

Geometry-Dependent Molecular Photoionization Dynamics

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Argonne National Laboratory



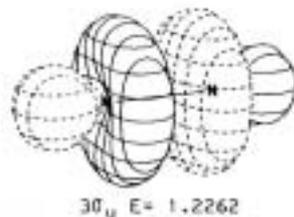
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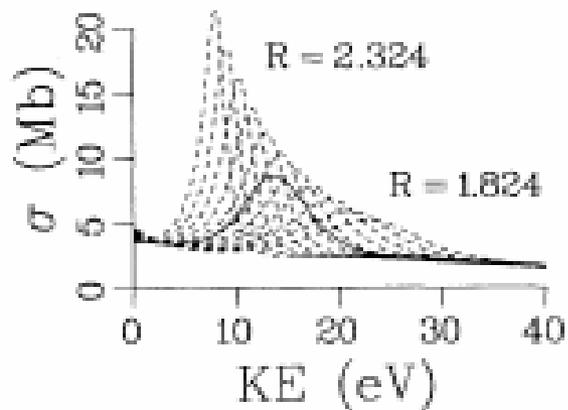
WHY IS GEOMETRY DEPENDENCE IMPORTANT?

- Correlations between resonance positions and bond lengths, angles, and more generally, geometries
- Identification of near-threshold features, i.e., shape resonances, doubly excited states, etc.
- Understanding vibronically induced effects in molecular photoionization dynamics
- Connection between shape resonances and LUMOs, theories of chemical reactivity
- Resonance positions and orbital energies are closely connected to quantum defects
- Geometry-dependent quantum defects describe nonadiabatic interactions that drive many important chemical processes

R-DEPENDENCE OF THE f_{σ_u} SHAPE RESONANCE IN N_2

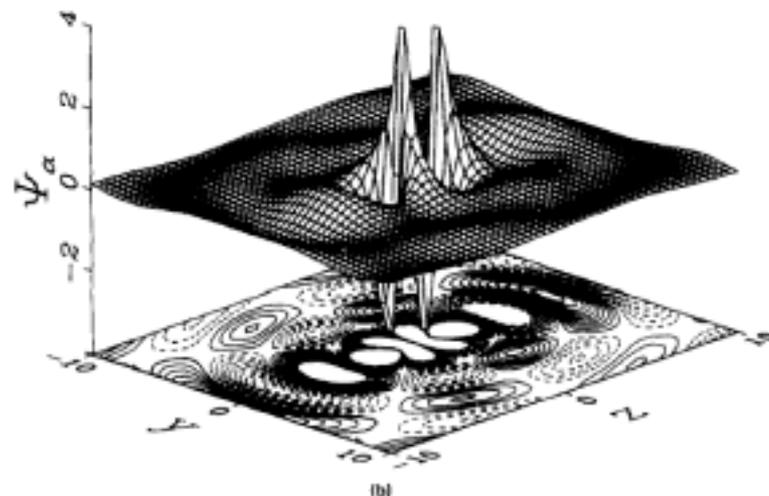


At smaller R , the nodes are squeezed, and the resonance energy goes up. At larger R there is better overlap with the initial state, and the cross section goes up



J. L. Dehmer, D. Dill and S. Wallace
Phys. Rev. Lett. **43**, 1005 (1979).

Excitation from $3\sigma_g$ orbital

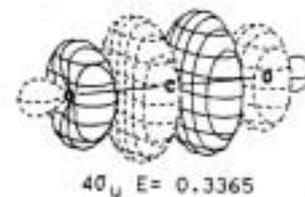
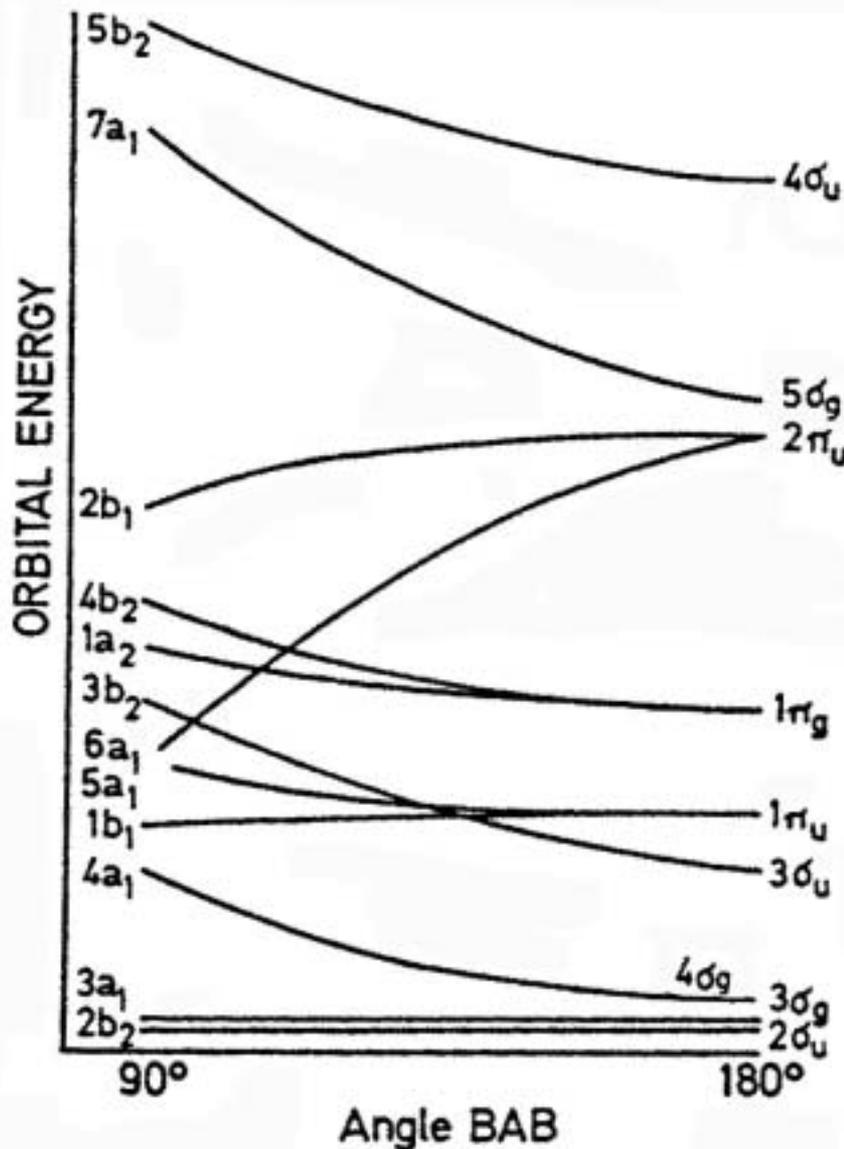


D. Loomba, S. Wallace, D. Dill, and J. L. Dehmer
J. Chem. Phys. **75**, 4546 (1981).

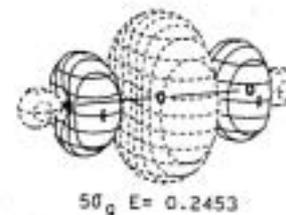
f_{σ_u} resonance wavefunction



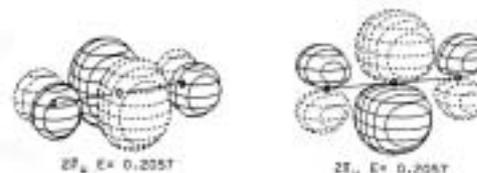
WALSH DIAGRAM FOR BENDING A BAB MOLECULE (E.G. CO₂, NO₂...)



1 ~ 5



1 ~ 4



1 ~ 3

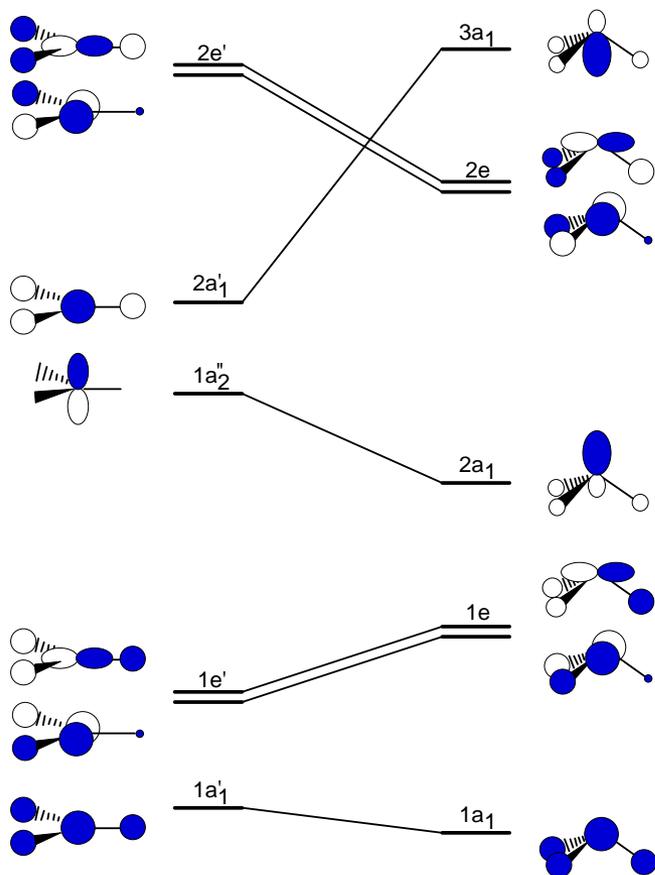
In valence-shell spectra, both the initial-state and final-state orbitals may show strong geometry dependences. Interpretation of inner-shell spectra is simplified because the initial state is highly localized.



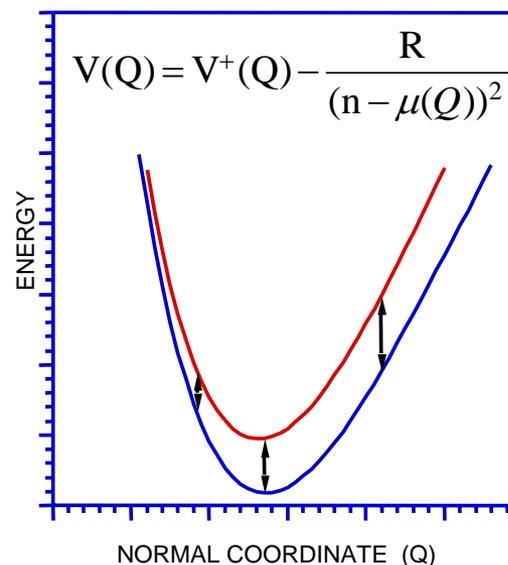
CORRELATION DIAGRAMS AND WALSH DIAGRAMS

How orbital energies change with geometry

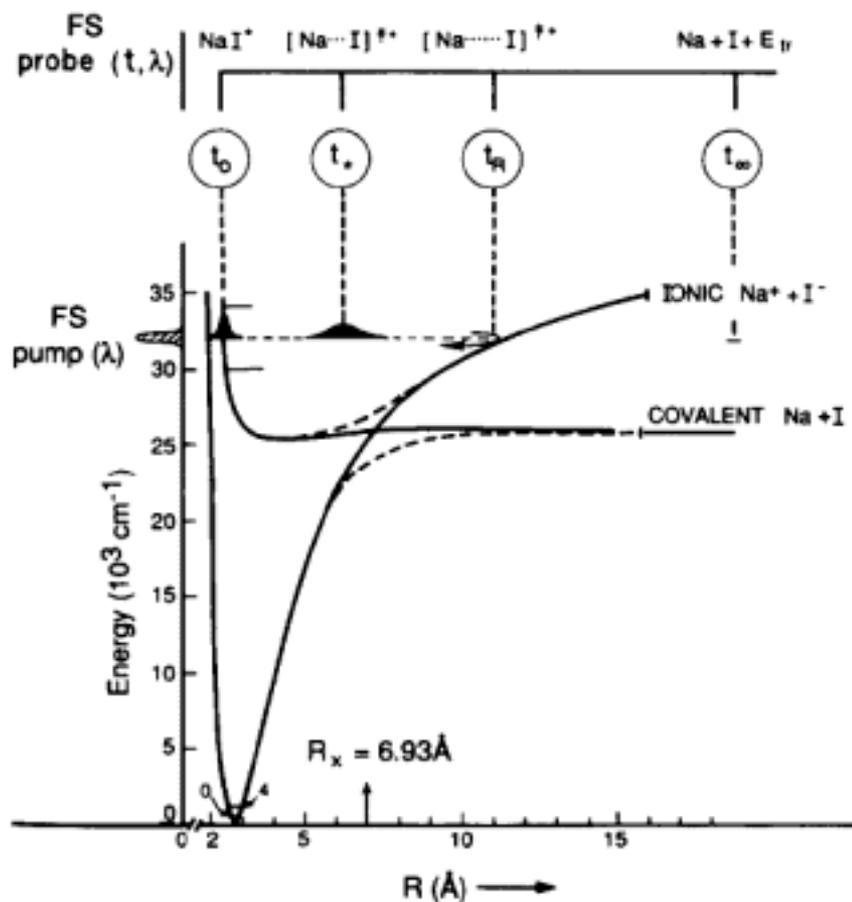
Walsh Diagram for an AH₃ Molecule



What is plotted is the "orbital energy", essentially the IP of the orbital. These quantities are closely related to the geometry dependent quantum defects, $\mu(Q)$.



TIME-DOMAIN VIBRATIONAL WAVEPACKETS



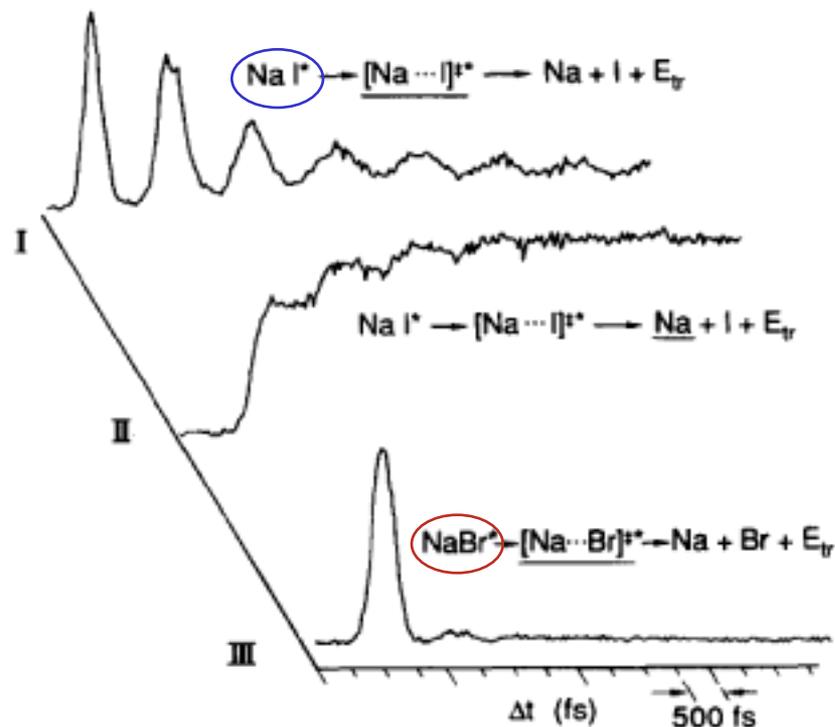
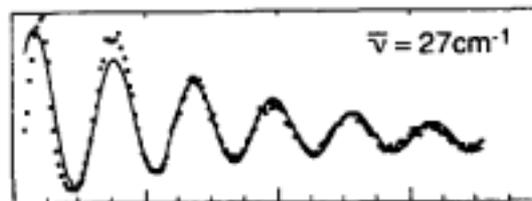
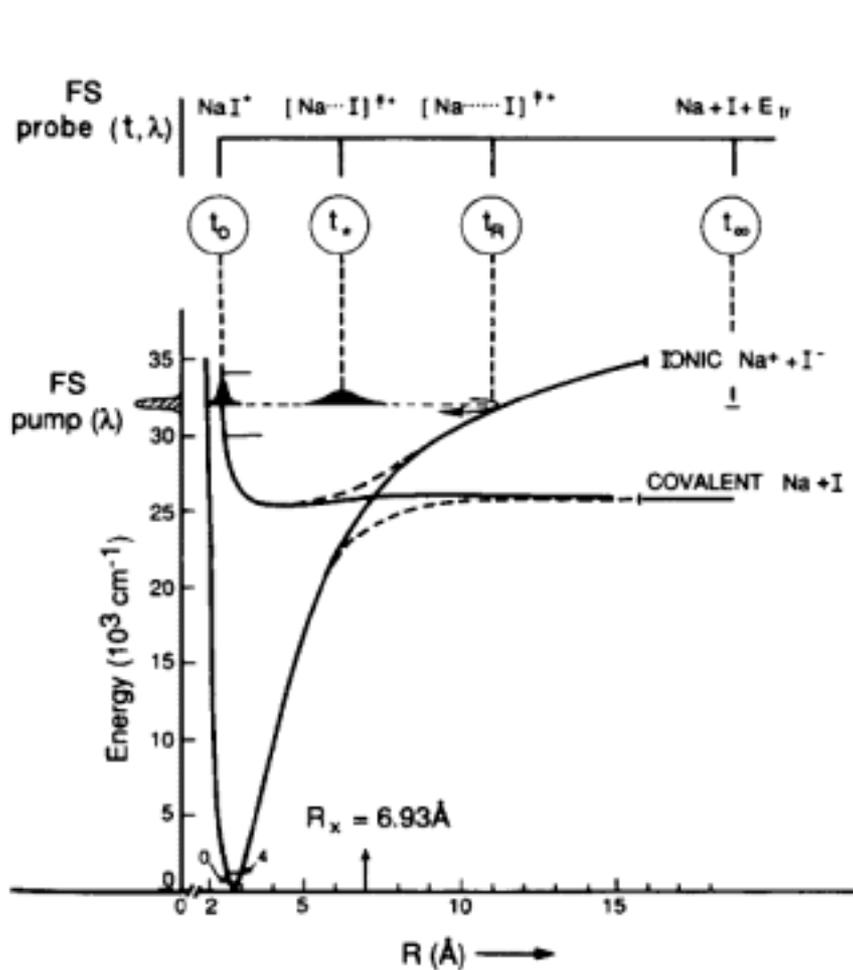
T. S. Rose et al., J. Chem. Phys. **88**, 6672 (1988).

- Correlation between time delay and R ("geometry")
- Direct measurements of core excitation vs. R or bend angle
- Dipole approximation vs. R
- Oscillations in the optical experiments imply geometry dependent cross sections
- In principle, dissociative states are of interest if the kinetic energy release is very small
- Interesting effects near curve crossings?

EXAMPLE NaI

Very low-frequency vibration, feasible for LCLS, but still too fast for standard APS pulse

T. S. Rose et al., J. Chem. Phys. **88**, 6672 (1988).



ISSUES WITH APS

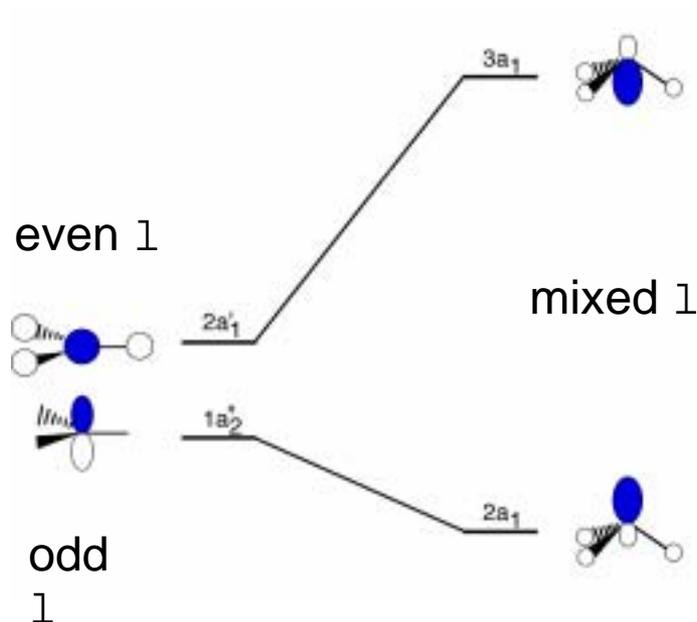
- Pulse durations too long for vibrational wavepackets
- Slicing the x-ray beam is possible, but big loss of photons
- Even rotational wavepackets dephase too fast to be adequately probed by a 90 ps pulse
- Frequency-domain studies may be more effective for this these phenomena at the APS?

IR-X-RAY PUMP-PROBE EXPERIMENTS

- Frequency-domain approach to geometry-dependent dynamics
- Enhance vibrationally induced symmetry breaking
- Enhance vibronic interactions
- Feasibility demonstrated at ALS by X. -M. Xian et al., Phys. Rev. Lett. 91, 233001 (2003)
- Poled LiNbO₃ optical parametric oscillator provides a reasonable IR source [C. -S. Yu and A. H. Kung, J. Opt. Soc. Am. B 16, 2233 (1999)].
- Alternative approaches (pump-dump, STIRAP, control) may provide feasible complementary approaches for vibrational excitation

VIBRATIONALLY ENHANCED EFFECTS

In the planar geometry,
even \perp \rightarrow odd \perp , and
odd \perp \rightarrow even \perp



In the pyramidal
geometry, transitions
from both orbitals to
even and odd \perp are
allowed

Excitation of the umbrella vibration will enhance transitions
that are forbidden in the equilibrium geometry.

Rovibrational-State-Selected Photoionization of Acetylene by the Two-Color IR + VUV Scheme: Observation of Rotationally Resolved Rydberg Transitions

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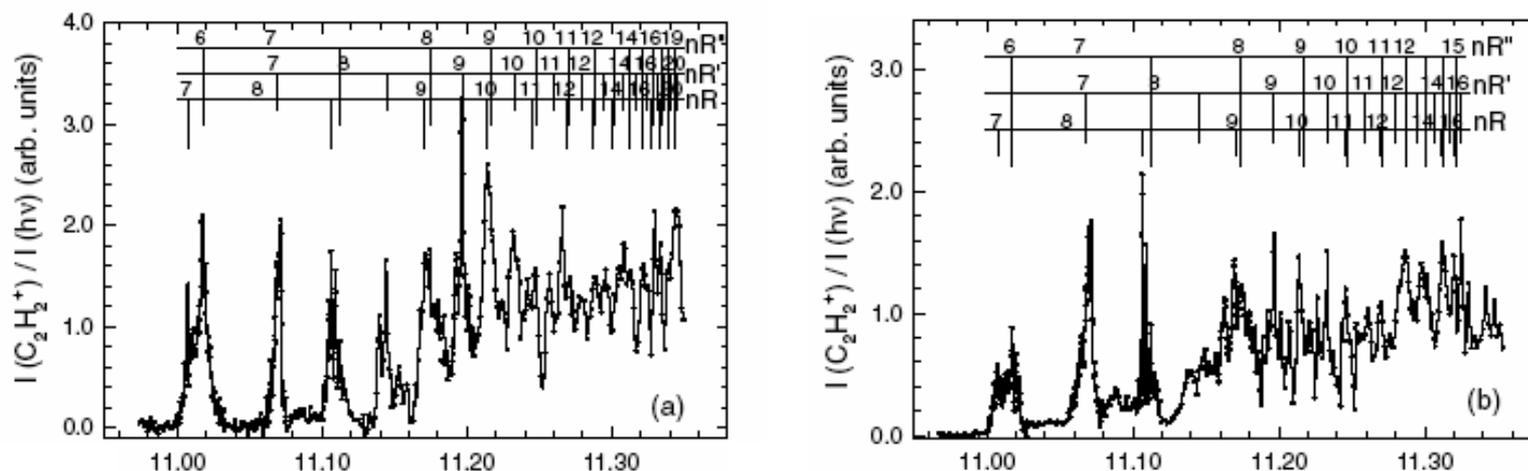


FIG. 1. IR-VUV photoion spectra for $C_2H_2^+$ in the VUV range of 10.97–11.35 eV obtained with the IR-OPO frequency set at (a) the $P(9)$ and (b) the $P(11)$ transitions of ν_3 . The labels on top mark the assignment of the three Rydberg series (nR , nR' , and nR'') converging to the excited $\nu_3^+ = 1$ state of the ion. The assigned positions correspond to VUV energies of the $\Delta J = 0$ transitions.

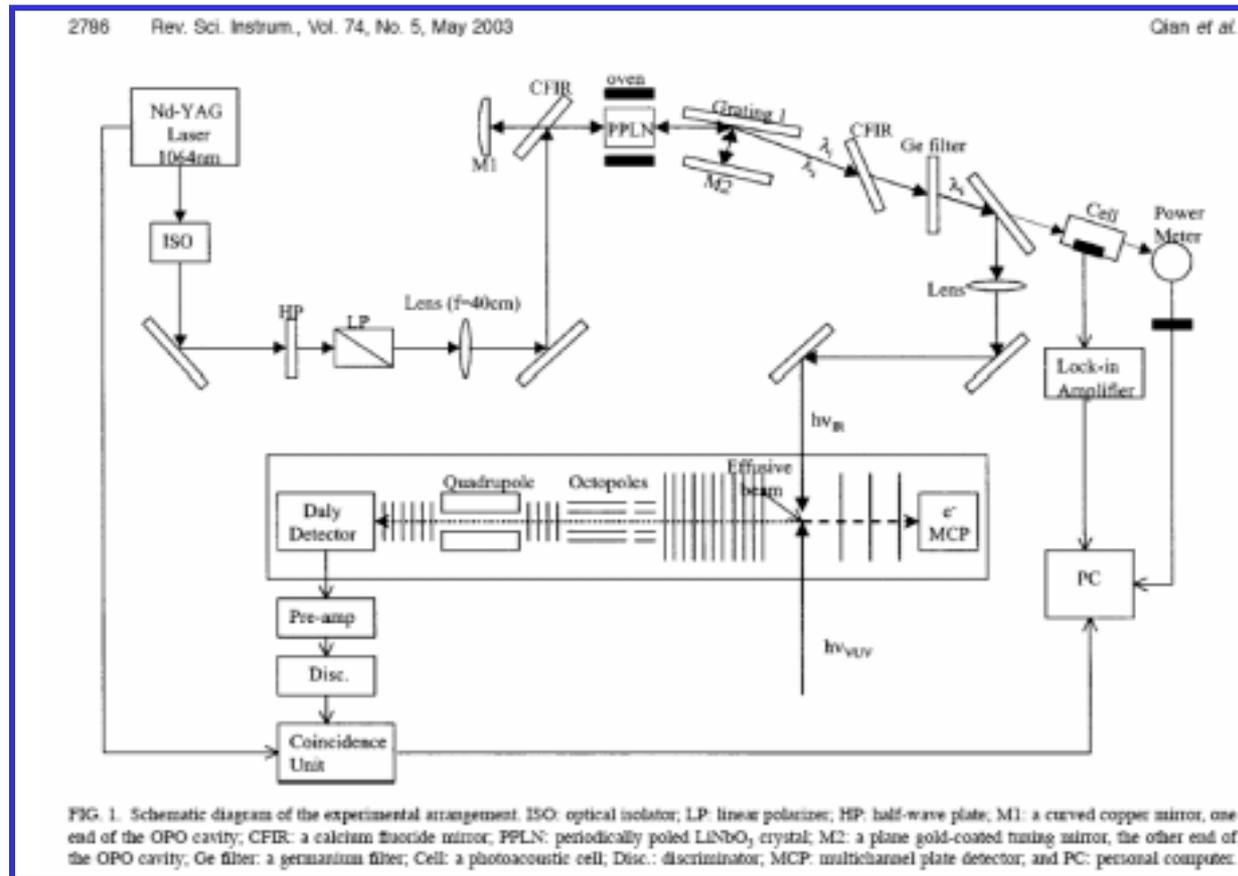


IR LiNbO₃ Optical Parametric Oscillator

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TECHNICAL ISSUES

- Not an issue at ALS, as pulse duration (~ 15 ns) \gg vuv pulse spacing (2 ns)
- Possible issues at APS, especially in Top-Up Mode, where pulse spacing is 153 ns, but with synchronization, no problems
- Duty cycles not a great match, but ir-radiative lifetimes are long
- Improved signal-to-noise with co-linear ir and collision-free molecular beams
- X-ray only subtraction should be possible
- IR frequencies are best matched to CH stretches, where shape-resonant effects may be small

**Observation of the Symmetry-Forbidden $5\sigma_u \rightarrow k\sigma_u$ CS₂ Transition:
A Vibrationally Driven Photoionization Resonance**

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- Title transition is forbidden in the Born-Oppenheimer approximation
- It is vibronically allowed through coupling with the asymmetric stretch
- Analysis suggests the resonance results from zero-point vibrations along this mode (ν_3)
- By exciting the ν_3 fundamental or overtones, the strength of the resonance should increase substantially
- Calculations suggest the resonance position is independent of vibrational displacement. For real?
- Access via multiple paths



WHAT CAN BE EXPECTED?

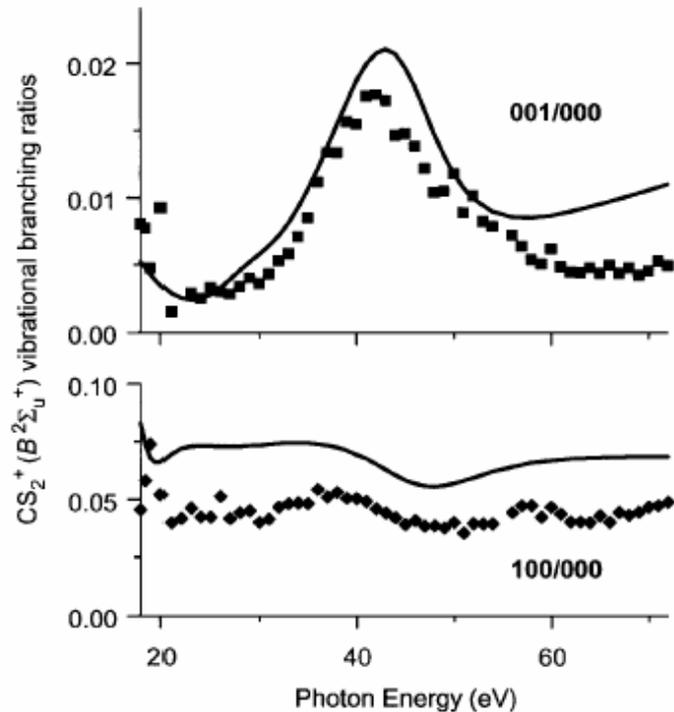
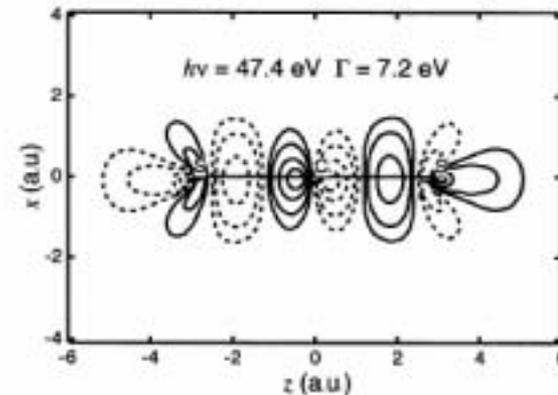


FIG. 1. Selected vibrational branching ratios for the CS₂⁺ (B²Σ_u⁺) state, demonstrating that the $\nu^+ = (001)$ level is very sensitive to the resonance, whereas the $\nu^+ = (100)$ branching ratio exhibits contrasting, energy-independent Franck-Condon behavior.

- Increase the magnitude of the effect
- Confirm the interpretation, or...
- Identify uncharacterized features
- Control: for a given resonance, which vibrations affect intensity, position, branching ratios, ...?



G. J. Rathbone et al., Phys. Rev. Lett. **92**, 143002 (2004).

ALTERNATIVE APPROACHS

- Not all vibrational modes are infrared active
- Raman transitions access complementary vibrations
- Optical control of stimulated Raman scattering can optimize production of specific vibrational levels (c.f., S. A. Malinovskaya, P. H. Bucksbaum, and P. R. Berman, Phys. Rev. A **69**, 013801 (2004).)
- Stimulated Raman Adiabatic Passage (STIRAP) can selectively transfer significant populations to excited vibrational levels

CONCLUSIONS

- Geometry-dependent studies can provide a new perspective
- With inner-shell excitation, the initial state is localized, simplifying the characterization of final-state effects...
- Studies using time-domain techniques and vibrational wavepackets have potential at fourth-generation facilities, but the x-ray pulse duration makes them difficult at the APS
- Frequency-domain pump-probe experiments can provide complementary information and are feasible with third-generation sources