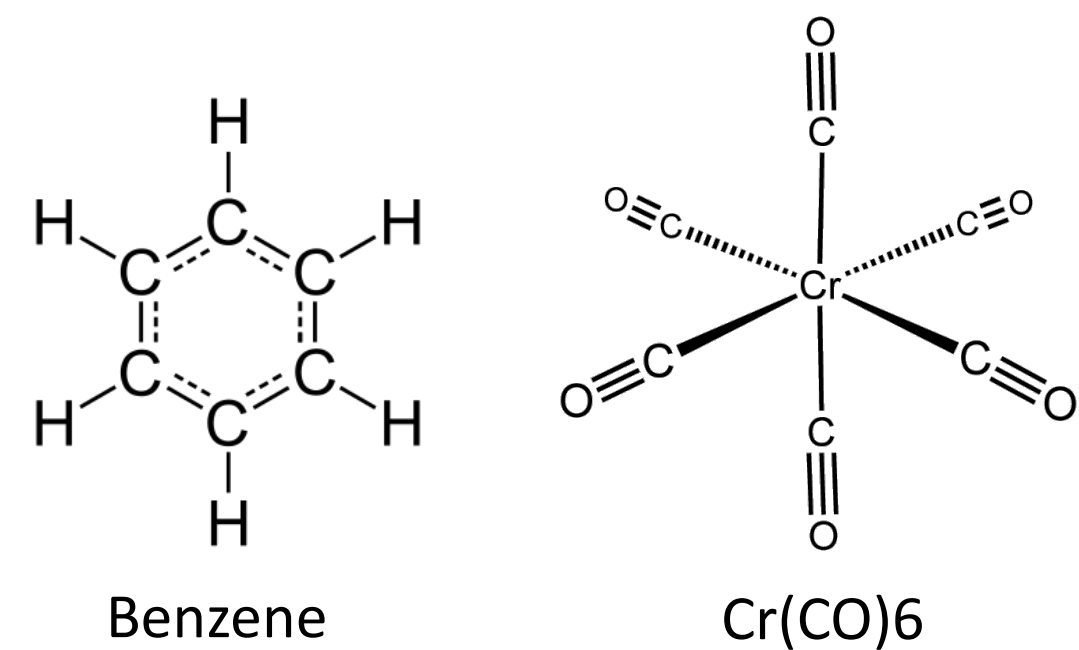


Raman Resonance Scattering: Depolarization Ratio for Benzene and Cr(CO)6 with Irreducible Tensor Method

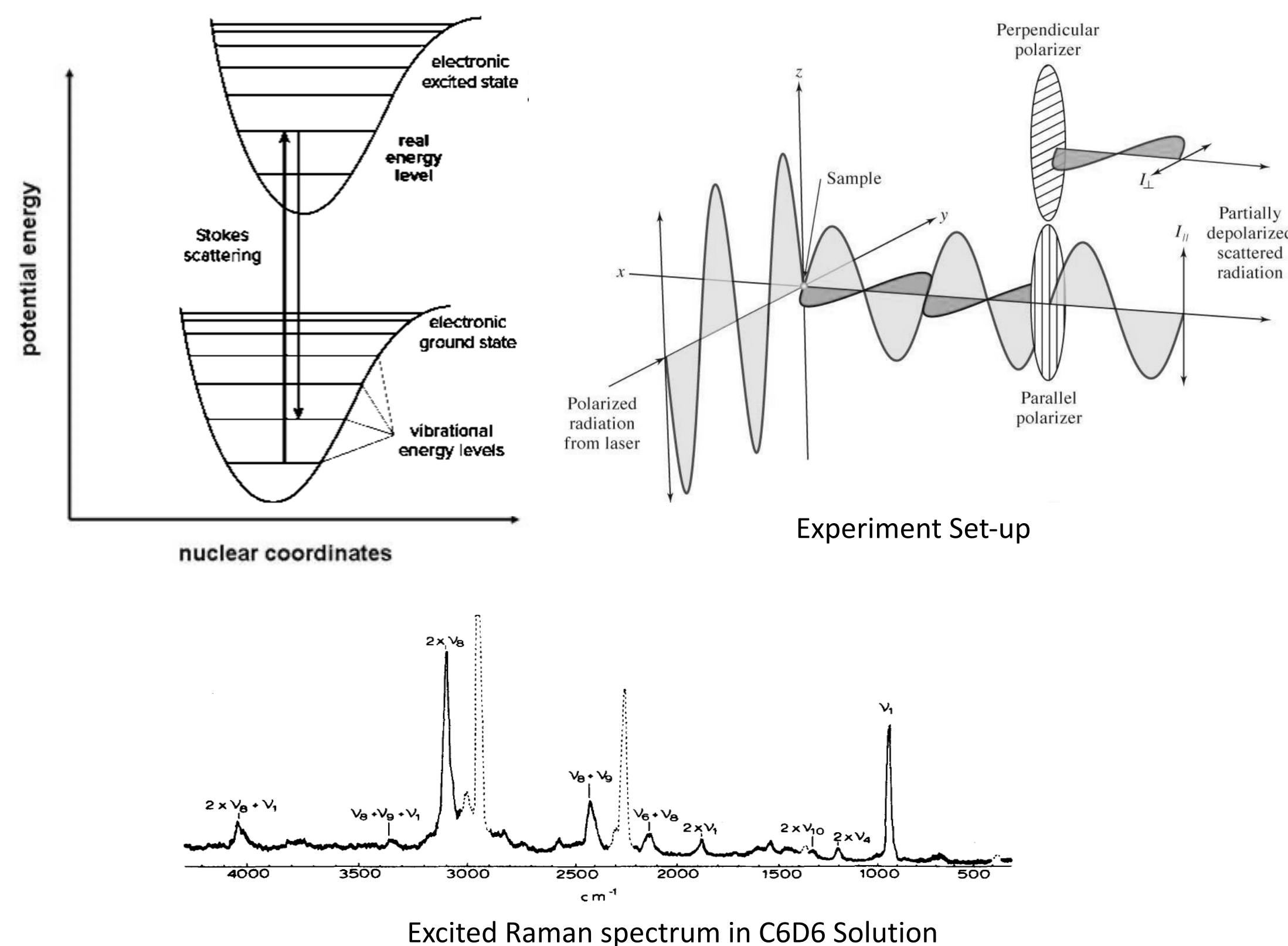
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Motivation

- Check assumptions from vibronic coupling
- Help with synthesizing inorganic materials

Resonance Raman Scattering



Depolarization Ratio

- Definition of Depolarization Ratio

$$\rho_l = \frac{I_{\perp}}{I_{\parallel}}$$

- Kramers-Heisenberg Relation (Polarizability tensor elements):

$$\alpha_{\rho\sigma} \approx \frac{1}{hc} \frac{\langle \Psi_F | \mu_{\rho} | \Psi_E \rangle \langle \Psi_E | \mu_{\sigma} | \Psi_G \rangle}{\nu_{GE} - \nu_L + i\Gamma_E}$$

- Invariants: a^2, γ^2, δ^2 (explain invariants)

- Depolarization Ratio Calculation

$$\rho_l = \frac{I_{\perp}}{I_{\parallel}} = \frac{3\gamma^2 + 5\delta^2}{45a^2 + 4\gamma^2}$$

Make Use of Symmetry

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1		
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1	(R_x, R_y)	(xz, yz) $(x^2 - y^2, xy)$
E_{1g}	2	1	-1	2	0	0	2	1	-1	-2	0	0		
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	z	
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1		
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1	(x, y)	
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0		
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

- The point group (e.g. D_{6h}) defines the symmetry of a molecule geometrically.
- Quantum mechanical operators, coordinates, electronic state, vibrational mode transform as one (or linear combination) of the symmetry representations.
- Criteria for vanishing integrals

$$I = \int f_1 f_2 f_3 d\tau = 0?$$

Decompose direct product $\Gamma_{f_1} \otimes \Gamma_{f_2} \otimes \Gamma_{f_3} = \sum_i \Gamma_i$. If no $\Gamma_i = A_{1g}$ exists, then $I = 0$.

Decomposition of Direct Products

- Benzene**
- Overtones: $(E_{2g})^2 = A_{1g} \oplus E_{2g}$
 - Binary Combinations: $E_{2g} \otimes E_{2g} = A_{1g} \oplus A_{2g} \oplus E_{2g}$
- Cr(CO)6**
- Overtones: $(T_{1u})^2 = (T_{2u})^2 = A_{1g} \oplus E_g \oplus T_{2g}$
 - Binary Combinations: $T_{1u} \otimes T_{1u} = T_{2u} \otimes T_{2u} = A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$
 - Binary Combinations:
 - $T_{1u} \otimes T_{2u} = A_{2g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$

Summary of Results

Benzene	$(E_{2g})^2$	$E_{2g} \otimes E_{2g}$	$E_{2g} \otimes E_{2g}$ (omit A_{2g})
B1u	7/16	3/4	7/16
B2u	7/16	3/4	7/16
Experiment (Stewart & Clark)	7/16	7/16	

We assume that the Reduced Matrix Elements (RME) for $\langle \phi_e || Q_j || \phi_f^r \rangle = \sqrt{\lambda(\Gamma)} \cdot \langle \phi_e || Q_j || \phi_f^{A_1} \rangle$.

Cr(CO)6	(t1u^2)	(t2u^2)	(t1u*t1u)	(t2u*t2u)	(t1u*t2u)
T1u	1/4	1/4	1/2	1/2	7/6
T2u	1/4	1/4	1/2	1/2	7/6
E2g	11/28	11/28	/	/	/
Experiment	/				

Vibronic Coupling

- Selection rule: If $M = 0$, then intensity of a spectral line depends on the (electric) transition is 0 (forbidden transition).

$$M = \langle \psi_g | \mu | \psi_e \rangle$$

- Born-Oppenheimer approximation: $\Psi_{\text{tot}} = \psi_{\text{ele}} \phi_{\text{nuc}}$

- Forbidden transition to excited electronic state ψ_e

$$\alpha_{\rho\sigma} = \frac{1}{hc} \frac{\langle \phi_f | \langle \psi_f | \hat{\mu}_{\rho} | \psi_e \rangle \langle \phi_E | \langle \psi_e | \hat{\mu}_{\sigma} | \psi_g \rangle \langle \phi_G \rangle}{\nu_{GE} - \nu_L + i\Gamma_E} = 0$$

- Breakdown of B-O approximation
Observation of forbidden electronic transition
- Herzberg-Teller Coupling
Electronic Hamiltonian operator to have some dependence on the vibration (Taylor expansion)

$$|\psi_e\rangle = |\psi_e^o\rangle + \sum_{s \neq r} \sum_k \frac{\langle \psi_s^o | \left(\frac{\partial \hat{H}_e}{\partial Q_k} \right)^o | \psi_r^o \rangle}{E_r - E_s} |\psi_s^o\rangle$$

- Wigner-Eckart Theorem

$$\langle a\alpha | T_{\beta}^b | c\gamma \rangle = \langle a || T^b || c \rangle \lambda(a)^{-1/2} \langle b\beta c\gamma | a\alpha \rangle$$

Following Work

1. Reason for A2g not contributing to the intensity for Benzene combination bands.
2. Relative Intensities for combination bands and overtones.

Acknowledgments

Thanks for Dr. Jane Galbraith Shell Raymond Student Research Fellowship to support my summer research in chemistry. I would like to thank Prof. Dan Gerrity for inspiring discussions and the freedom to explore things in research.

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