PHY 745 Group Theory
11-11:50 AM MWF Olin 102

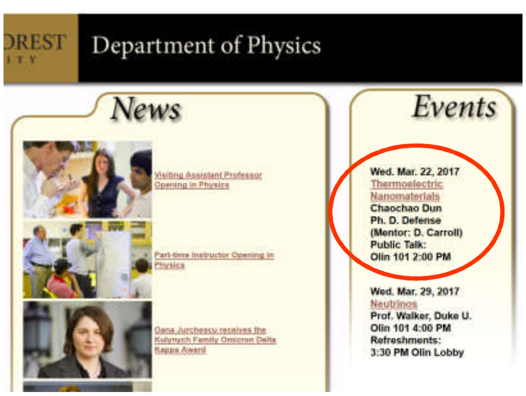
Plan for Lecture 24:

Jahn-Teller Effect
Section 7.7 in DDJ

Example of tetrahedral molecule with doubly or triply degenerate electronic states.

Ref: Grosso and Pastori Parravinci, SSP, Chap. 8, Wang et al. JCP 93, 6318 (1990)

	Fri: 03/17/2017		*APS Meeting - no class*		
23	Mon: 03/20/2017	Chap. 7.7	Jahn-Teller Effect	#15	03/24/2017
24	Wed: 03/22/2017	Chap. 7.7	Jahn-Teller Effect		
25	Fri: 03/24/2017				
26	Mon: 03/27/2017				
27	Wed: 03/29/2017				
28	Fri: 03/30/2017				
29	Mon: 04/03/2017				
30	Wed: 04/05/2017				
31	Fri: 04/07/2017				
32	Mon: 04/10/2017				
33	Wed: 04/12/2017				
	Fri: 04/14/2017		*Good Friday Holiday -- no class*		
34	Mon: 04/17/2017				
35	Wed: 04/19/2017				
36	Fri: 04/21/2017				
	Mon: 04/24/2017		Presentations I		
	Wed: 04/26/2017		Presentations II		

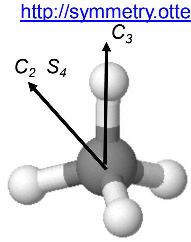


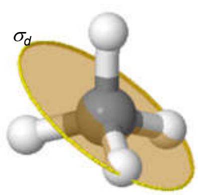
Symmetry analysis of vibrations of tetrahedral system

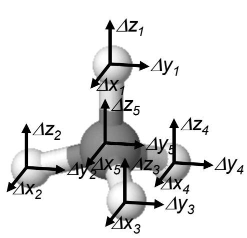
Table 3.34: Character Table for Group T_d

T_d ($\bar{4}3m$)		E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
	A_1	1	1	1	1	1
	A_2	1	1	1	−1	−1
	E	2	−1	2	0	0
(R_x, R_y, R_z)	T_1	3	0	−1	−1	1
(x, y, z)	T_2	3	0	−1	1	−1

Visualization of symmetry elements
http://symmetry.otterbein.edu/tutorial/methane.html

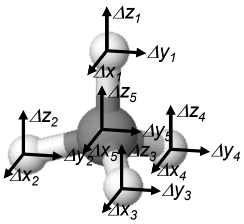




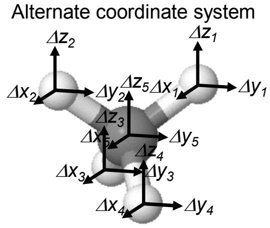


Construct 15-component vector V describing the 3-dimensional motion of the 5 atoms in CH_4

$$V = \begin{pmatrix} \Delta x_1 \\ \Delta y_1 \\ \Delta z_1 \\ \Delta x_2 \\ \Delta y_2 \\ \Delta z_2 \\ \Delta x_3 \\ \vdots \\ \Delta z_5 \end{pmatrix}$$



Alternate coordinate system



Compute characters of transformations:

$\chi(E)=15 \quad \chi(C_3)=0 \quad \chi(C_2)=-1 \quad \chi(\sigma_d)=3 \quad \chi(S_4)=-1$

T_d ($\bar{4}3m$)		E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
	A_1	1	1	1	1	1
	A_2	1	1	1	−1	−1
	E	2	−1	2	0	0
(R_x, R_y, R_z)	T_1	3	0	−1	−1	1
(x, y, z)	T_2	3	0	−1	1	−1
χ		15	0	−1	3	−1

Decomposition of the displacement representation into irreducible representations

$$\chi(R)=\sum_i a_i \chi^i(R)$$

$$a_i=\frac{1}{h}\sum_R \left(\chi^i(R)\right)^* \chi(R)$$

All motions: ➔ $A_1+E+T_1+3T_2$
Translations: T_2
Rotations: T_1
Vibrations: A_1+E+2T_2

Photoelectron spectroscopy and electronic structure of clusters of the group V elements. II. Tetramers: Strong Jahn–Teller coupling in the tetrahedral ^2E ground states of P_4^+, As_4^+, and Sb_4^+

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High resolution HeI (584 Å) photoelectron spectra have been obtained for the tetrameric clusters of the group V elements: P_4, As_4, and Sb_4. The spectra establish that the ground ^2E states of tetrahedral P_4^+, As_4^+, and Sb_4^+ are unstable with respect to distortion in the $\nu_2(e)$ vibrational coordinate. The $E \otimes e$ Jahn–Teller problem has been treated in detail, yielding simulated spectra to compare with experimental ones. Vibronic calculations, extended to second order (quadratic coupling) for P_4^+, account for vibrational structure which is partially resolved in its photoelectron spectrum. A Jahn–Teller stabilization energy of 0.65 eV is derived for P_4^+, which can be characterized in its ground vibronic state as being highly distorted, and highly fluxional. Linear-only Jahn–Teller coupling calculations performed for As_4^+ and Sb_4^+, show good qualitative agreement with experimental spectra, yielding stabilization energies of 0.84 and 1.4 eV, respectively.

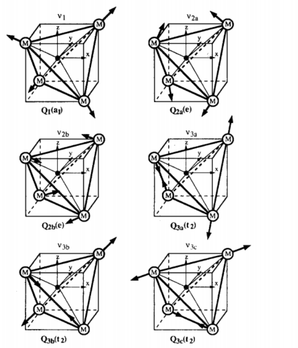
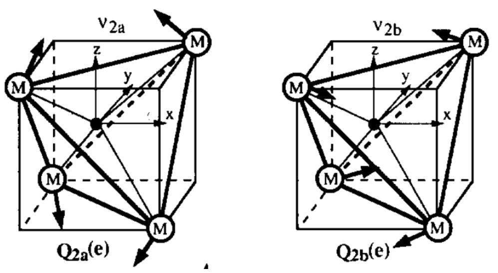


FIG. 4. The normal modes of vibrations for tetrahedral M_4 molecules. The x, y, and z axes lie along the three twofold axes.



Some equations

$$H_{\text{tot}} = T_N(R) + T_e(r) + V(r, R),$$

nuclei electrons

$$\Psi(r, R) = \sum_{n=1}^{v} \chi_n(R)\psi_n(r; R_0),$$

Electronic part:

$$\left(T_e(r) + V(r,R)\right)\psi_n(r;R) = E_n(R)\psi_n(r;R)$$

Nuclear part:

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2}\chi_m(R) + \sum_{n=1}^{v} U_{mn}(R)\chi_n(R) = W\chi_m(R)$$

Some equations -- continued

$$U_{mn}(R) = E_m(R_0)\delta_{mn} + \langle \psi_m(r;\, R_0)|V(r,\, R) - V(r,\, R_0)|\psi_n(r;\, R_0)\rangle.$$

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2}\chi_m(R) + \sum_{n=1}^{\nu} U_{mn}(R)\chi_n(R) = W\chi_m(R)$$

with

$$U_{mn}(R) = E_m(R_0)\delta_{mn} + \langle \psi_m(r;\, R_0)|V(r,\, R) - V(r,\, R_0)|\psi_n(r;\, R_0)\rangle.$$

Transform coordinates to q_1 and q_2 amplitudes of the two E symmetry normal modes

$$H = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial q_1^2} - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial q_2^2} + \gamma\begin{pmatrix} -q_1 & q_2 \\ q_2 & q_1 \end{pmatrix} + \frac{1}{2}C(q_1^2 + q_2^2)$$

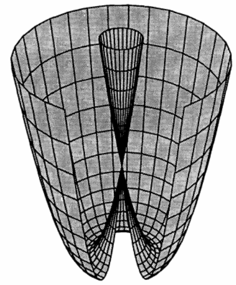


FIG. 5. Diagram showing the adiabatic potential energy surfaces of the linear $E \otimes e$ Jahn–Teller Hamiltonian. $E(\rho,\phi)$ is plotted according to Eq. (2), for $k = 5.75$, a value deduced from spectral simulations to be that most appropriate for P_4^+. The floor of the potential lies at an energy of 16.5, in units of the zeroth-order harmonic frequency, below the conical intersection.

Some equations -- continued

$$\text{Further transform} \quad (q_1, q_2) \rightarrow (q, \theta)$$

Diagonalize nuclear Hamiltonian

$$E_1(q) = -\gamma q + \frac{1}{2}Cq^2, \qquad E_2(q) = \gamma q + \frac{1}{2}Cq^2.$$

More detailed Hamiltonian from JCP paper:

$$\left\{ T_N\mathbf{1} + \begin{bmatrix} \frac{\rho^2}{2} & k\rho e^{-i\phi} + \frac{g\rho^2 e^{2i\phi}}{2} \\ k\rho e^{i\phi} + \frac{g\rho^2 e^{-2i\phi}}{2} & \frac{\rho^2}{2} \end{bmatrix} \right\} \times \begin{bmatrix} \chi_+ \\ \chi_- \end{bmatrix} = W\begin{bmatrix} \chi_+ \\ \chi_- \end{bmatrix},$$

Solved numerically

P_4^+

Wang *et al.*: Photoelectron

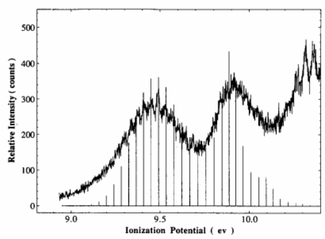


FIG. 7. Linear Jahn–Teller fit to the vibronic profile of the $(1e)^{-1}$ band of the photoelectron spectrum of P_4^+. The linear coupling parameter k in units for which the harmonic force constant is 1, is 5.75. The progression of transitions to $j = 1/2$ radial harmonics originates at an adiabatic ionization energy of 8.95 eV. Positions and intensities were obtained at the converged eigenvalues and eigenvectors of Eq. (5) for $g = 0$, diagonalized exactly in a basis of 800 two-dimensional harmonic oscillator wave functions.

As_4^+

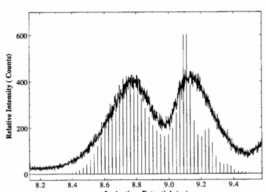


FIG. 10. Linear Jahn–Teller fit to the $(1e)^{-1}$ band of the As_4^+ photoelectron spectrum. The linear coupling parameter k in units for which the harmonic force constant is 1, is 9.7. The progression of transitions to $j = 1/2$ radial harmonics originates at an adiabatic ionization energy of 7.83 eV. Positions and intensities were obtained as in Fig. 7.

Sb_4^+

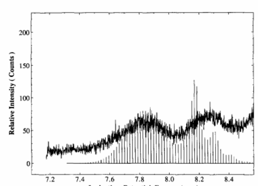


FIG. 11. Linear Jahn–Teller fit to the $(1e)^{-1}$ band of the Sb_4^+ photoelectron spectrum. The linear coupling parameter k in units for which the harmonic force constant is 1, is 12.5. The progression of transitions to $j = 1/2$ radial harmonics originates at an adiabatic ionization energy of 6.61 eV. Positions and intensities were obtained as in Fig. 7.