Applications of Quantum Chemistry

$$H\Psi = E\Psi$$

Areas of Application

- Explaining observed phenomena (e.g., spectroscopy)
- Simulation and modeling: make predictions
- New techniques/devices use special quantum properties

Q.M. Required to Explain Many Observed Phenomena

- Blackbody radiation
- Photoelectric effect: makes no sense without the idea of photons
- H atom spectrum (and other spectra) explained extremely well by Q.M.
- Two-slit experiment: interference patterns caused by wave-like properties of matter
- Many others!

Simulation and Modeling

- Electronic Structure Theory: Solve for electronic Schrödinger Equation, get electronic properties and potential energy surfaces.
- Dynamics: Solve for motion of nuclei on the potential energy surfaces. Important for detailed understanding of mechanisms.

Electronic Structure Theory

Electronic wavefunction and its derivatives give...

- Dipole moment, polarizability,...
- Spectra: electronic, photoelectron, vibrational, rotational, NMR, ...
- Equilibrium geometry is one with minimum energy

Electronic Structure Methods

Method	Accuracy	Max atoms
Semiempirical	Low	2000
Hartree-Fock & Density Functional	Medium	500
Perturbation & Variation Methods	High	50
Coupled-Cluster	Very High	20

High-Accuracy Quantum Chem

Typical accuracy of coupled-cluster methods

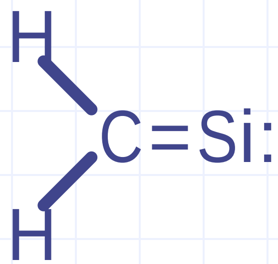
Property	Accuracy
Bond lengths	± 0.004 Å
Bond angles	± 0.03°
Vibrational frequencies	± 2%
Dipole moments	± 0.05 D
Relative energy	± 1.5 kcal/mol

Example Applications

- Predicting/confirming spectra
- Sructures/energies of highly reactive molecules
- Interaction between possible drugs and enzyme active sites
- Computational materials science

Interstellar Molecule Spectra

- 1-Silavinylidene has been predicted to be abundant in interstellar space



- Could search for it if we knew what its microwave/infrared spectra looked like
- Bengali and Leopold performed tricky experiments and requested theoretical confirmation.

Theory Confirms Assignment

Mode	Theory	Experiment
ω_1(CH sym str)	3084	2980 $\pm$ 20
ω_2(CH_2 scissor)	1345	1250 $\pm$ 30
ω_3(Si-C str)	927	930 $\pm$ 20
ω_4(Si oop bend)	690	
ω_5(CH asym str)	3165	
ω_6(CH_2 rock)	305	~ 265

Using TZ2Pf CCSD(T) theoretical method.

Sherrill and Schaefer, J. Phys. Chem. **99**, 1949 (1995).

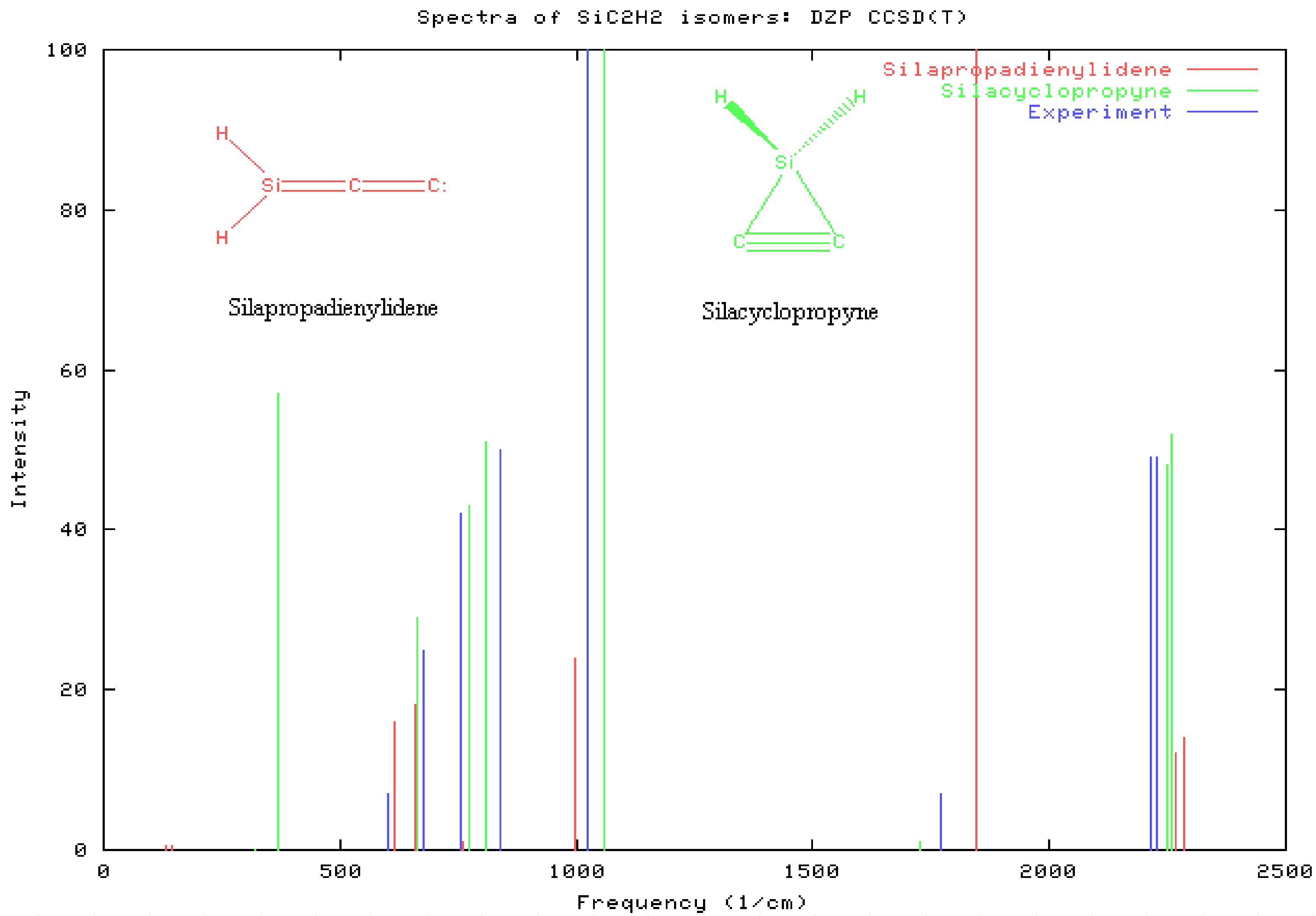
Vibrational Spectra of SiC_2H_2 Species

- Maier et al. isolated a new, unknown SiC_2H_2 species
- The matrix IR spectrum indicated an SiH_2 group (absorption at 2229 and 2214 cm^{-1}).
- Theory shows which species was seen.

Maier et al. Angew. Chem. Int. Ed. Eng. **33**, 1248 (1994).

Sherrill et al. J. Am. Chem. Soc. **118**, 7158 (1996).

Theory Shows Silacyclopropyne Seen



Highly Reactive Systems

- Many molecules are hard to study experimentally: e.g., radicals, diradicals, highly strained molecules.
- Theory can be helpful in understanding such systems.

N_8: Possible Rocket Fuel

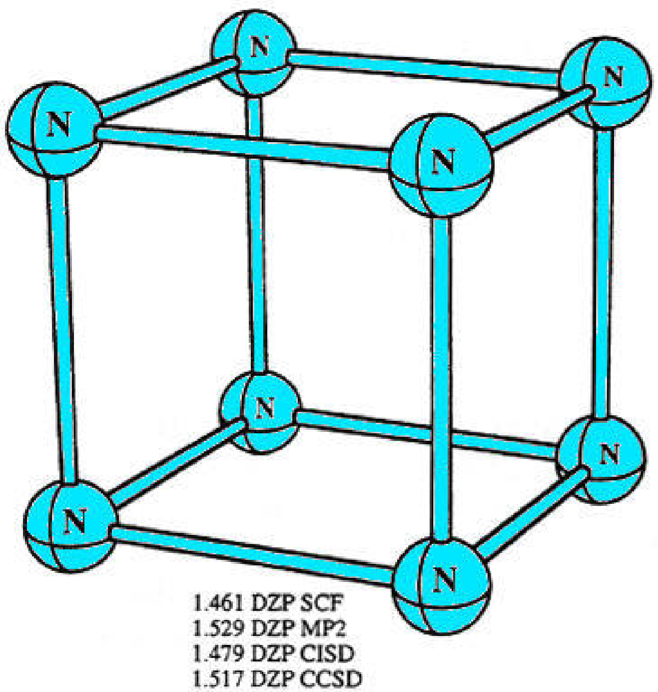


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Figure 1. Theoretical equilibrium geometries of the O_h symmetry octahedral structure of N_8. Bond lengths are in angstroms, and bond angles are in degrees.

- ❖First studied theoretically.
- ❖Energy for decomposition $N_8 \rightarrow 4\ N_2$ is computed as 423 kcal/mol !
- ❖Efforts underway to synthesize it.

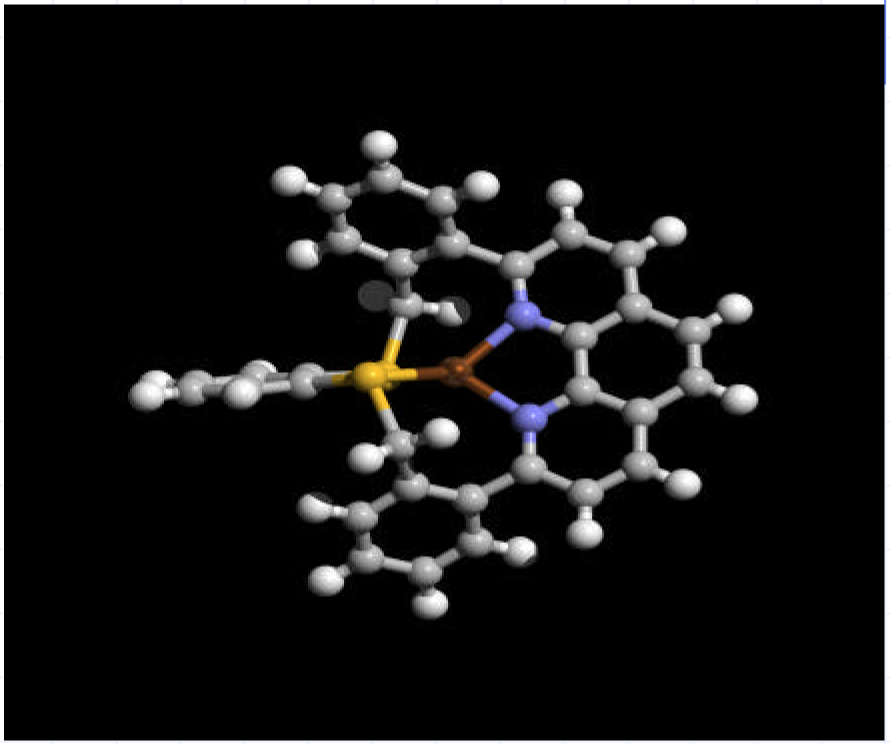
Leininger, Sherrill, and Schaefer, J. Phys. Chem. **99**, 2324 (1995).

Design of New Molecules

- Often need to design a molecule for a specific purpose (e.g., N_8 for rocket fuel).
- Theory is useful for narrowing down the list of candidate molecules.
- Ruling out bad candidates early saves time: no need to synthesize something which won’t work.
- This strategy used by many pharmaceutical companies.

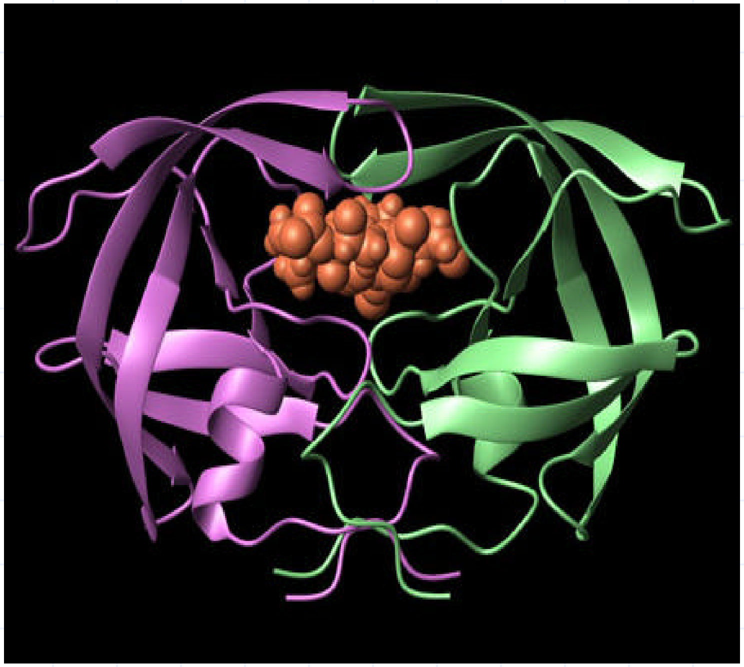
Fluorescent Copper(I) Probes

- Collaboration with Prof. Christoph Fahrni
- Need a way to track Cu(I) ions in the body to understand their biochemical role
- Use theory to predict structures and spectra of possible Cu(I) probes



Rational Drug Design

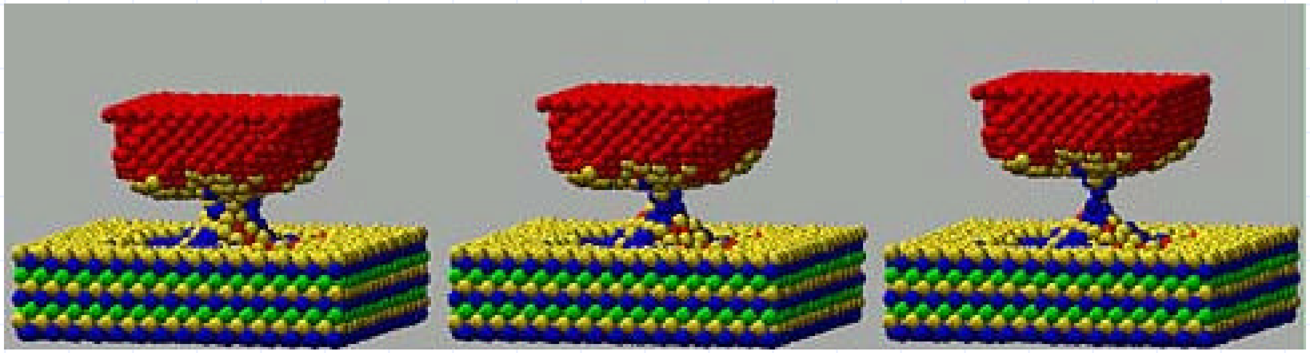
- Take structure of enzyme and model interaction with possible drugs
- Often uses classical mech. models but sometimes refined by Q.M.
- Promising new drug design approach.



Model of candidate inhibitor for HIV-1 protease.
(Physical Computing Group, Rice U.)

Computational Materials Science

- Study larger systems with more approximate methods (DFT at best). Examples from GT:
- Prof. Peter Ludovice (CHE): simulation of polymers.
- Prof. Uzi Landman (PHYS): simulation of surfaces and interactions of surfaces.



Ni tip on Au surface

New Devices/Techniques

- Quantum Computing: The ultimate "parallel computer." Potentially billions of times faster than conventional computers.
- Quantum Cryptography: Use Uncertainty Principle to keep out eavesdroppers.

Quantum Computing

- Conventional computers are being improved by smaller and smaller chips. This will end when the features become so small that quantum effects become important (10-15 years?).
- Need to investigate new ways to make computers.

Power of Quantum Computing

- Before the wavefunction collapses, quantum system is in multiple states simultaneously --- 2n states for n qbits (very large!).
- Take advantage of this to process in parallel: In 1994, Peter Shor (AT&T) showed how to use this to factorize numbers (important in encryption).
- Factoring 400 digits might take 1 year on quantum computer, billions of years on supercomputer!

Quantum Computing Scheme

- Basic idea: take advantage of special quantum properties of superposition and measurement.
- A conventional bit is either 0 or 1. A *quantum bit* (qbit) can have any value between 0 and 1 but is only 0 or 1 when measured (somewhat like z-projection of angular momentum).

$$\Psi = c_0 \Psi_0 + c_1 \Psi_1$$

Computation exploits fact that all states are present at the same time.

Quantum Cryptography

- Potential new method for secure communications.
- Basic idea: a sender ("Alice") prepares a physical system in a known quantum state and sends it to a receiver "Bob."
- Bob measures the system's state. Process is repeated so the string of measurements can be decoded to give a message.
- Eavesdroppers can't listen in without disturbing the system (Uncertainty Principle)!

Conclusions

- Quantum Mechanics is how the world works at small scales: vital for understanding physics/chemistry.
- Can be used to model molecular behavior and speed up research.
- Unique features of Q.M. may be exploited in quantum computing and quantum cryptography.