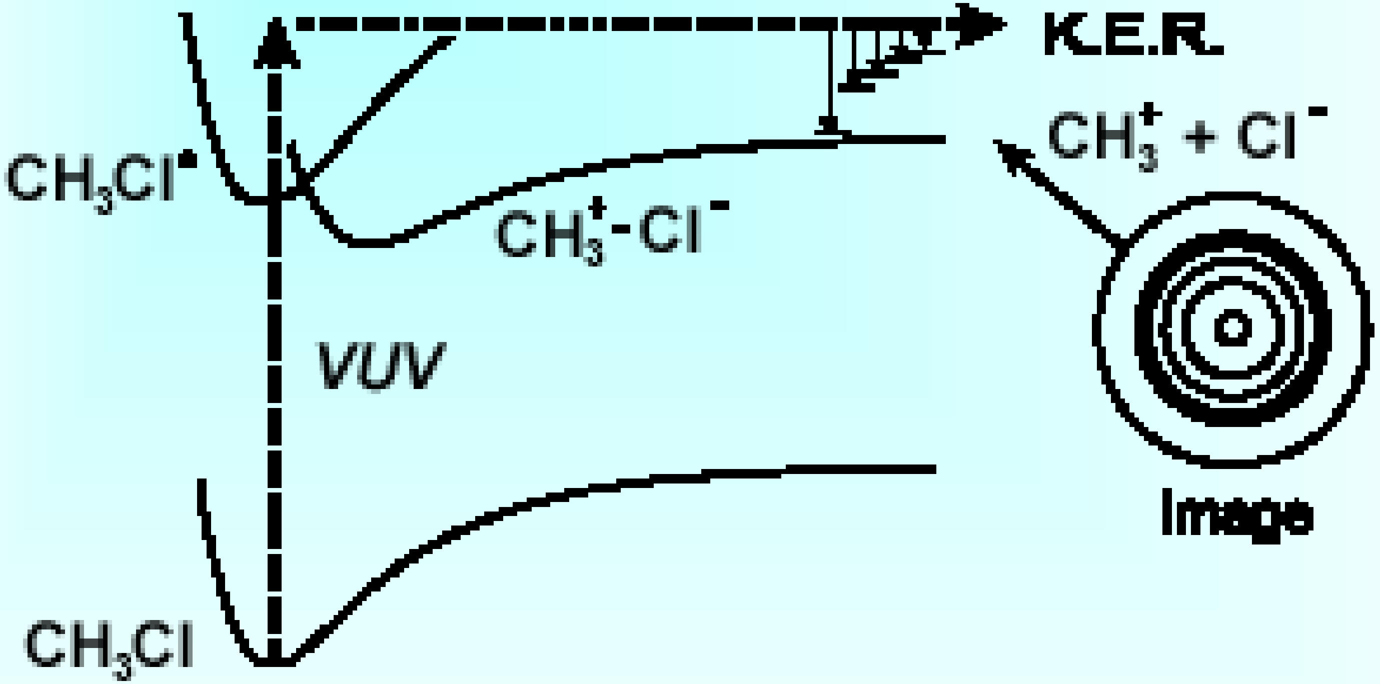
For example:

$Cl + CH_3CH_2CH_3 \Rightarrow$
$CH_2CH_2CH_3 + HCl$
or $CH_3CHCH_3 + HCl$

Isomers have same mass, but slightly different IP's

Ion Pair Formation

VUV excitation of CH_3Cl



Arthur Suits SUNY-SB/BNL

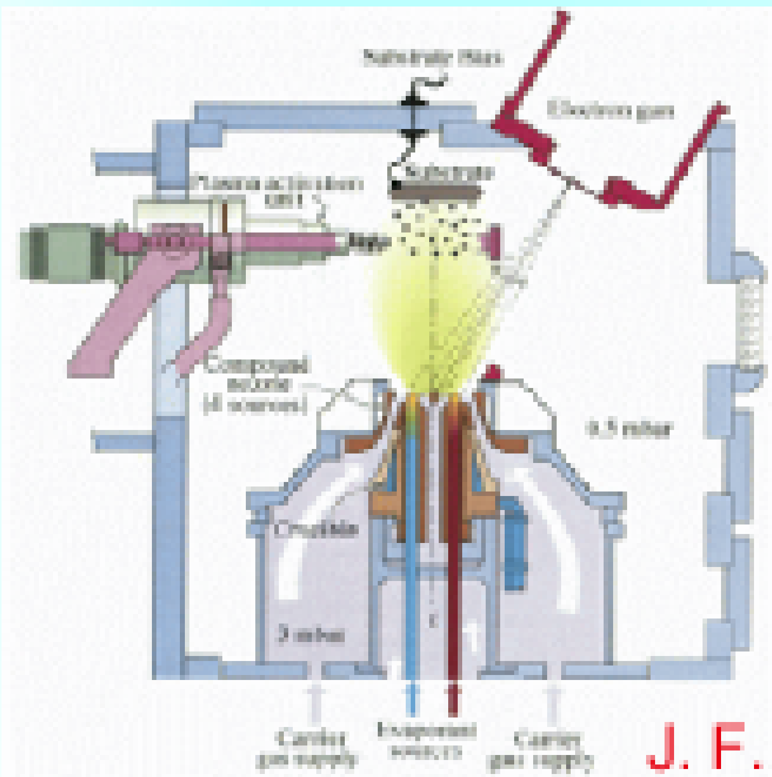
FEL Requirements

For single molecule ionization

- Tunable VUV (8-20 eV)
  - 10^{19} photons/sec, bandwidth of 10^{-3}-10^{-4}
  - High repetition-rates needed for coincidence experiments
- Extension (alternative method) to time-dependent structural dynamics?
  - Intense narrow bandwidth x-ray pulse synchronized with excitation

Molecular Precursors in Crystal Growth Processes

Closer to current capability



- Current interest in nanostructure materials
  - Coatings
    - Surface properties
  - Electronic structure
    - New devices
  - Chemical properties
    - New catalysts

J. F. Groves et al., UVa,...

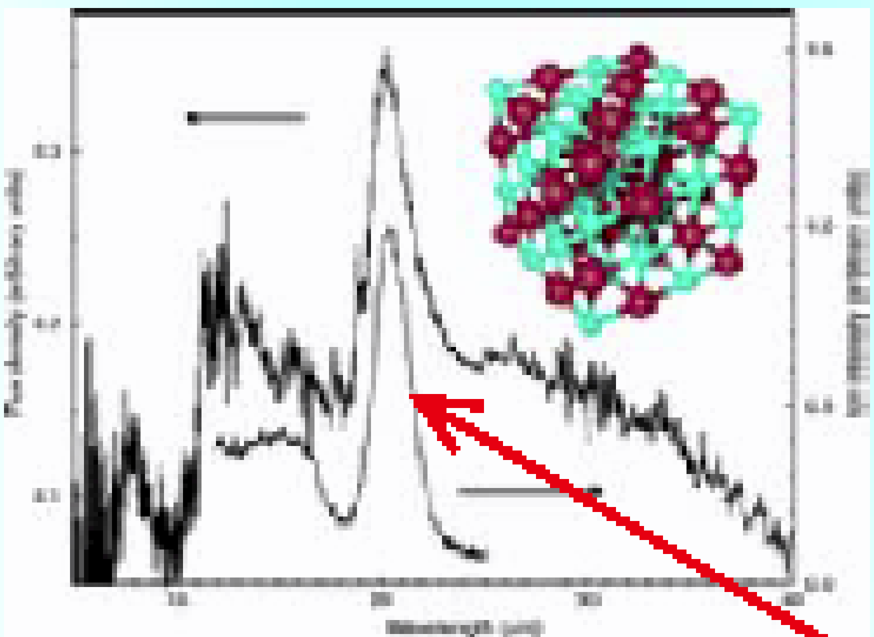
New Catalysts

For example, *MoC*-based systems

- Show great promise
  - Replacements for noble metal-based catalysts (expensive) in methane reforming, hydro-desulfurization
- Reactivity studies
  - Large variations in activity with size and structure
- Gas phase precursors?
  - Molecular description of the active site!!!

Molecular Cluster Characterization

Example of Ti-metcar clusters



- IR Spectra at FELIX
  - Resonant IR absorption is followed by increasingly strong photon absorption to ionization
  - Detect mass-analyzed ions as function of IR wavelength

G. Von Helden et al. Science **288**, 313 (2000).

IR band near 20 μm

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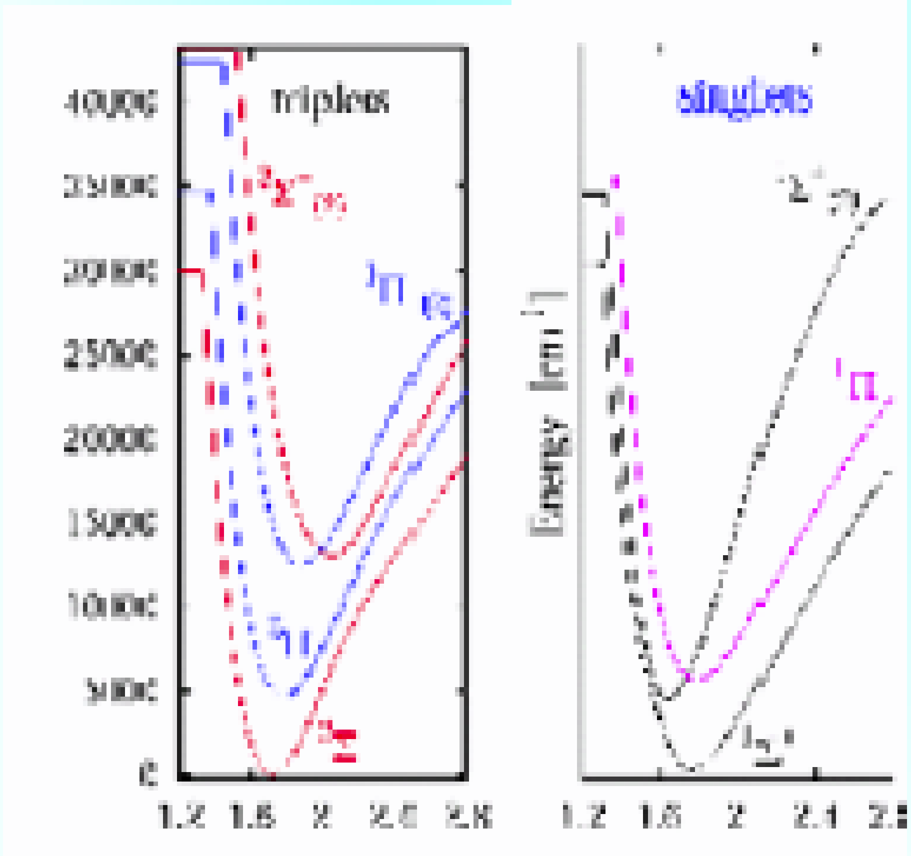
diatomic TiC

IC-MRCI, all electrons



- Computed PE curves for lowest states
  - Lowest state is triplet (just)
    - Electronic spectrum near 2μm
    - Huge number of low-lying states (within 2 eV)

Jim Muckerman, Nicolas Poulin, BNL

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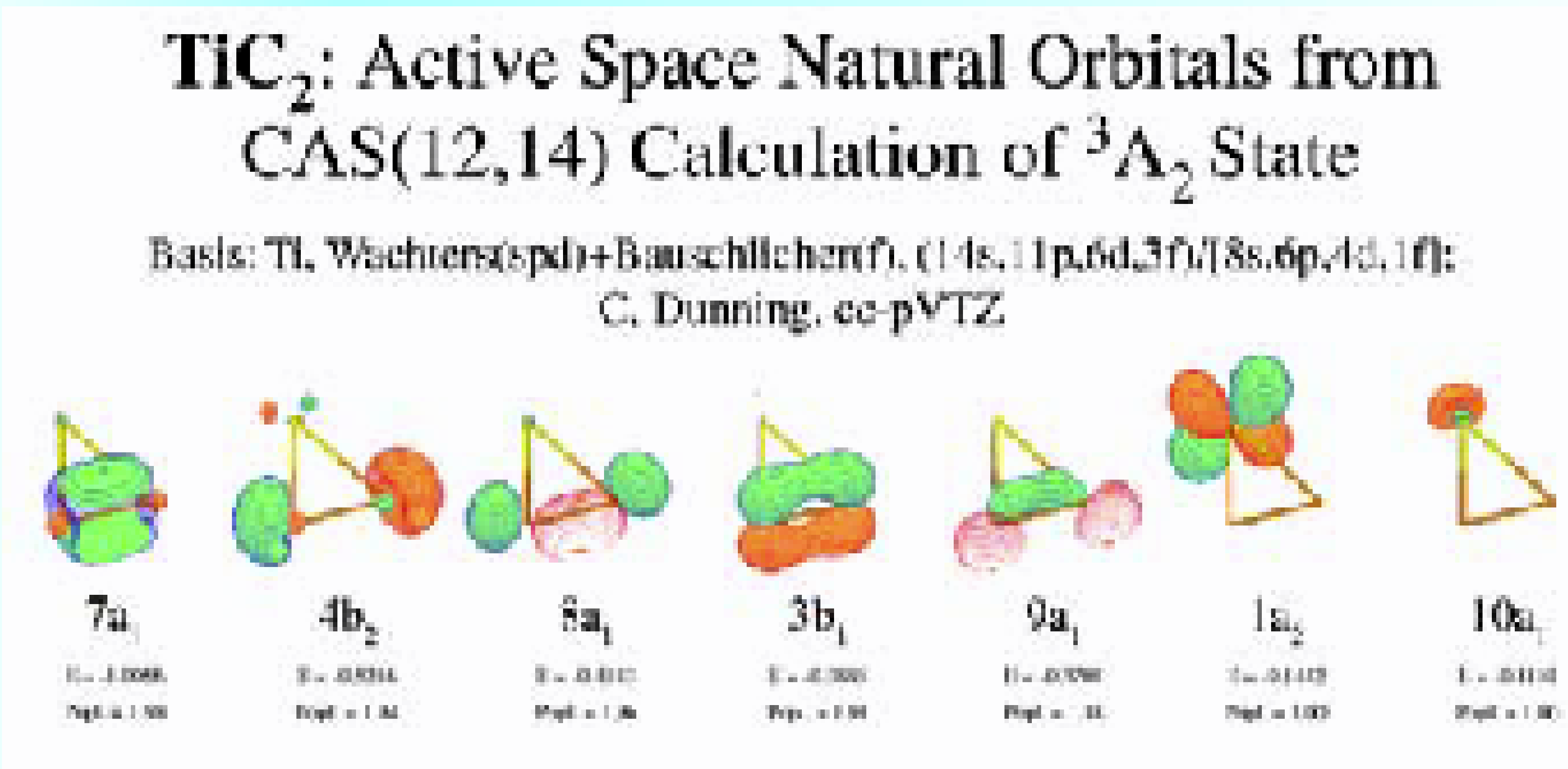
TiC_2 and larger

Computed structures:



Nicolas Poulin and Jim Muckerman, BNL

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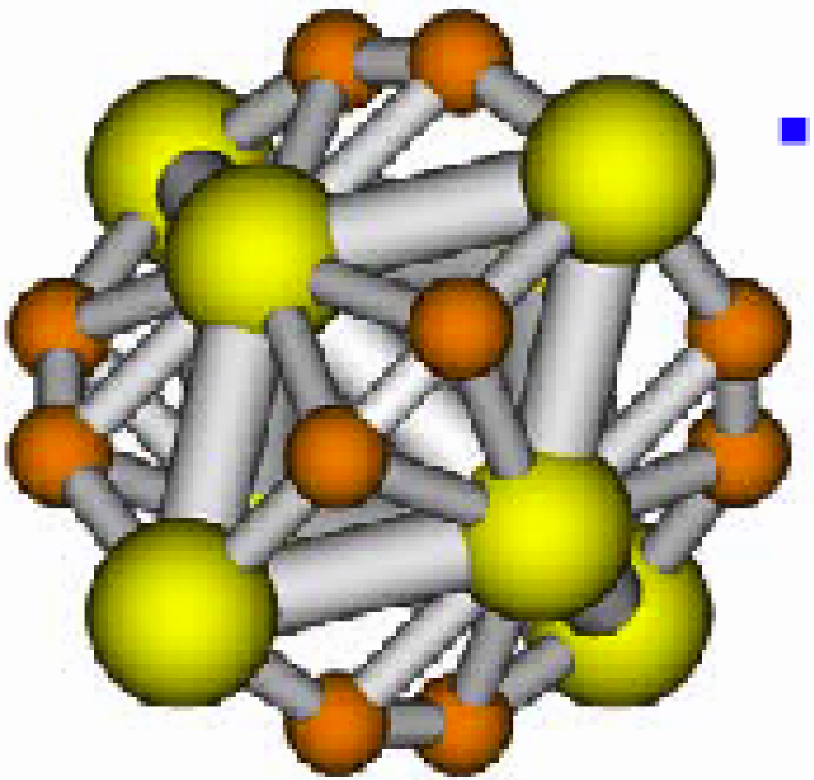
Ti_8C_{12}



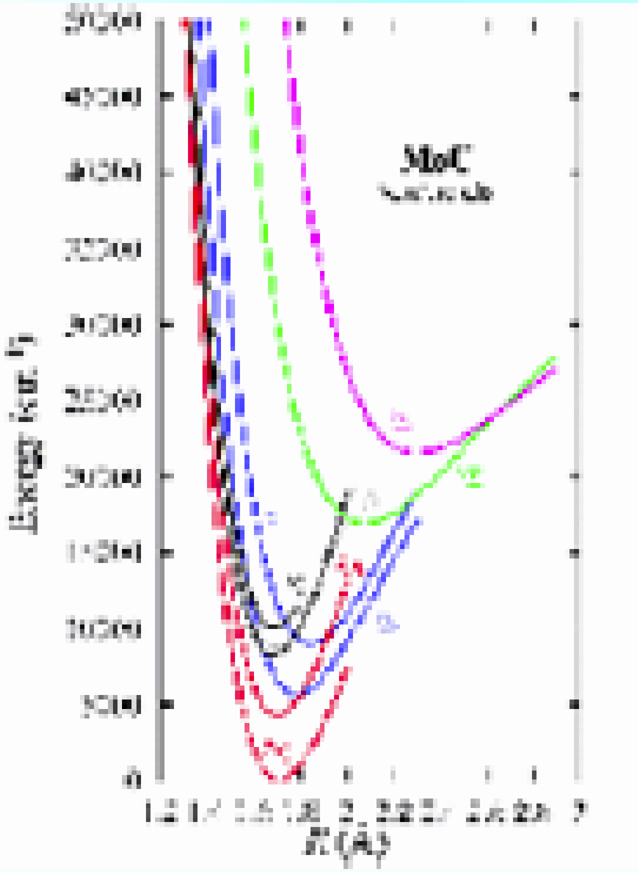
D_2 Symmetry: HF/3-21G Calculations
E(RHF) = -7205.60428719 Hartree
(No Imaginary Frequencies)

- Recognize TiC_2 fragments
  - D_2 symmetry? (Some degenerate vibrations)
  - Lower energy for less symmetrical configuration, but find imaginary frequencies

Jim Muckerman, BNL

Plasma Characterization

Vibrational or electronic spectra?



- Early transition metal carbides (TiC and MoC) have very complex electronic structure
  - But diatomic species seem generally to have first excited state at energy near 2 μm.
- No optical spectroscopic data exists for these species!

Jim Muckerman, Nicolas Poulin, BNL

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Summary

Potentially numerous applications for current and future FELs

- Present:
  - Investigation of molecular and cluster precursor species in materials production
  - IR absorption spectroscopy with indirect detection methods
- Future
  - Chemical control (in IR with pulse shaping)
  - Chemical control (in UV via electronic transitions)
  - Single molecule ionization as exquisite detection method

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