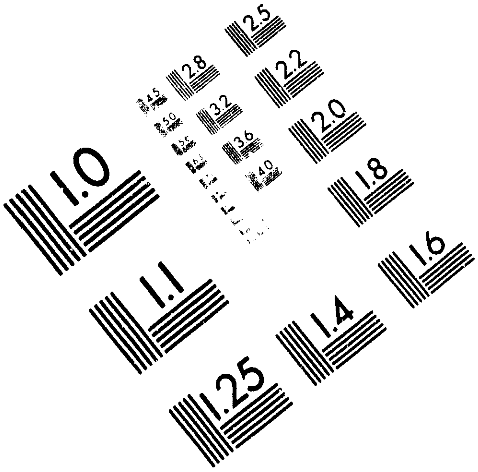

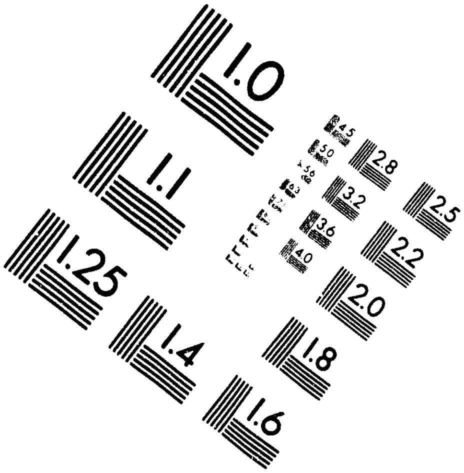

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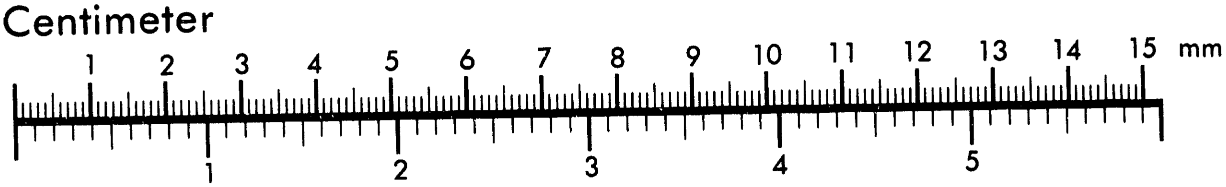

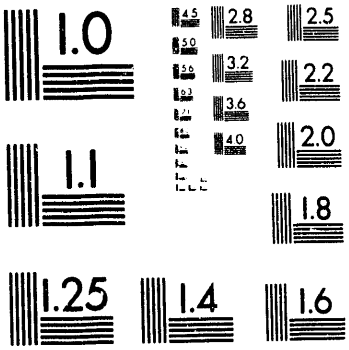

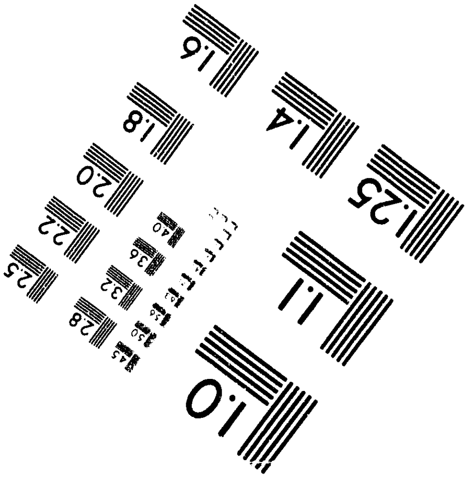

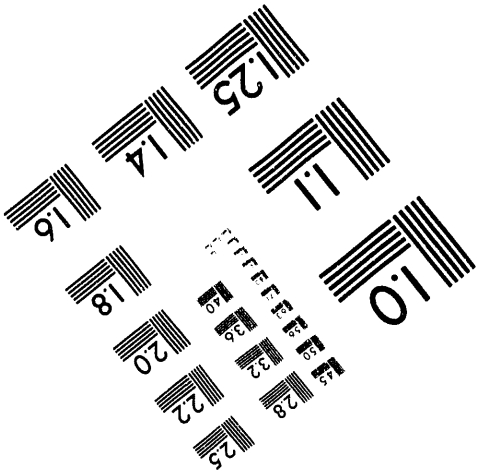

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INFRARED SPECTROSCOPY OF ORGANIC FREE RADICALS RELATED TO COMBUSTION PROCESSES

(DE-FG02-92ER14306)

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Program Definition

The primary long-term goal of this work is to develop new techniques for measuring vibrational spectra of polyatomic neutral free radicals. We will explore a variation of resonant two-photon ionization (R2PI) in which tunable ω_{IR} excites the radical vibrationally and ω_{UV} selectively ionizes only the vibrationally excited molecules. Development of the IR + UV R2PI experiment is underway. In the meantime, we have used optical R2PI and pulsed field ionization (PFI) detection to obtain new vibrational spectra of species such as the benzyl and phenylsilane cations. In benzyl, we have learned a great deal about the vibronic coupling mechanism in the mixed 1^2A_2-2^2B_2 system near 450 nm by projecting the mixed states onto the manifold of cation vibrational states. In phenylsilane$^+$, we find that the sixfold barrier to internal rotation of the silyl group is small ($V_6 = +19$ cm^{-1}). We are beginning to understand the mechanisms of coupling of torsional states with vibration, overall rotation, and other electronic states. In addition, we are developing a new model of internal rotation in aromatic compounds based on Prof. Frank Weinhold's natural resonance theory.

Recent Progress

1. Benzyl Radical

We create a skimmed beam of internally cold neutral benzyl radicals by 193 nm photolysis of toluene several mm downstream in a pulsed nozzle expansion.[1] Internally cold benzyl radical is probed by two-color, resonant two-photon ionization (R2PI) through vibronically mixed 1^2A_2-2^2B_2 excited states near 450 nm.[2,3,4] We obtain R2PI spectra of three isotopomers, benzyl$^+$-h_7, benzyl$^+$-αd_2, and benzyl$^+$-d_7. By tuning ω_1 to a particular resonance, scanning ω_2, and detecting electrons produced by delayed, pulsed field ionization (PFI),[5] we obtain vibrational spectra of the corresponding cations primarily in the range 0-650 cm^{-1}. We assign the low frequency bands by comparison with harmonic, normal mode frequencies from *ab initio* calculations of the X^1A_1 state of benzyl$^+$.

The origin bands provide the following adiabatic ionization potentials: 58465 ± 5 cm^{-1} = 7.2487 ± 0.0006 eV for benzyl-h_7; 58410 ± 5 cm^{-1} for benzyl-αd_2; and 58382 ± 5 cm^{-1} for benzyl-d_7. The benzyl-h_7 value refines our previous measurement[6] of 58456 ± 14 cm^{-1} from extrapolation of cation yield curves to zero field as well as the earlier value[7] of 58100 ± 160 cm^{-1}. The accurate IP is important in thermochemical cycles.

In benzyl$^+$, we observe several low-frequency vibrational states for each isotopomer. Table I collects the measured frequencies for all three isotopomers in the range 0-650 cm^{-1} and compares experiment with *ab initio* calculations of harmonic frequencies. The vibronic mixing in the intermediate states[8,9] allows us to observe benzyl$^+$ vibrational states of both a_1 and b_1 symmetry (C_{2v} point group) in the PFI spectrum. The frequencies of the out-of-plane modes of benzyl$^+$, which we obtain indirectly from combination bands and from *ab initio* calculations, provide a quantitative measure of the bond order between the exocyclic CH_2 group and the benzene ring. The cation clearly has substantially greater double-bond character than the neutral.

In addition, the intensities of the cation bands provide a measure of the vibrational character of the excited states of neutral benzyl, complementing recent dispersed fluorescence measurements.[3a] Our new data indicate that previous models[8,9] of the vibronically mixed 1^2A_2-2^2B_2 system have included unimportant modes and neglected important ones. In particular, certain low frequency *combination* states of overall a_1 or b_1 symmetry induce vibronic mixing efficiently.

Table I. Experimental and Calculated Vibrational Levels of X^1A_1 State of Benzyl Cation.[a]

		benzyl$^+$-h_7		benzyl$^+$-αd_2		benzyl$^+$-d_7	
Level[b]	symm	expt	calc	expt	calc	expt	calc
$\nu_{36}+\nu_{17}$	b_1	487	480	456	452	423	418
$\nu_{36}+\nu_{35}$	a_1	--	552	--	540	488	494
ν_{13}	a_1	526	537	504	524	500	511
ν_{28}	b_1	598	613	596	612	575	588

[a] Calculated harmonic frequencies using Gaussian-90, MP2/6-31G*.

[b] Approximate mode descriptions (op = out-of-plane, ip = in-plane): ν_{36} = ring and CH_2 op wag; ν_{35} = op CH ring wag; ν_{28} = ip ring deform; ν_{17} = op ring + CH_2 torsion; ν_{13} = ip CCC bend.

2. Phenylsilane

Resonant two-photon ionization (R2PI) and pulsed field ionization (PFI) were used to measure S_1-S_0 and cation-S_1 spectra of phenylsilane cooled in a pulsed nozzle expansion.[12] We obtain the adiabatic ionization potentials IP(phenylsilane) = 73680 ± 5 cm^{-1}, IP(phenylsilane·Ar) = 73517 ± 5 cm^{-1} and IP(phenylsilane·Ar_2) = 73359 ± 5 cm^{-1}. We also resolve and assign many low lying torsion-vibration levels of the S_1 (X^1A_1) state of phenylsilane and of the X^2B_1 state of phenylsilane$^+$. In both states, the pure torsional transitions are well fit by a simple sixfold hindered rotor Hamiltonian. The results for the rotor inertial constant B and internal rotation potential barrier V_6 are: in S_1, $B = 2.7 \pm 0.2$ cm^{-1} and $V_6 = -44 \pm 4$ cm^{-1}; in the cation, $B = 2.7 \pm 0.2$ cm^{-1} and $V_6 = +19 \pm 3$ cm^{-1}. The sign of V_6 and the conformation of minimum energy are inferred from spectral intensities of bands terminating at the $3a_1''$ and $3a_2''$ torsional levels.[10,11] In S_1 the staggered conformation is most stable, while in the cation ground state the eclipsed conformation is most stable.

In phenylsilane$^+$ we find experimental evidence of coupling between torsion and vibration.[12] For small V_6, the term $P_\alpha P_a$ in the rigid-frame model Hamiltonian strongly mixes the $6a_1'$ and $6a_2'$ torsional states, which mediates further torsion-vibrational coupling. In addition, the cation X^2B_1 vibrational structure is badly perturbed, apparently by strong vibronic coupling with the low-lying A^2A_2 state. Accordingly, our *ab initio* calculations find a substantial in-plane distortion of the equilibrium geometry of the X^2B_1 state, while the A^2A_2 state is planar and symmetric.

For all sixfold potentials whose absolute phase is known experimentally, the most stable conformer is staggered in the neutral states (S_0 and S_1 *p*-fluorotoluene, S_1 toluene, S_1 *p*-fluorotoluene)[10] and eclipsed in the cationic states (ground state toluene$^+$ [11] and phenylsilane$^+$ [12]). We find that *ab initio* calculations correctly predict the lowest energy conformer for S_0 states and for cation ground states. In addition, we adapt the natural resonance theory (NRT) of Glendening and Weinhold[13] to explain why sixfold barriers for methyl and silyl rotors are uniformly small, while some threefold barriers are quite large. The phase of the sixfold potential is apparently determined by a subtle competition between two types of rotor-ring potential terms: attractive donor-acceptor interactions and repulsive van der Waals interactions (steric effects).[14]

Future Plans

We have obtained high quality PFI spectra of the cations toluene$^+$·Ar, *p*-fluorotoluene$^+$, *p*-fluorotoluene$^+$·Ar, and phenylsilane$^+$·Ar. Analysis of the data will provide a detailed picture of the interaction between the two low frequency motions: van der Waals bending and internal rotation of the methyl or silyl group.

In collaboration with Prof. Frank Weinhold, we have carried out high quality *ab initio* calculations of the equilibrium geometries and vibrational frequencies of toluene (S_0), toluene$^+$, and many related molecules with sixfold and threefold symmetric torsional potentials. We plan to use the natural resonance theory to try to understand the underlying electronic factors that dictate the widely varying magnitudes of threefold potentials.

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