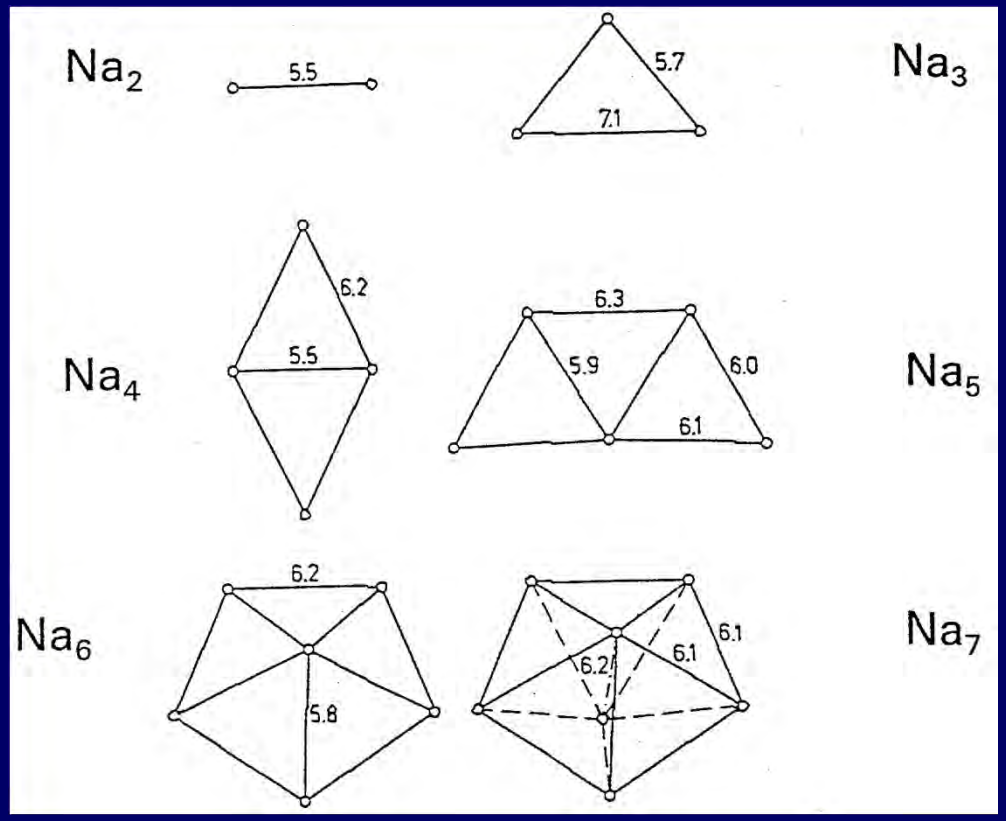
Shell Models for Alkali Metal Trimers: Electronic Level Structure and Magnetic Properties from Experimental and Theoretical Investigations

Lecture I

- introduction: metal clusters, jellium, shell structure, molecule?
- Na_3 electronic excitation
- pseudorotation – Jahn-Teller or pseudo Jahn-Teller?
- K_3 on argon clusters, K_3 femtosecond pump-probe
- *ab initio* K_3 and Rb_3 doublet states
- doublet state shell structure
- the ultimate resolution: electron spin density at the 3 nuclei

Introduction: metal clusters, jellium, shell structure, molecule?

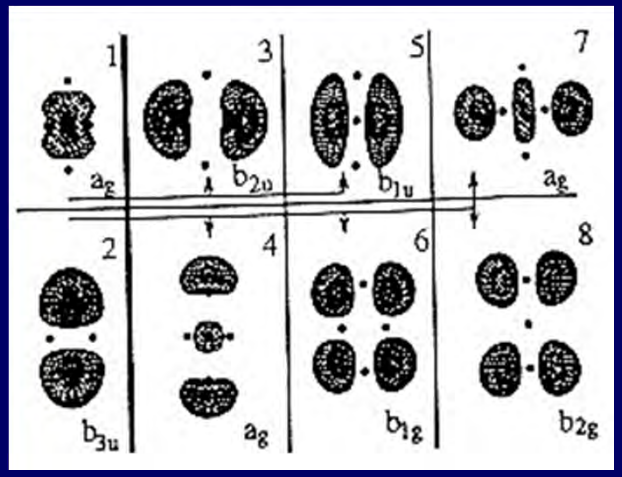
Metal Clusters



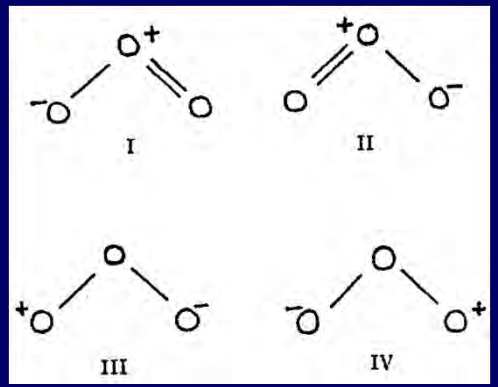
from Martins, Buttet, Car, *Phys. Rev. B (1985)*

Valence electrons?

shell model, e.g. Na_4 (Andreoni, PRL 75, 818 (1995)):



"regular molecule", e.g. ozone:



EXPERIMENTS ON ALKALI CLUSTERS, SOME HISTORY

- Schumacher, Kappes, et al.: ionization threshold
- Knight, de Heer et al.: optical spectra (neutrals)
- C. Brechignac et al.: optical spectra (ions)

jellium or molecules?

M. Kappes (experiment) & Koutecky, Bonacic-Koutecky (theory)

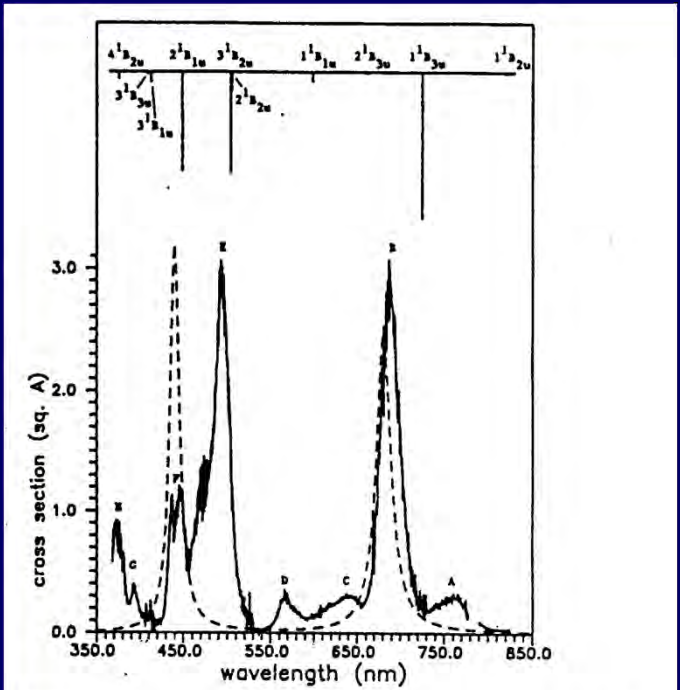


FIG. 7. Na_4 depletion spectrum. The measurement is contrasted to (i) *ab initio* calculations of vertical allowed transitions from rhombic Na_4 (D_{2h}) (Ref. 26) and (ii) electrostatic prediction of optical response (dotted line) for an appropriate metal spheroid ($\alpha_{Na_4}/4\alpha_{Na} = 0.857, \delta = 0.67, \Gamma = 0.03\ \omega_0$).

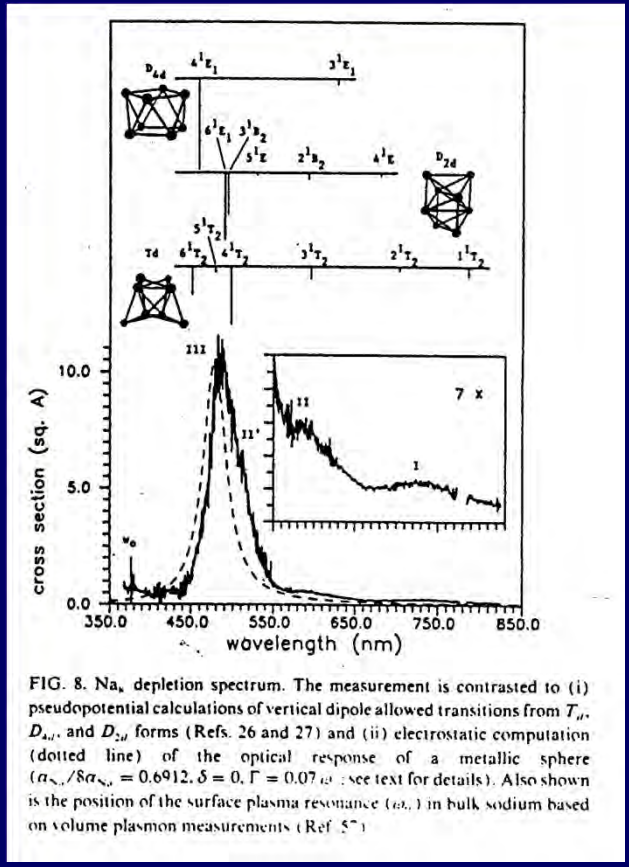
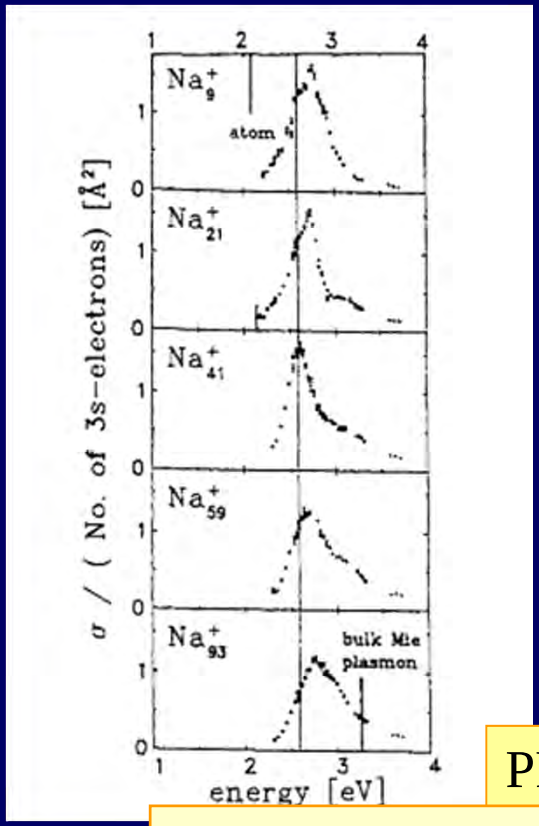


FIG. 8. Na_8 depletion spectrum. The measurement is contrasted to (i) pseudopotential calculations of vertical dipole allowed transitions from T_d, D_{4d}, and D_{2d} forms (Refs. 26 and 27) and (ii) electrostatic computation (dotted line) of the optical response of a metallic sphere ($\alpha_{Na_8}/8\alpha_{Na} = 0.6912, \delta = 0, \Gamma = 0.07\ \omega$; see text for details). Also shown is the position of the surface plasma resonance (ω_s) in bulk sodium based on volume plasmon measurements (Ref. 57).

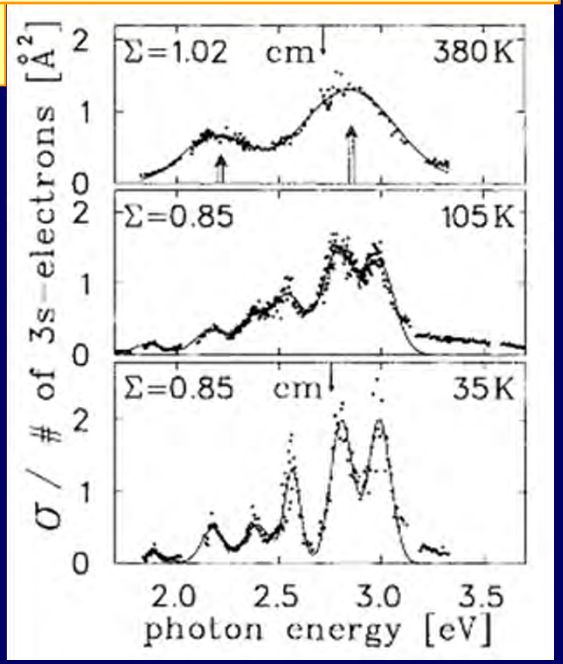
From Wang et al., JCP 1990

EXPERIMENTS ON ALKALI CLUSTERS, SOME HISTORY



Optical spectrum of Na_{11}^+ at three different temperatures. The 6 lines observed for cold clusters become broader with increasing temperature and merge into 2 broad peaks at high T.

PRL 75, 1731 (1995)



- Haberland et al.

PRL 74, 1558 (1995)

Optical response of spherical sodium cluster ions. One large maximum is observed, accompanied by a shoulder on the high energy side.

- v. Issendorf et al.: photoelectron spectroscopy, PRA 65, 063201(2002)

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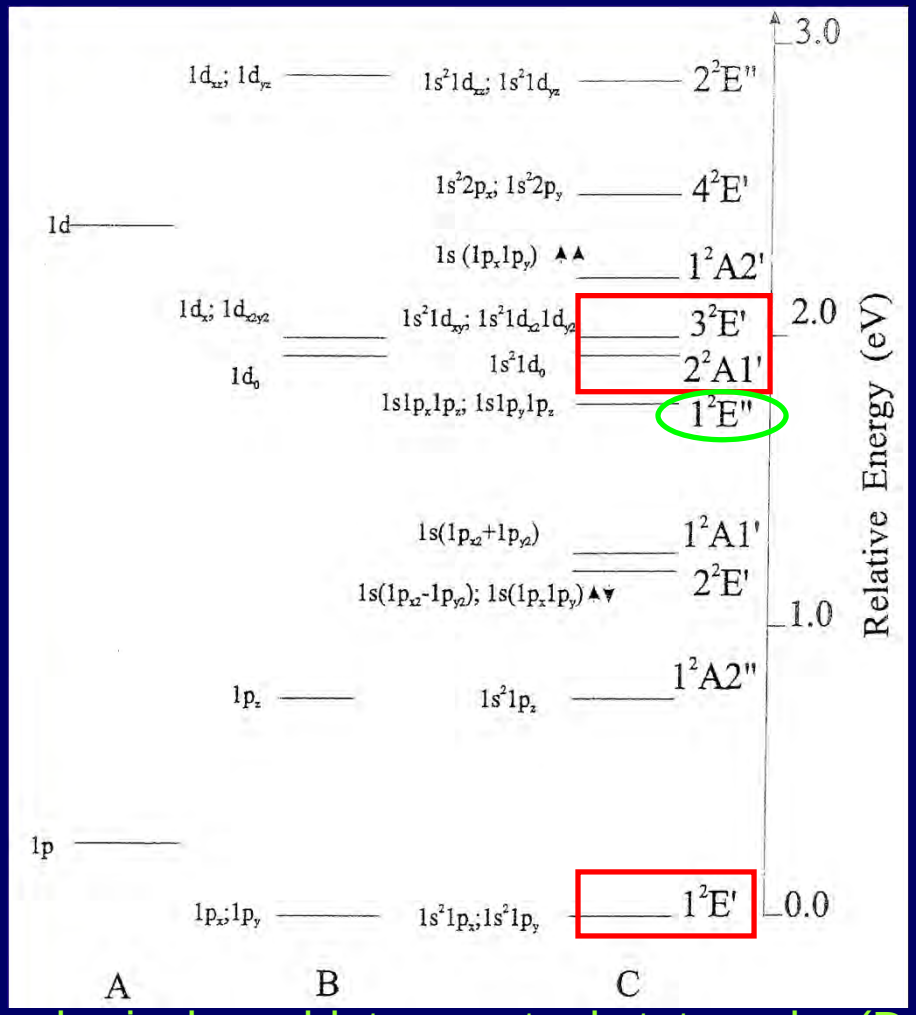
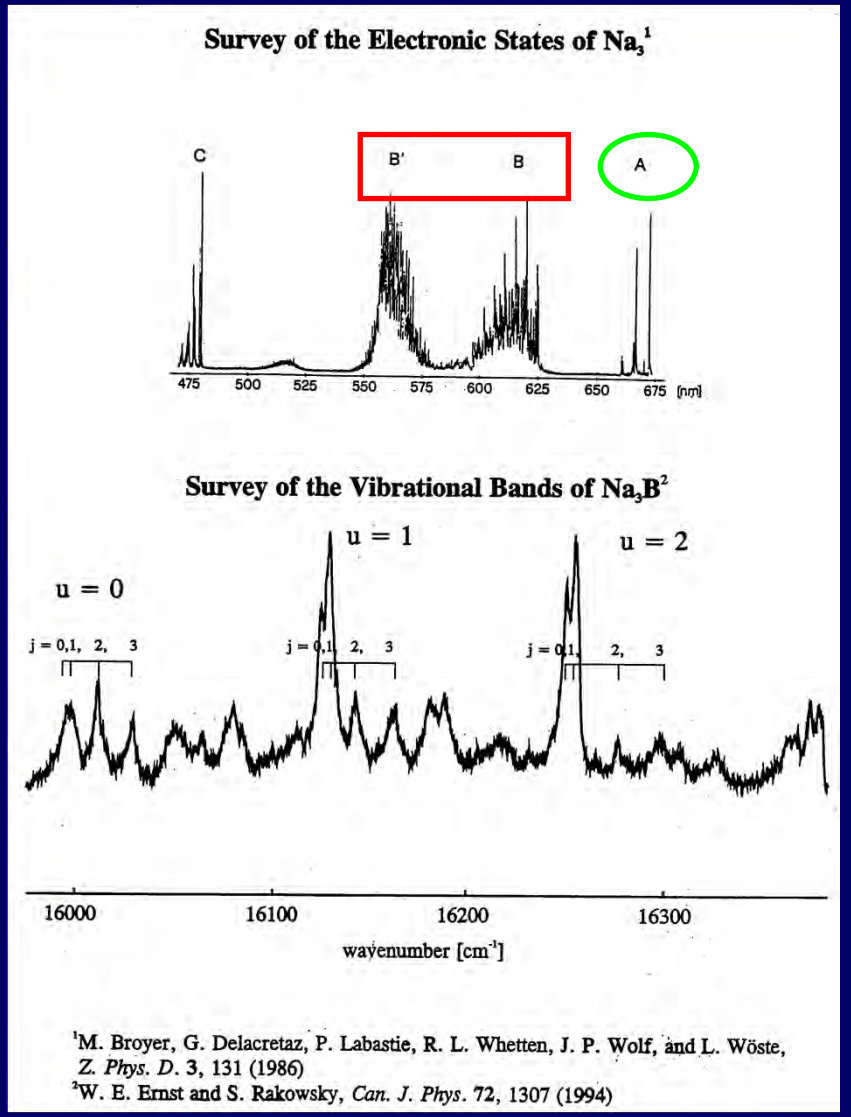
Shell Model for Metal Clusters

For Na_3: Cocchini, Upton, Andreoni 1988



spherical oblate actual state order (D_{3h})

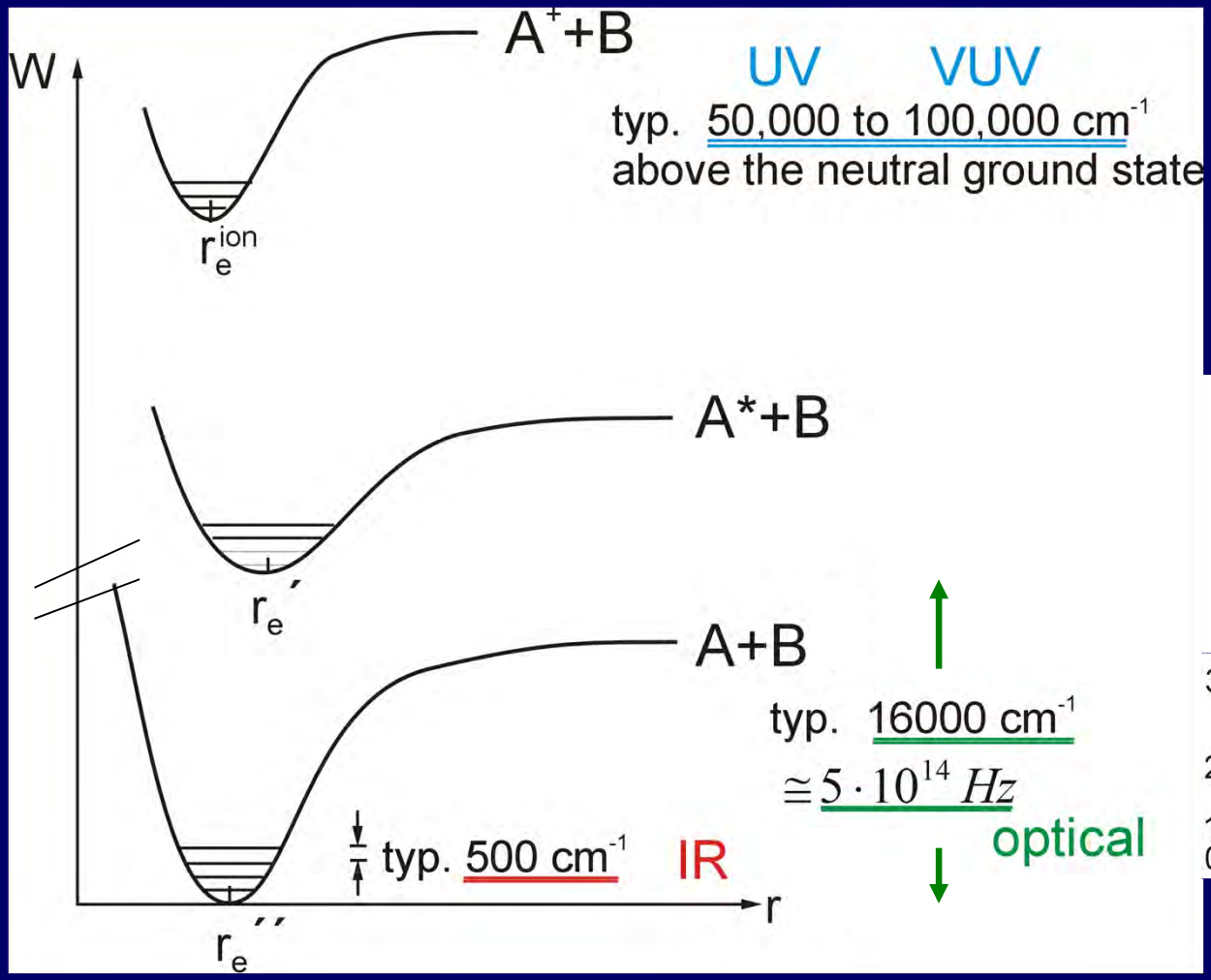
JCP 88, 6068 (1988)

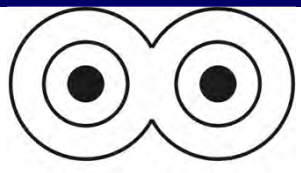


A-X rotational analysis:
Tiemann et al. (U. Hannover)
Demtröder, Meyer, et al. (U. Kaiserslautern)

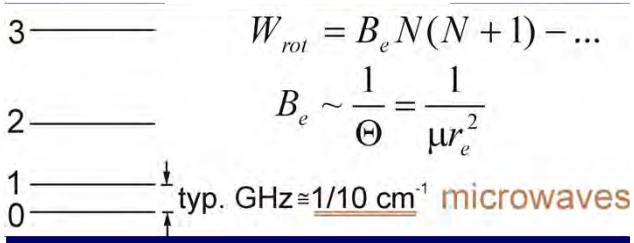
Molecular excitation – electronic, vibrational, rotational

Diatomic molecule and Born-Oppenheimer approximation





rotation



$$W_{rot} = B_e N(N+1) - \ldots$$

$$B_e \sim \frac{1}{\Theta} = \frac{1}{\mu r_e^2}$$

Molecular excitation – electronic, vibrational, rotational

- Polyatomic molecule of N atoms – 3N-6 normal modes of vibration

- crossing of potentials (electronic degeneracy) – due to symmetry or accidental

$\Rightarrow$ Breakdown of Born-Oppenheimer approximation

Here in case of trimers:

Degeneracy due to symmetry $\Rightarrow$ Jahn –Teller coupling

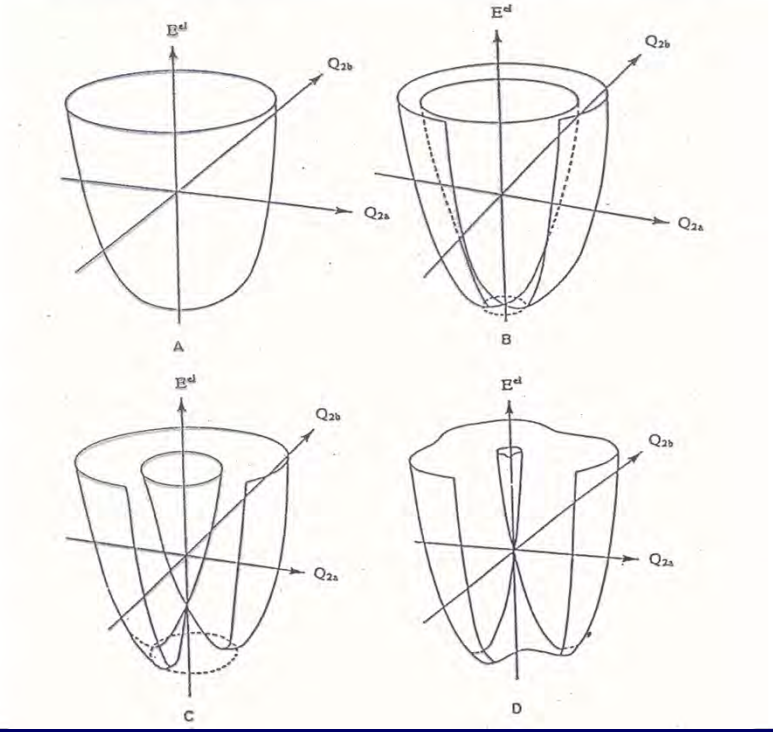
With additional accidental degeneracy,

i.e. three states interacting $\Rightarrow$ pseudo Jahn –Teller coupling

Jahn-Teller effect – from weak to strong coupling of electronic and nuclear motion

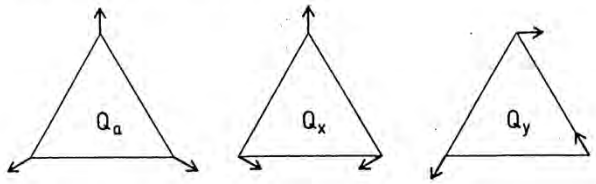
Jahn-Teller coupling

$$\left(H_0(Q) \begin{Bmatrix} 1 & 0 \\ 0 & 1 \end{Bmatrix} + \begin{Bmatrix} \frac{\rho^2}{2} & k\rho e^{-i\varphi} + g\rho^2 e^{2i\varphi} \\ k\rho e^{i\varphi} + g\rho^2 e^{-2i\varphi} & \frac{\rho^2}{2} \end{Bmatrix} \right) \begin{Bmatrix} \chi_+ \\ \chi_- \end{Bmatrix} = E \begin{Bmatrix} \chi_+ \\ \chi_- \end{Bmatrix}$$

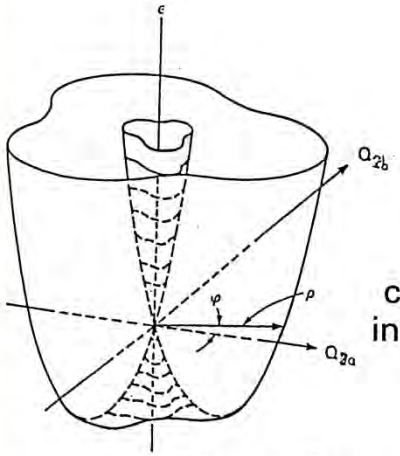


Na_3: Jahn-Teller effect

normal vibrations:

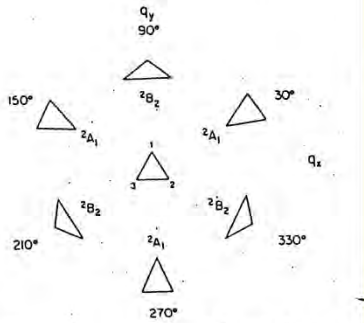


D_{3h}	A_1'	E'	
C_{2v}	A_1	A_1	B_2

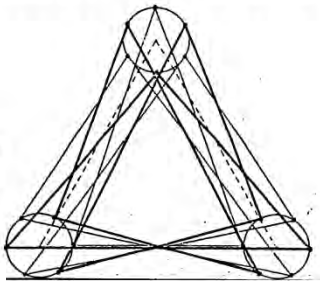


pseudorotation
vibronic angular momentum j

conical intersection



electronic phase $e^{ij\phi}$



CASES OF BERRY'S PHASE

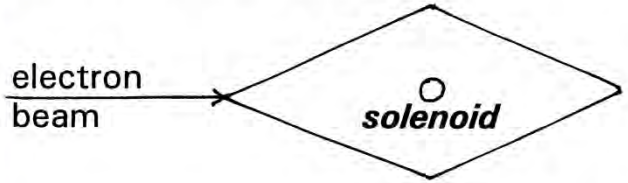
Potential of 3 nuclei with ***conical intersection*** ,
matrix element H_{ij} ~ nuclear displacement coord.

⇒ traversal of closed path around 0 leads to
sign change of wavefunction

$$\hat{H}_{nuc} = -1/(2M)\,\nabla_R^2 - 1/M\,\vec{F}(R)\cdot\vec{\nabla}_R - \ldots + U_i(R)$$

with $\vec{F}(R) = \langle \alpha_i(R) \,|\, \vec{\nabla}_R \alpha_i(R) \rangle$

Aharanov-Bohm effect:

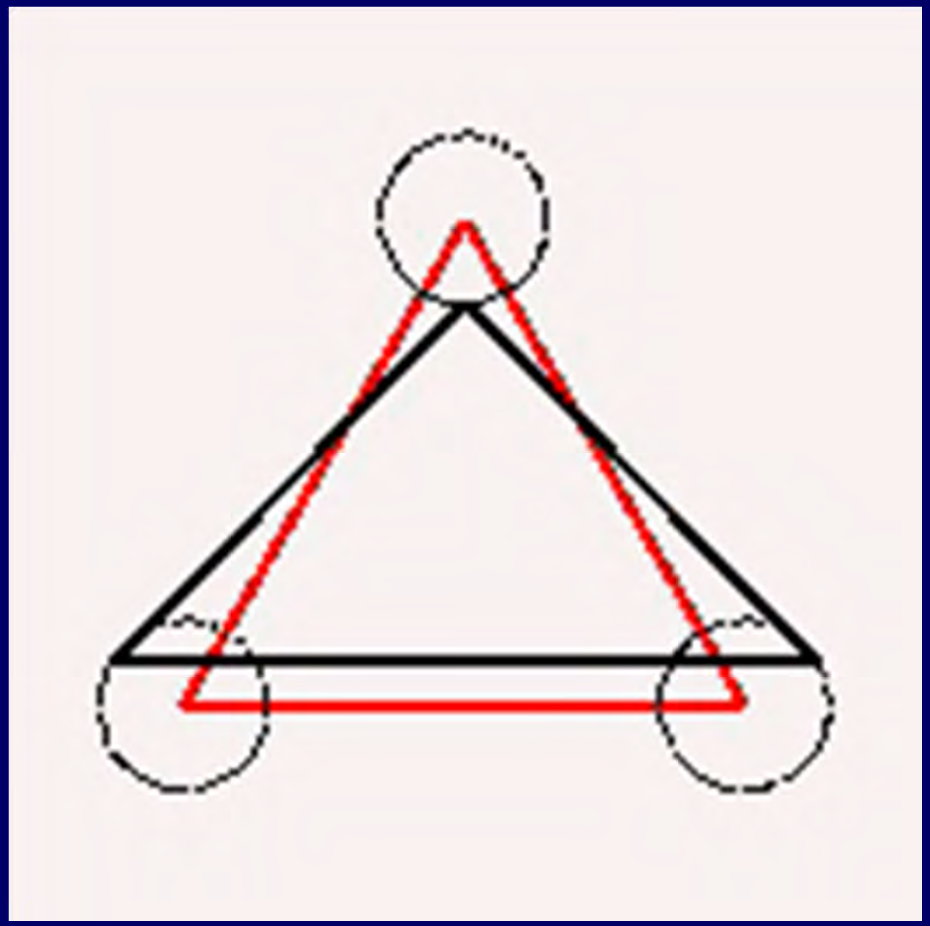


interference,

electron wavefunction experiences phase shift due to vector potential

$$\hat{H} = 1/(2m)\,[\hbar/i\ \mathrm{grad} + \vec{A}]^2 + V$$

$$= -\hbar 2/(2m)\,\nabla^2 + \hbar e/(2mi)\,\vec{A}\cdot\mathrm{grad} + \ldots + V$$



PSEUDOROTATION

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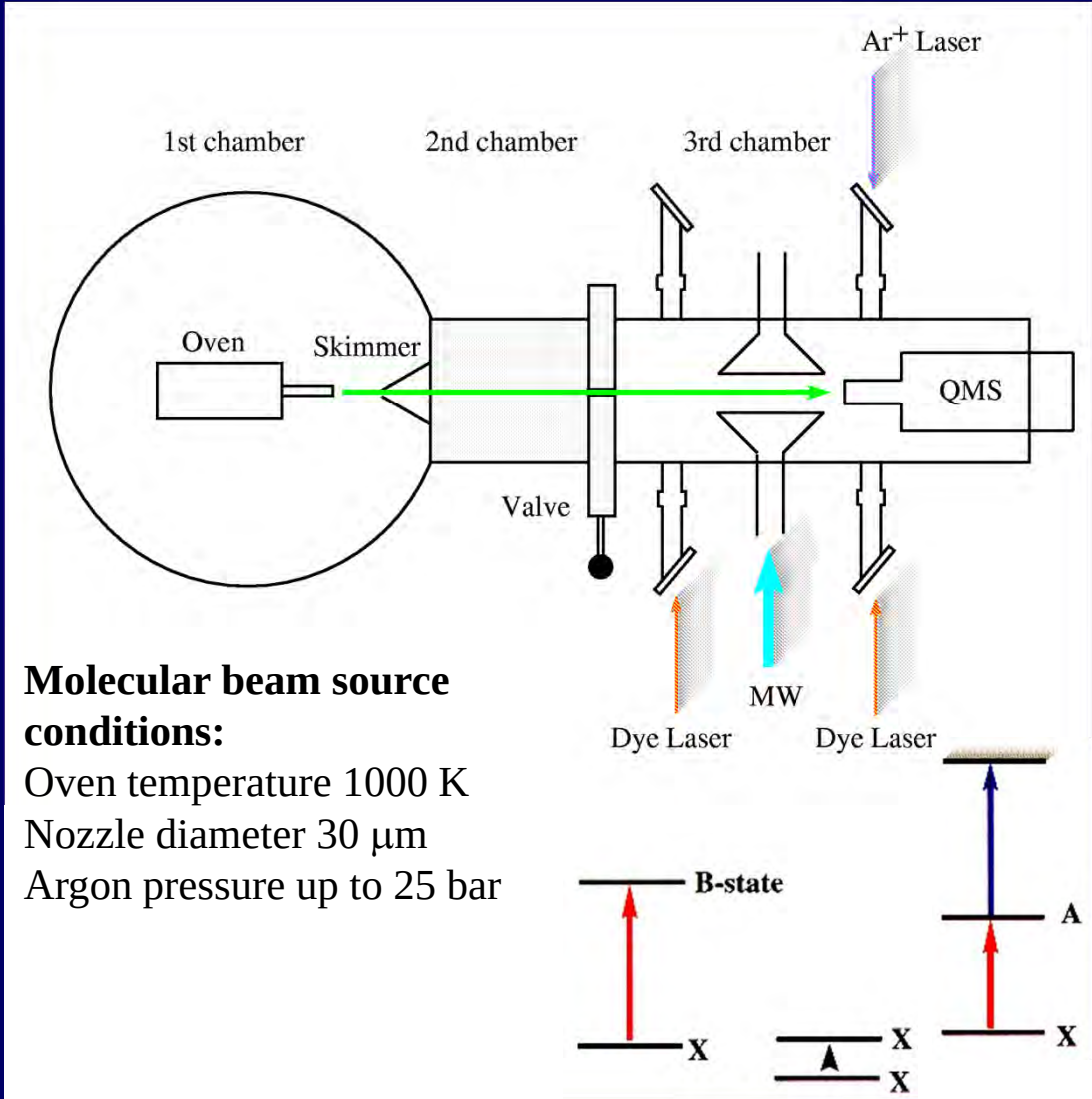
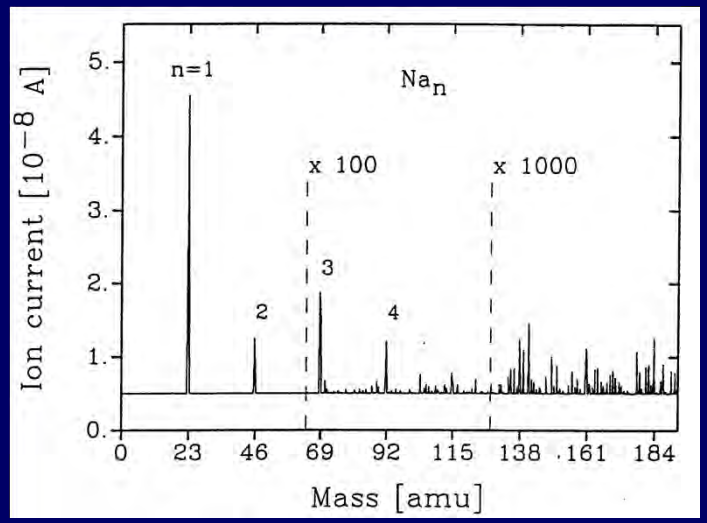
SPECTROSCOPY OF SODIUM CLUSTERS WITH MASS SELECTIVE DETECTION



Molecular beam source conditions:
Oven temperature 1000 K
Nozzle diameter 30 μm
Argon pressure up to 25 bar

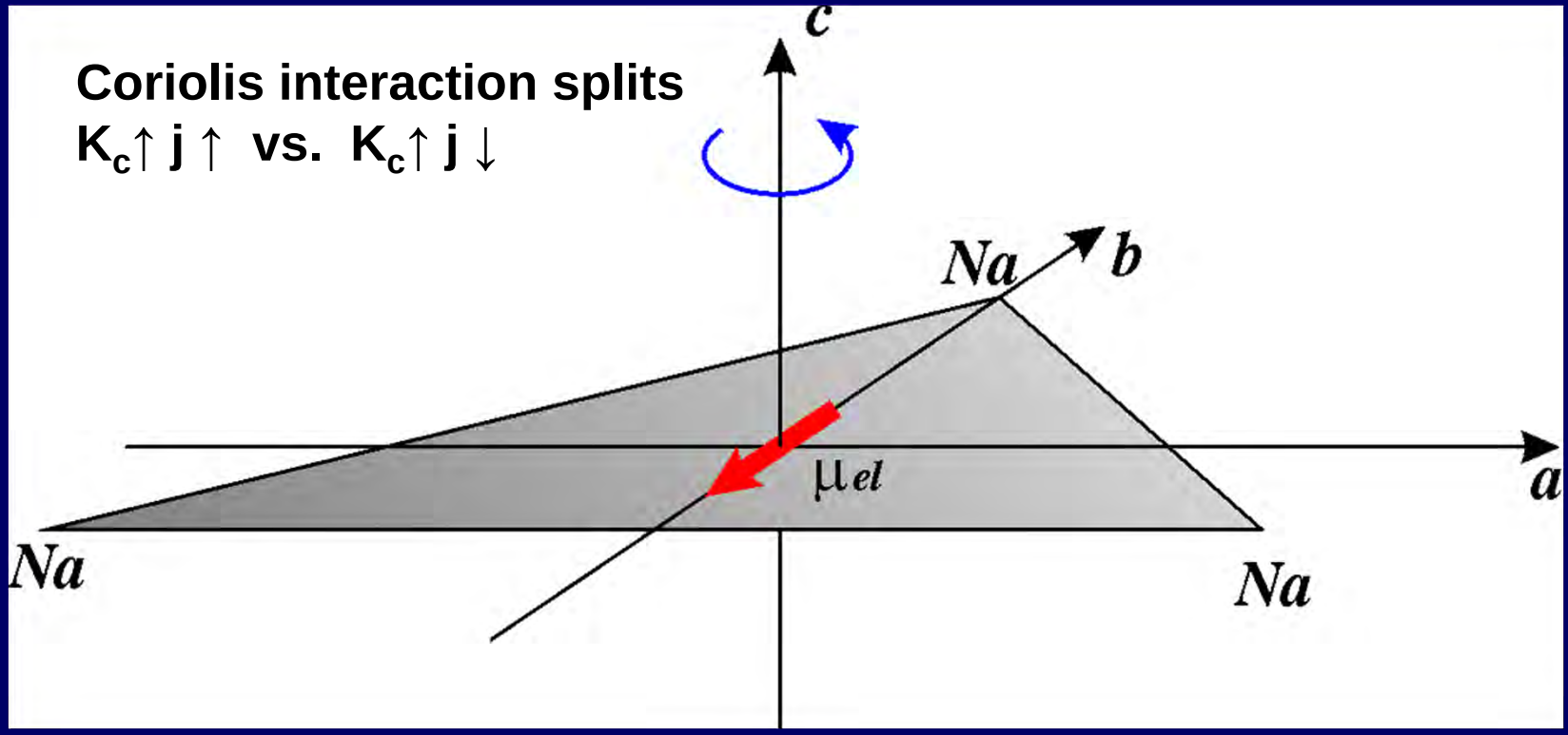


Typical mass spectrum with electron beam ionization

Na_3 – an asymmetric top molecule

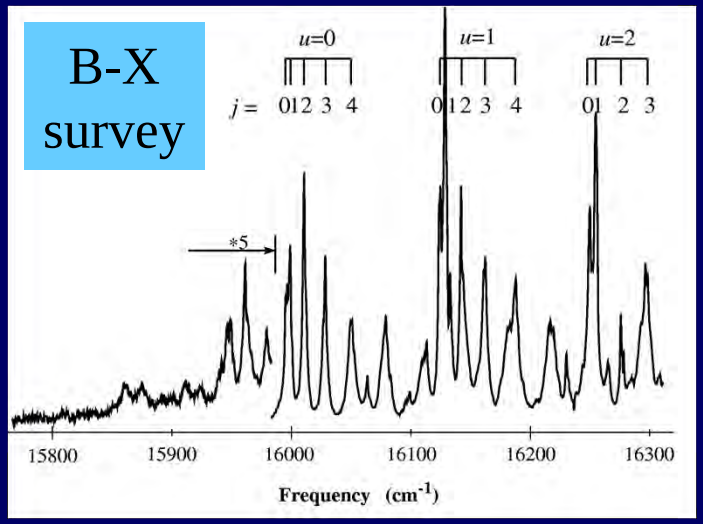
rotational quantum numbers N, K_a, K_c

pseudorotational quantum number j (a vibration!)

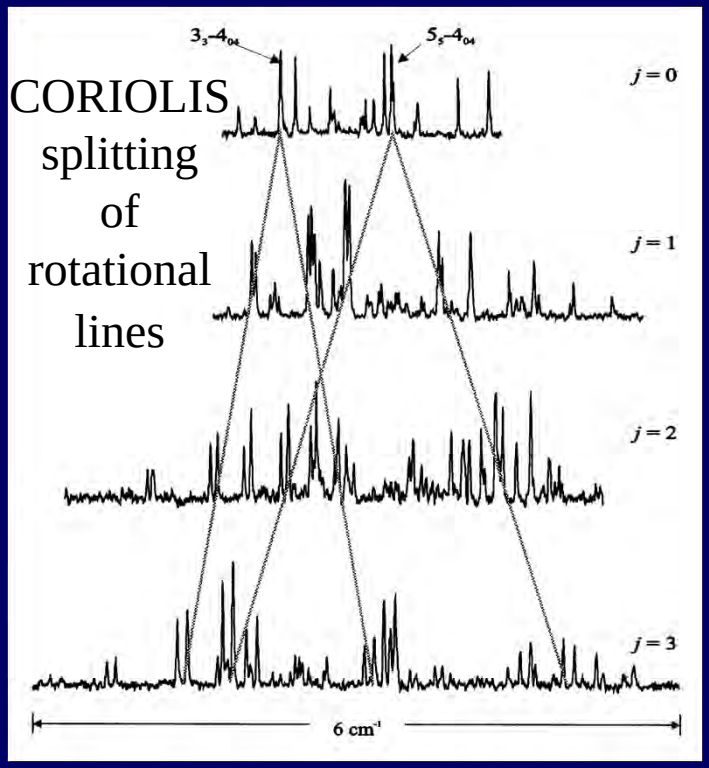


rotational constants A = 0.135, B = 0.076, and C = 0.052 cm^{-1}

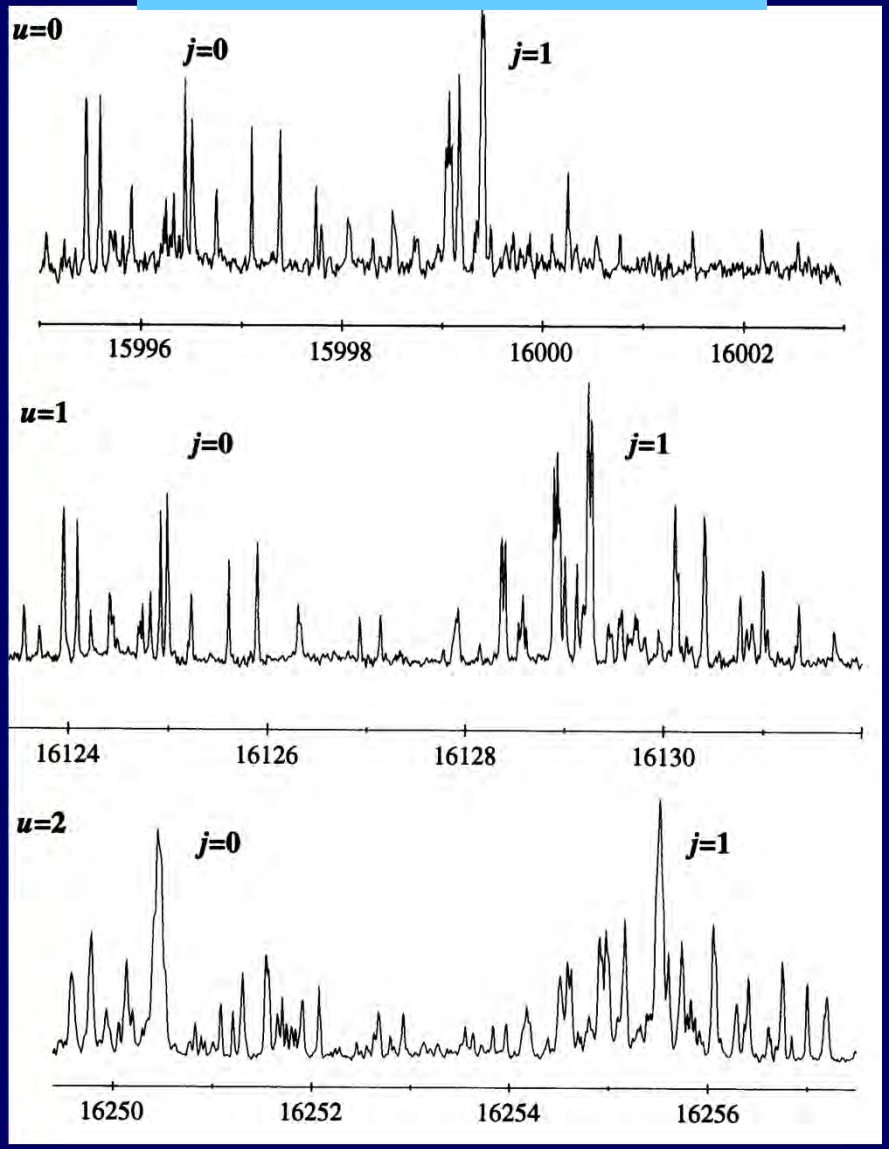
B-X survey



CORIOLIS splitting of rotational lines



B-X high resolution OODR



- Pseudorotation integer quantized: j= 0, 1, 2, 3, ...
- ⇒ no Berry phase (W.E. Ernst & S. Rakowsky PRL 1995)

Barrier to pseudorotation

Rotation-Pseudorotation Hamiltonian, vibrational part:

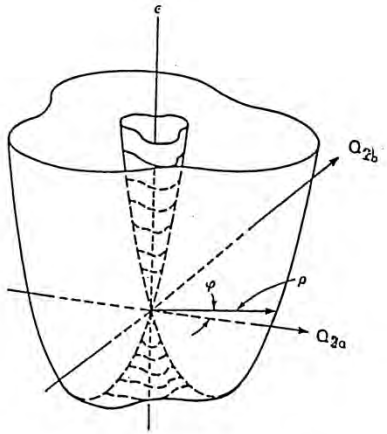
$$h_v = T_v + FJ_p^2 + \frac{1}{2}V_3(1-\cos(3\varphi))$$

Jahn-Teller Formalism (pr >> f(r)):

$$h_v = H_{Kinetic}(\rho,\varphi) + \frac{1}{2}\rho^2 - \sqrt{2}p\rho - f(\rho)\cos(3\varphi)$$

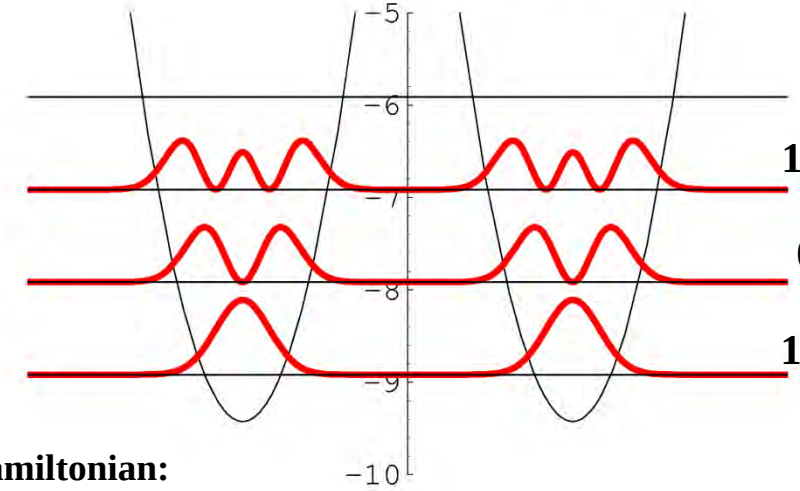
Vibrational wavefunction:

$$\chi^{u,j}(\rho,\varphi) = \psi^u(\rho)\, e^{ij\varphi}$$



Barrier to pseudorotation

$$V_3^u = 2\langle \psi^u(\rho)\,|f(\rho)|\,\psi^u(\rho)\rangle$$



V_3 in cm^{-1}

11.66

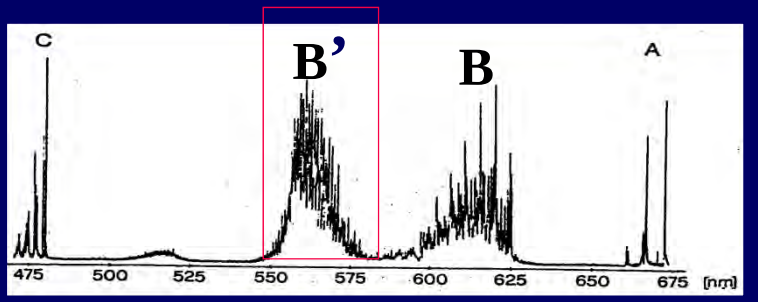
0.0

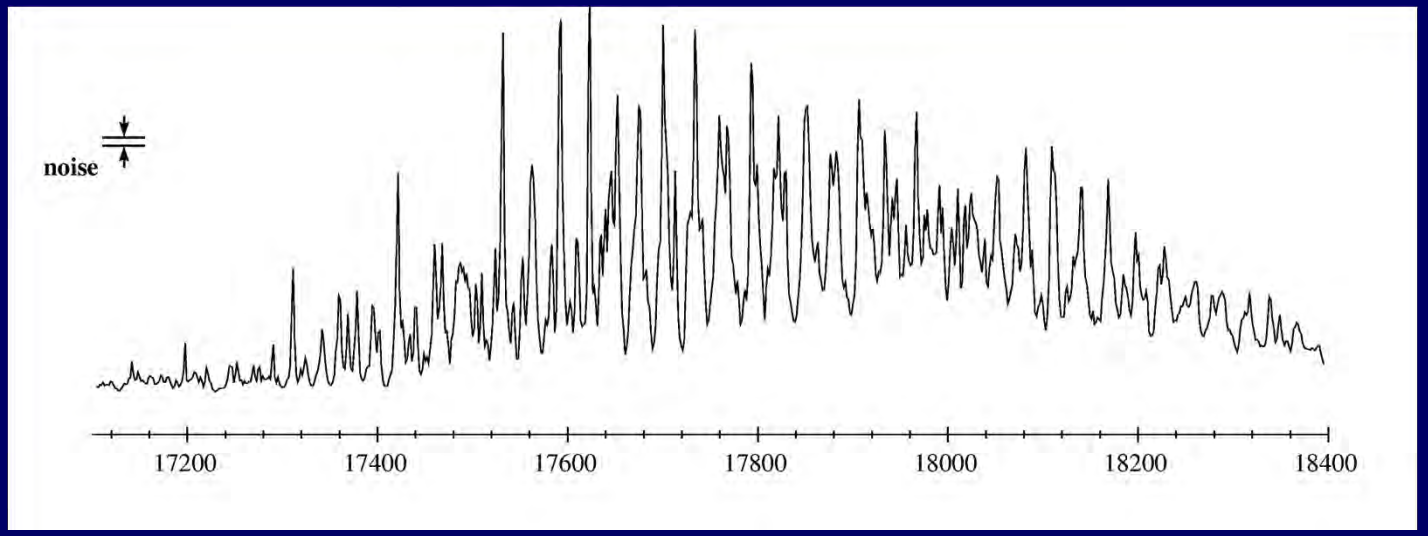
10.15

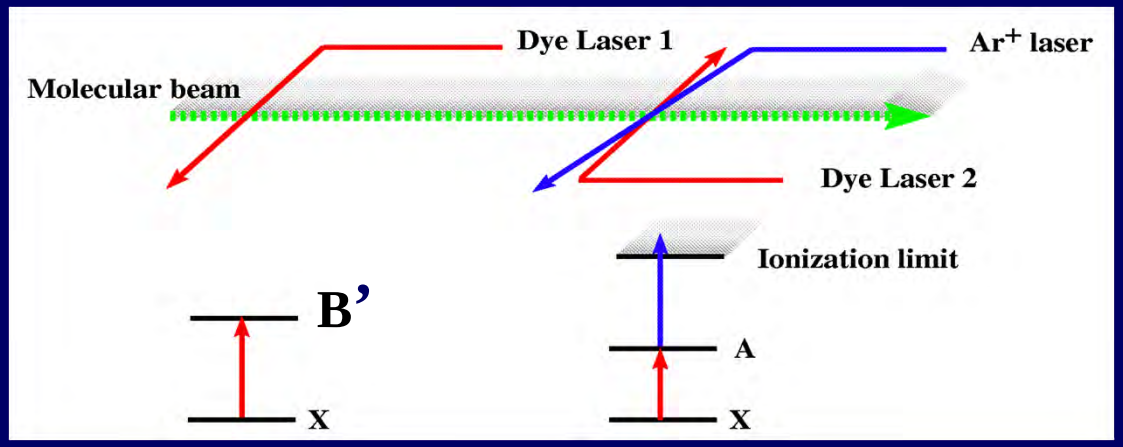
Hamiltonian:

N. Ohaski, M. Tsuura, J. T. Hougen, W. E. Ernst, S. Rakowsky, J. Mol. Spectrosc. 184, 22-34 (1997)

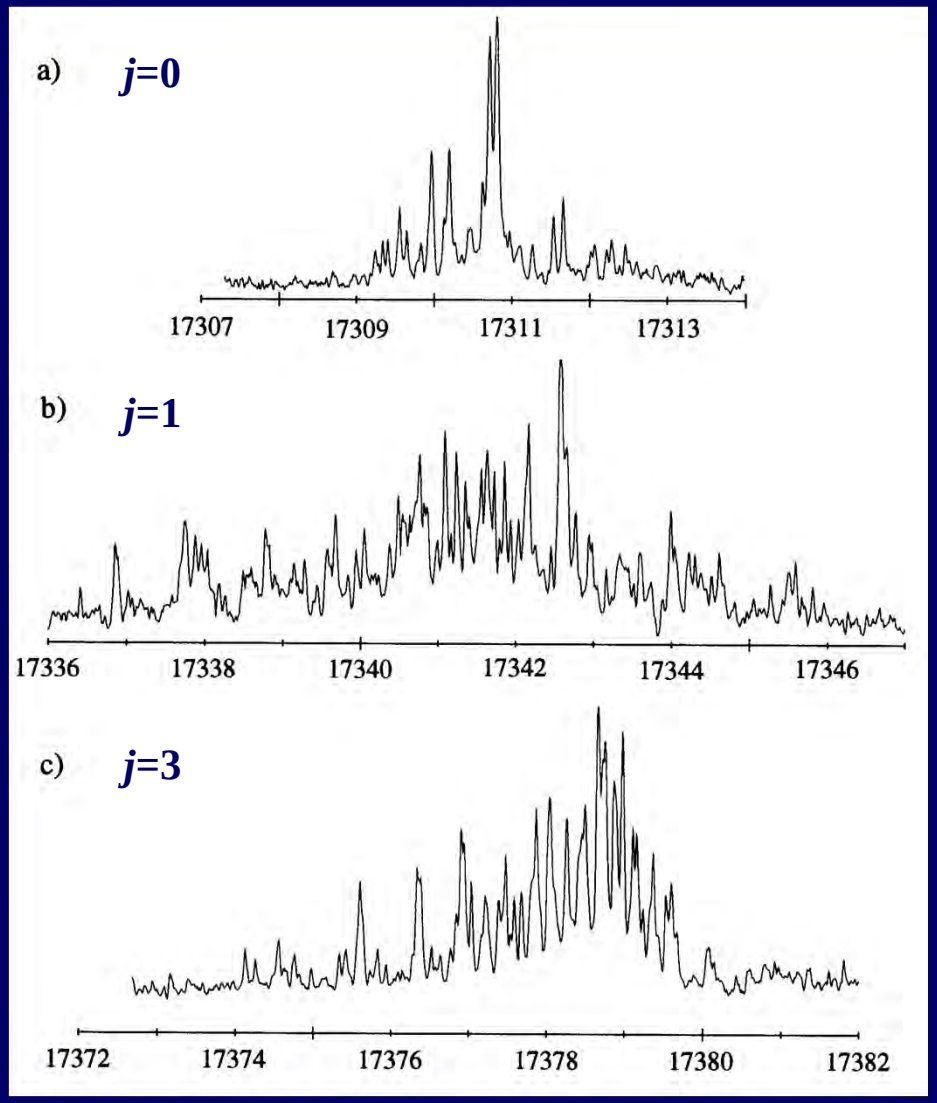
What is the B' State of Na_3?



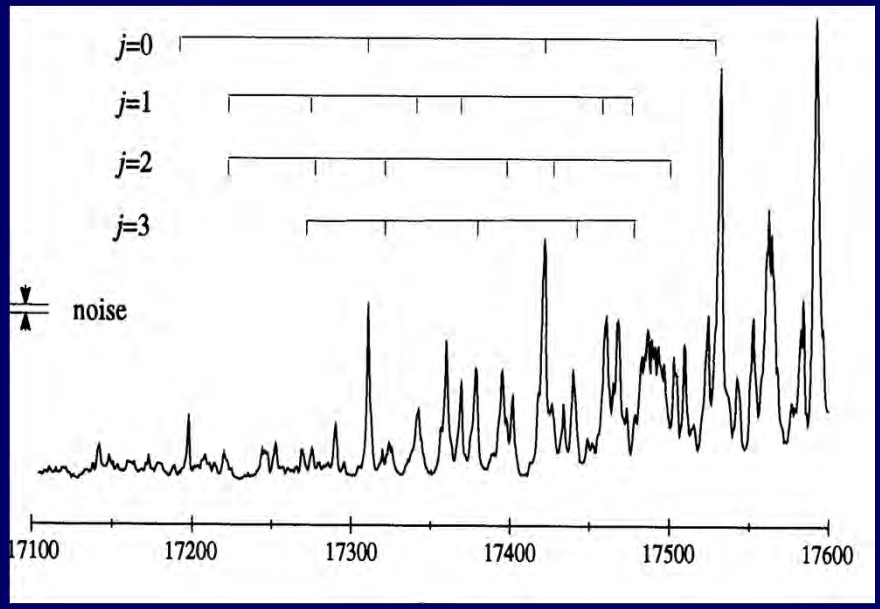




Vibronic assignments in the first part of the B'-X system of Na_3

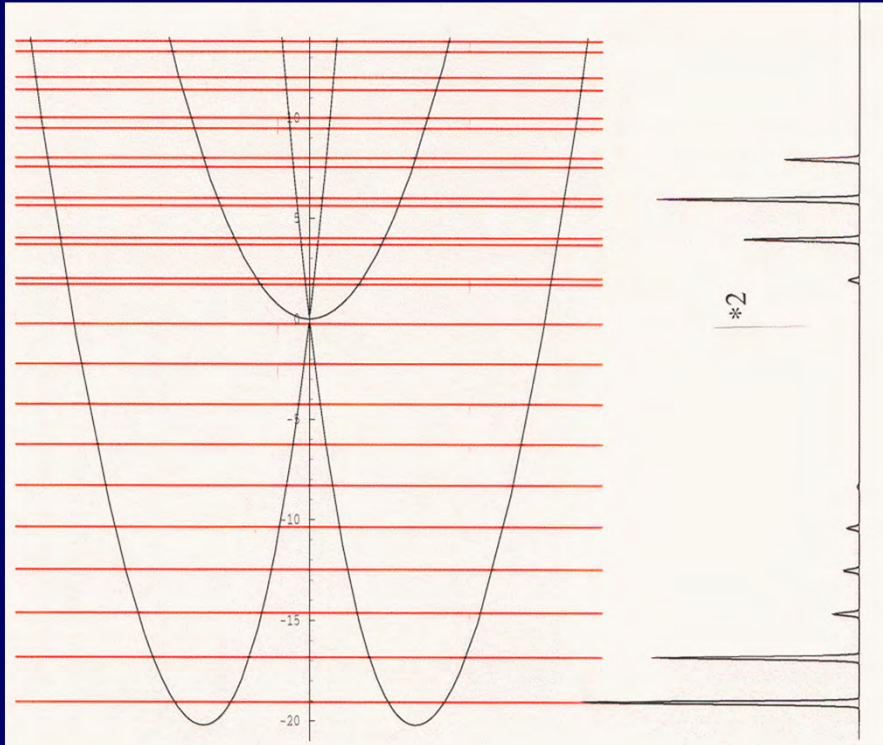


$j > 0$ bands twice as many rotational lines due to CORIOLIS interaction

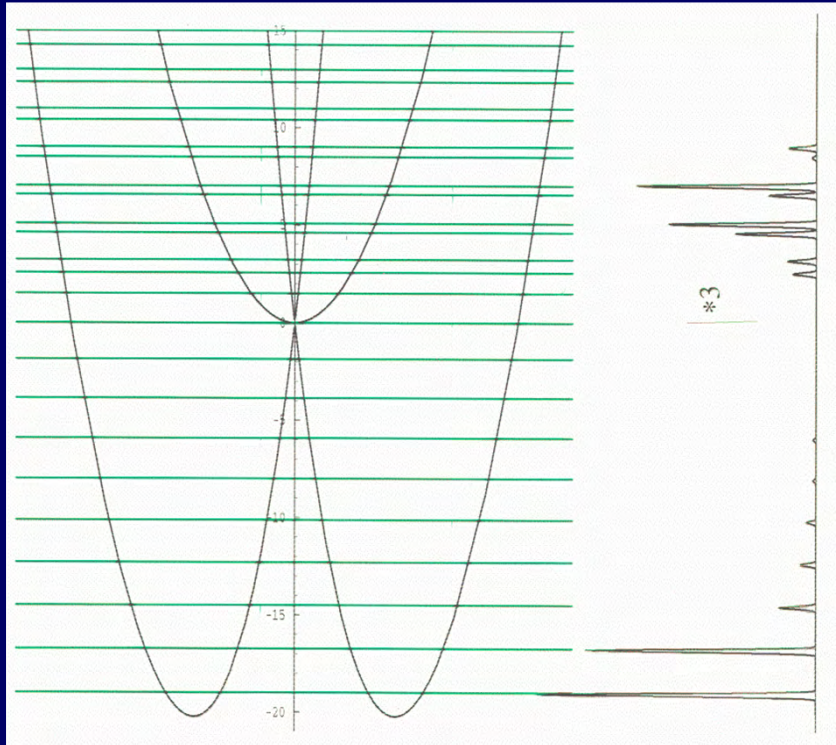


⇒ Largely pseudo Jahn-Teller interaction!

States of the Three-Surface Excited State Potential and Transition Probabilities

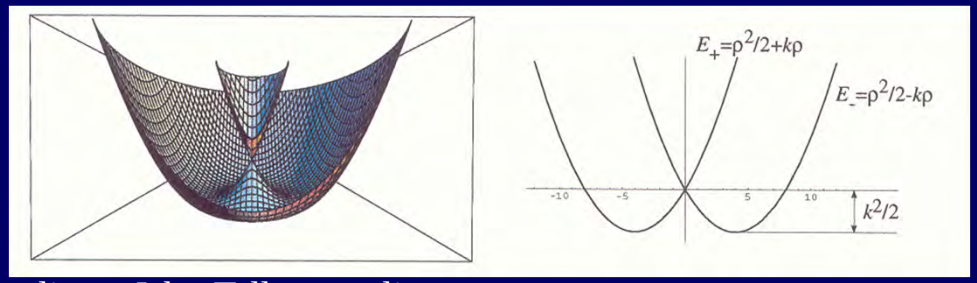


Intensity calculations for the transitions from the ground state of Na_3 (Jahn-Teller system, $k = 4.7$, $g = 0.076$, $\hbar\omega = 90\ cm^{-1}$) into $j = 0$ levels of a Pseudo Jahn-Teller system ($p = 7.98$, $d = 6.5$, $\hbar\omega = 56$

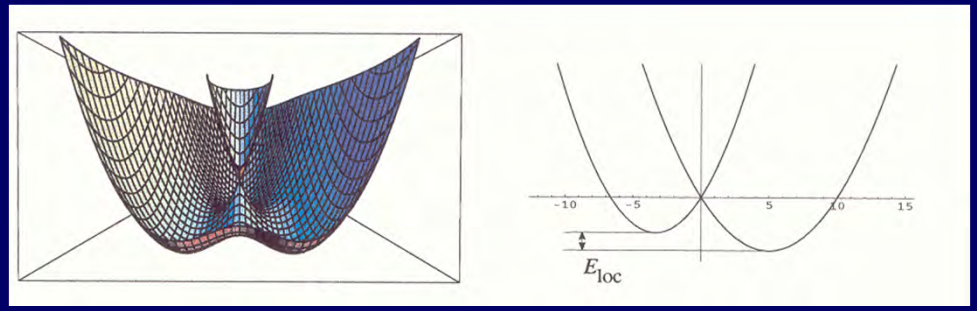


Intensity calculations for the transitions from the ground state of Na_3 (Jahn-Teller system, $k = 4.7$, $g = 0.076$, $\hbar\omega = 90\ cm^{-1}$) into $j = 1$ levels of a Pseudo Jahn-Teller system ($p = 7.98$, $d = 6.5$, $\hbar\omega = 56$

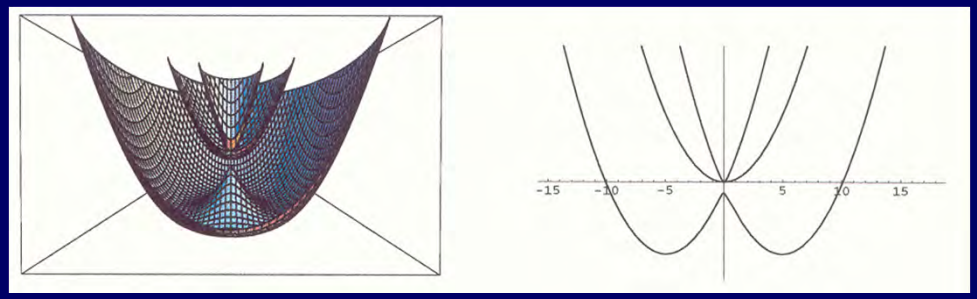
Adiabatic Potential Surfaces



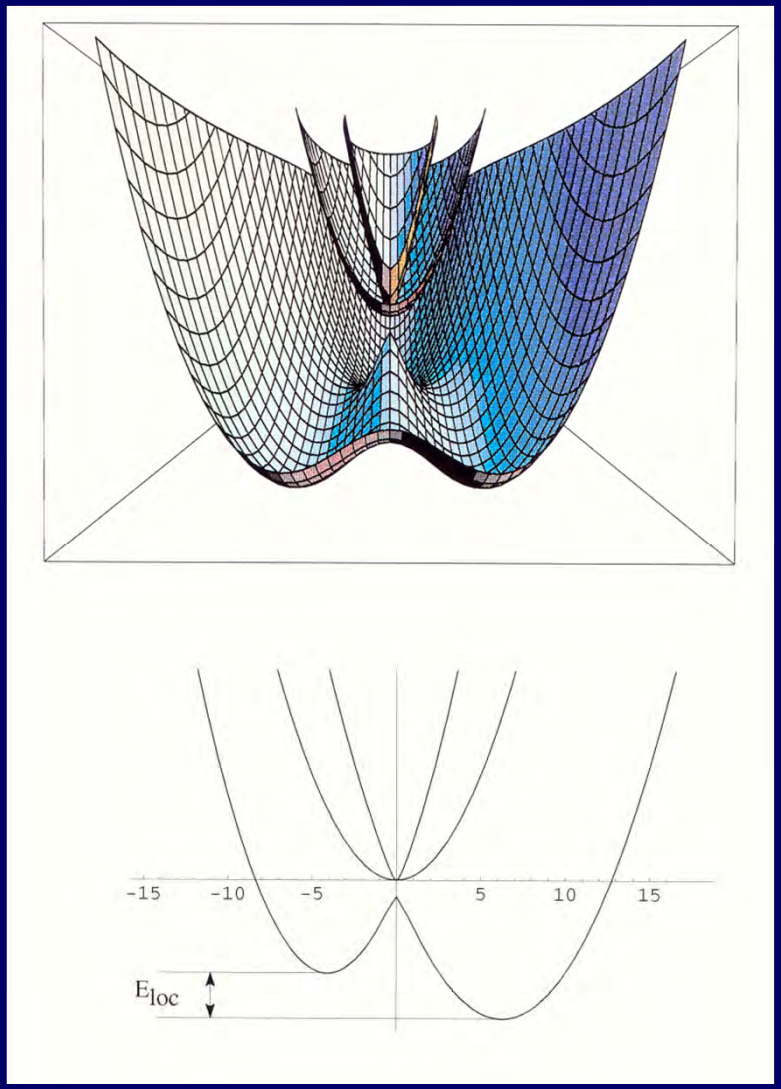
linear Jahn-Teller coupling



linear and quadratic Jahn-Teller coupling



linear pseudo Jahn-Teller coupling



Linear and quadratic pseudo Jahn-Teller coupling

Three-Surface Potential with Three-fold Barrier on the Lowest Sheet

Linear Pseudo Jahn-Teller and Linear Jahn-Teller Coupling

$$\begin{Bmatrix} \frac{1}{2}\rho^2 & k\rho e^{-i\varphi} & p\rho e^{i\varphi} \\ k\rho e^{i\varphi} & \frac{1}{2}\rho^2 & p\rho e^{-i\varphi} \\ p\rho e^{-i\varphi} & p\rho e^{i\varphi} & \varepsilon_0 + \frac{1}{2}d\rho^2 \end{Bmatrix}$$

$$f(\rho) \sim k\rho$$

Linear and Quadratic Pseudo Jahn-Teller Coupling

$$\begin{Bmatrix} \frac{1}{2}\rho^2 & 0 & p\rho e^{i\varphi} + \lambda\rho^2 e^{-2i\varphi} \\ 0 & \frac{1}{2}\rho^2 & p\rho e^{-i\varphi} + \lambda\rho^2 e^{2i\varphi} \\ p\rho e^{-i\varphi} + \lambda\rho^2 e^{2i\varphi} & p\rho e^{i\varphi} + \lambda\rho^2 e^{-2i\varphi} & \varepsilon_0 + \frac{1}{2}d\rho^2 \end{Bmatrix}$$

$$f(\rho) \sim \lambda\rho^2$$

Linear Pseudo Jahn-Teller Coupling with a "Proper" Anharmonicity Term

$$\begin{Bmatrix} \frac{1}{2}\rho^2 + 2\alpha\rho^3\cos(3\varphi) & 0 & p\rho e^{i\varphi} \\ 0 & \frac{1}{2}\rho^2 + 2\alpha\rho^3\cos(3\varphi) & p\rho e^{-i\varphi} \\ p\rho e^{-i\varphi} & p\rho e^{i\varphi} & \varepsilon_0 + \frac{1}{2}d\rho^2 + 2\alpha\rho^3\cos(3\varphi) \end{Bmatrix}$$

$$f(\rho) \sim \alpha\rho^3$$

Linear Pseudo Jahn-Teller, Linear Jahn-Teller and Quadratic Pseudo Jahn-Teller Coupling

$f(\rho) \sim k\rho - \lambda\rho^2$!!! (d=1, ε=0)

p=7.98 d=6.6 ε=-2 $\hbar\omega \cong 56$ cm^{-1}

k= 0.827 λ= 0.22

Linear and Quadratic Pseudo Jahn-Teller Coupling, and a „Proper“ Anharmonicity Term

$f(\rho) \sim \lambda\rho^2 - 2\alpha\rho^3$!!! (d=1, ε=0)

p=7.98 d=6.6 ε=-2 $\hbar\omega \cong 56$ cm^{-1}

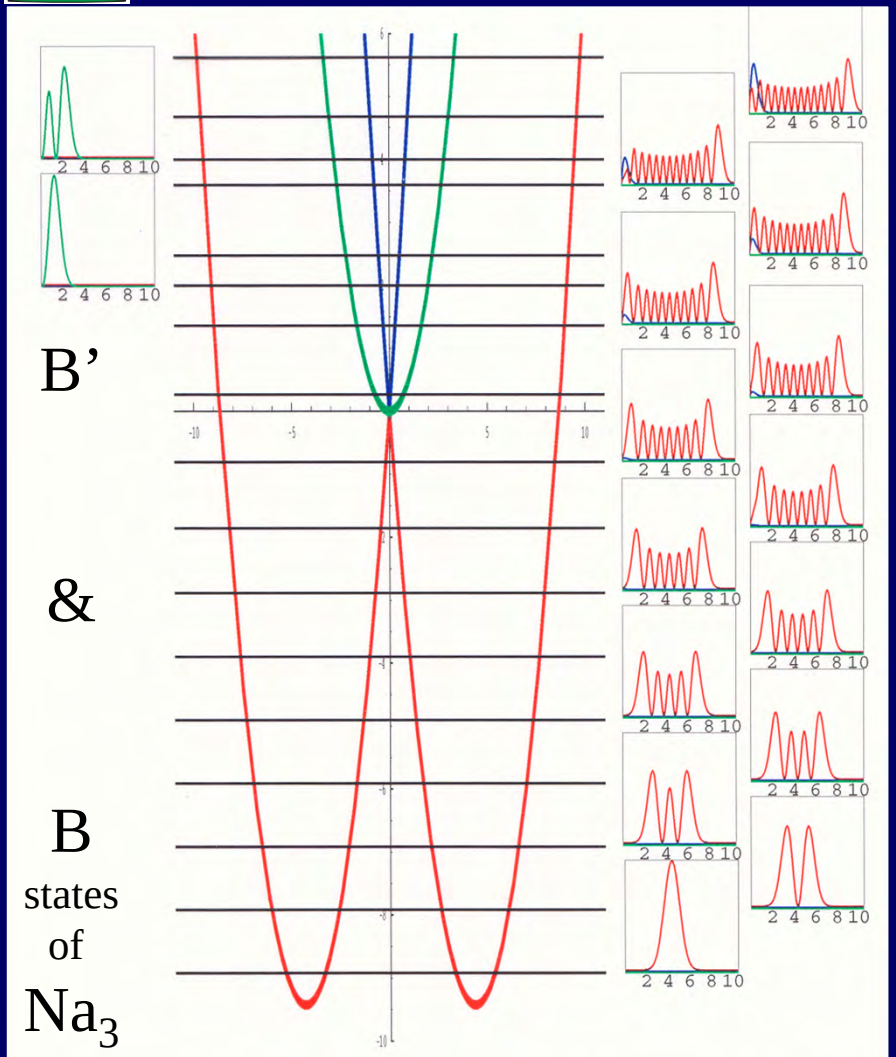
λ= 0.0598 α= 0.0033

Linear Pseudo Jahn-Teller, Linear Jahn-Teller Coupling and a „Proper“ Anharmonicity Term

$f(\rho) \sim k\rho - 2\alpha\rho^3$!!! (d=1, ε=0)

p=7.98 d=6.6 ε=-2 $\hbar\omega \cong 56$ cm^{-1}

k= 0.177 α= 0.003



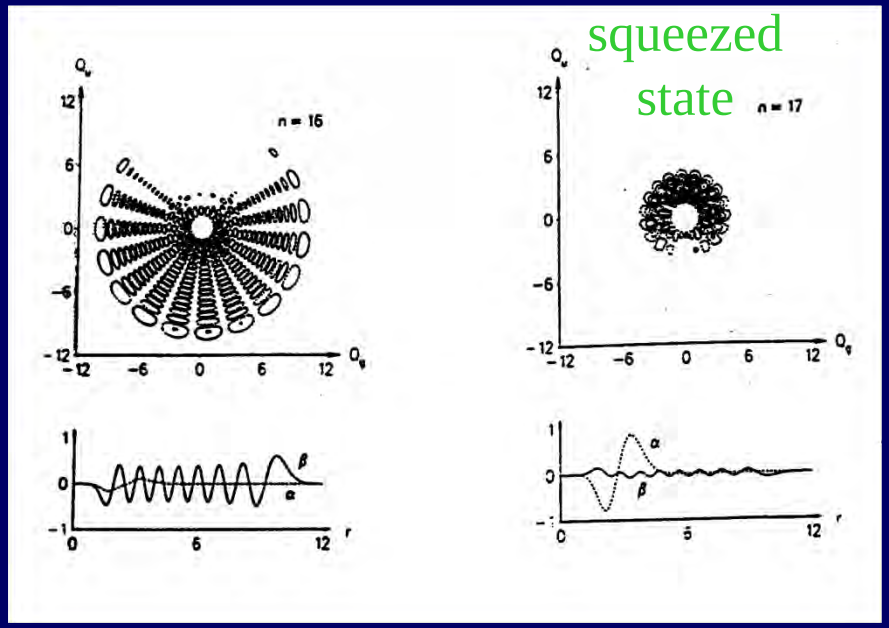
Probability density function $2\pi r \chi^*(\varphi, r)\, \chi(\varphi, r)$ for $j=0$ levels in a PJT system ($p=3.07$, $d=1$, $\varepsilon=0$) .

Energy is given in the units of $\hbar\omega = 127\ cm^{-1}$. For each energy level red, green and blue represent the probability functions associated with the lower , middle and upper sheets of the potential energy, respectively.

Similar: solid crystal exciton-phonon states

(Eiermann &Wagner 1996)

JCP 105, 6713



Na_3 B/B' surfaces:
PJT and JT coupling
+ anharmonicity

Lecture I

- introduction: metal clusters, jellium, shell structure, molecule?
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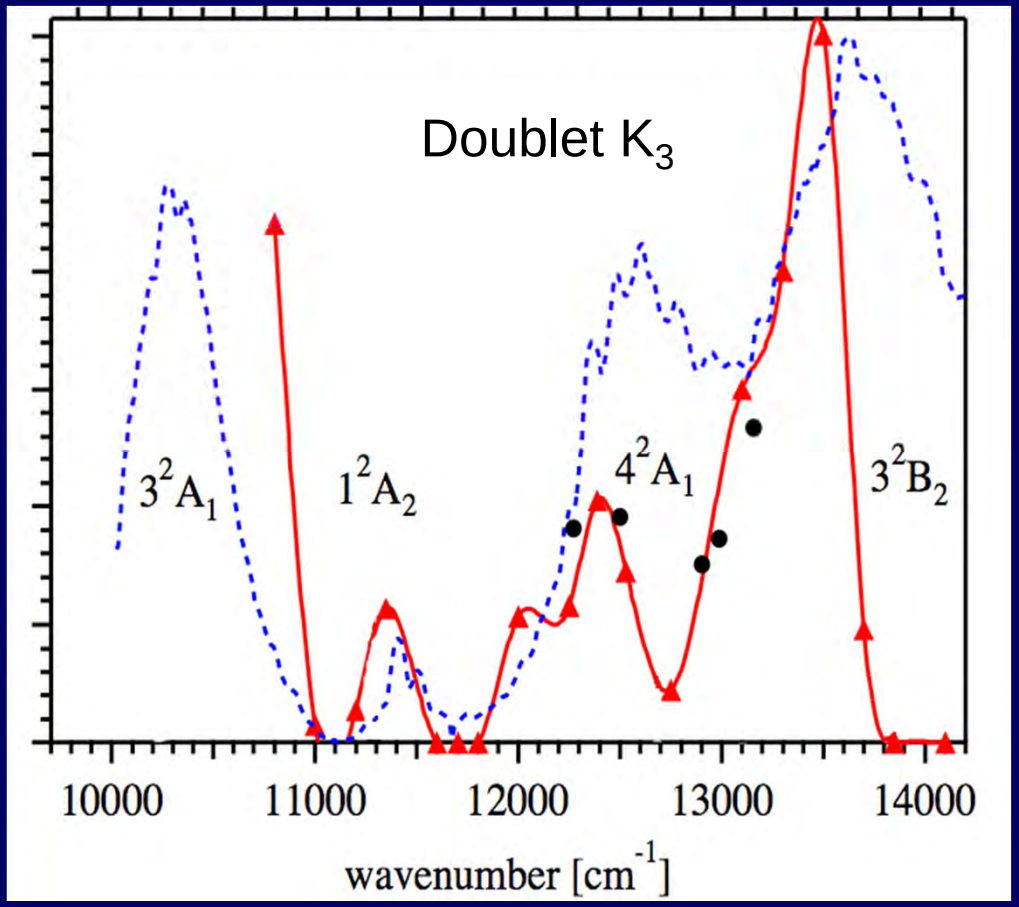
- K_3 on argon clusters, K_3 femtosecond pump-probe
- *ab initio* K_3 and Rb_3 doublet states
- doublet state shell structure
- the ultimate resolution: electron spin density at the 3 nuclei

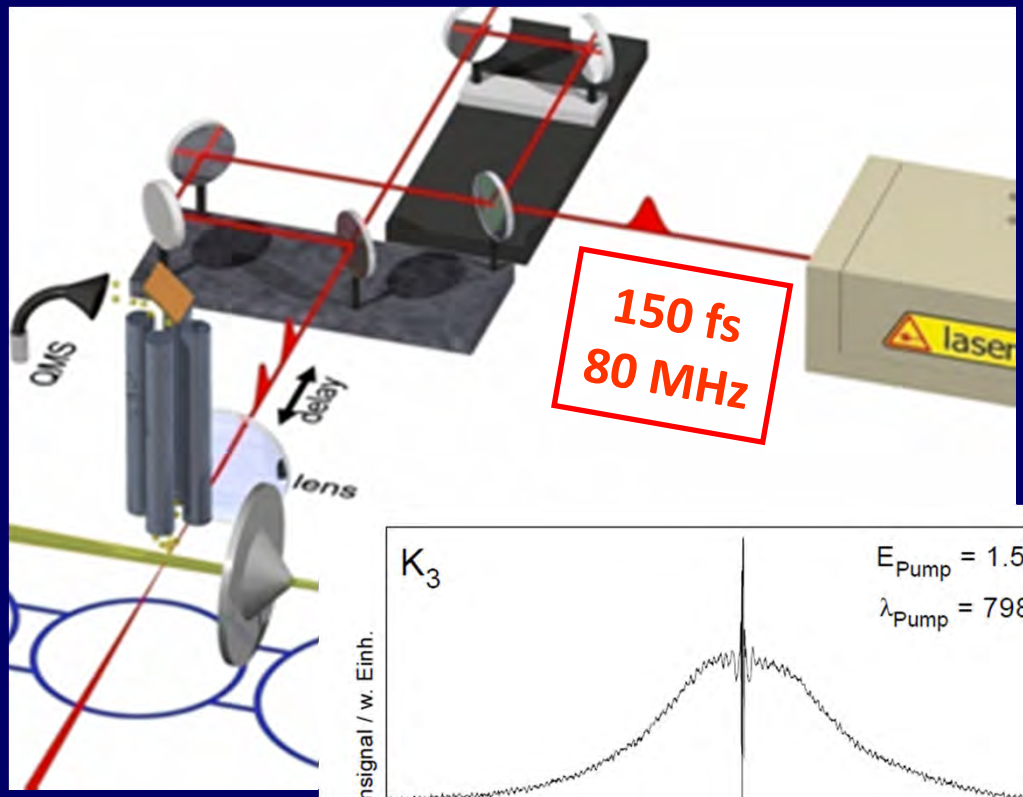


Alkali doped argon clusters:

potassium trimer detected

JPCA 111, 12386-12397 (2007):
J. Nagl, A.W. Hauser, G. Auböck, C. Callegari and W.E. Ernst:
Optical spectroscopy of potassium-doped argon clusters. Experiments and quantum-chemistry calculations

K_3 femtosecond pump-probe experiments
(PhD thesis S. Rupp (FU Berlin 1996)



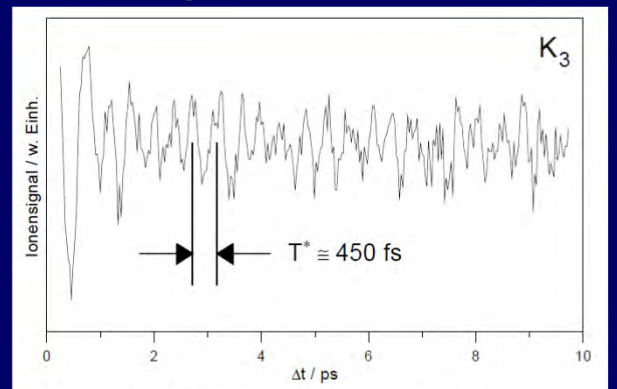


Abbildung 5.11: Normalisiertes Einfarben-Echtzeitspektrum an K_3 bei der Anregungsenergie E_{Pump} = 1.55 eV (λ_{Pump} = 798 nm). Die Periode der beobachteten Oszillation beträgt T^* ≅ 450 fs.

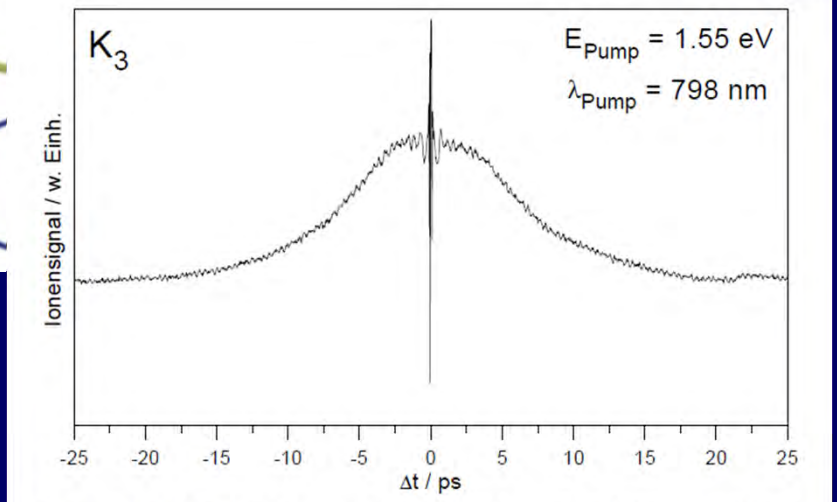


Abbildung 5.10: Einfarben-Echtzeitspektrum an K_3 bei E_{Pump} = 1.55 eV (λ_{Pump} = 798 nm). Dem beobachteten abfallenden Ionensignal ist eine Oszillationsstruktur überlagert.

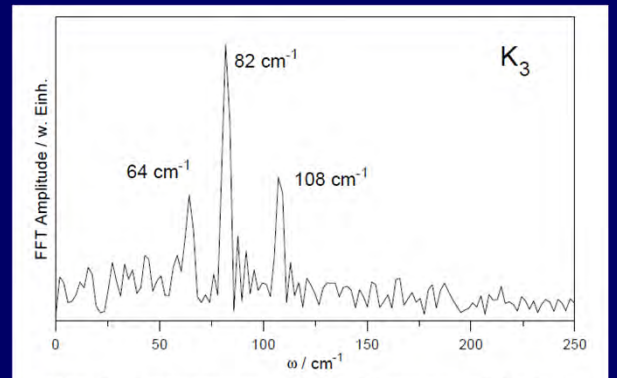


Abbildung 5.12: Fourierspektrum der normalisierten Echtzeitmessung an K_3 bei der Anregungsenergie E_{Pump} = 1.55 eV (λ_{Pump} = 798 nm).

	ω/cm^{-1}	T/fs	$I_{\omega_S^*}$
ω_S^*	82	406	1.00
ω_S^X	108	306	0.52
ω_V^X	64	505	0.45

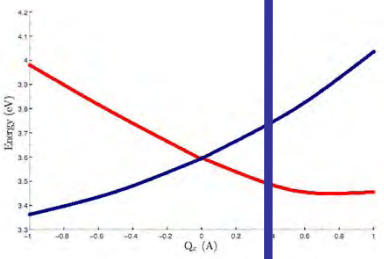
Femtosecond pump-probe scheme

Trimers – not so easy!

or ?

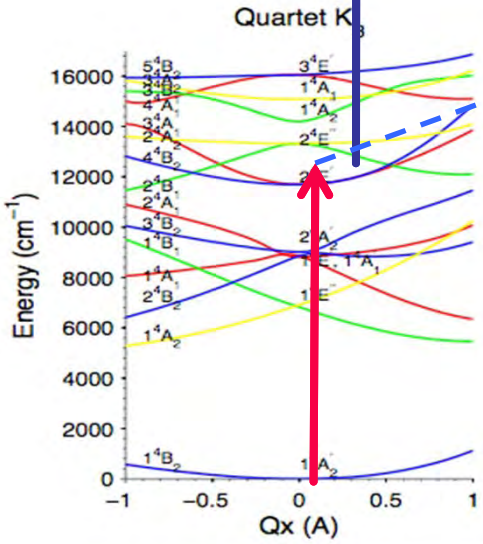
$1^3E'$

28,000 cm^{-1}



$2^4E'$

$1^4A_2'$



Vibronic level spacings vs. JT coupling strength

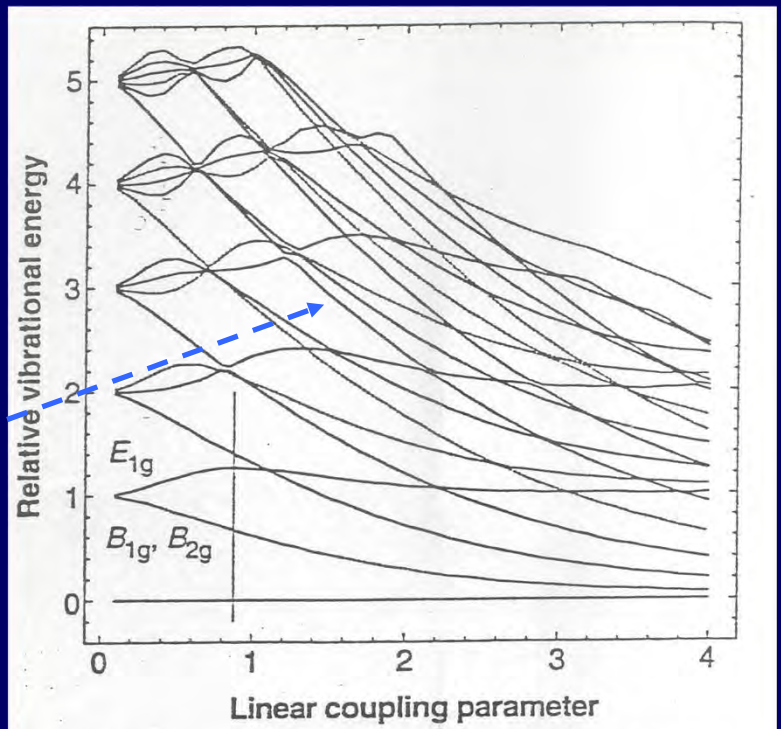


Fig. 3. Correlation diagram showing the level structure of the single-mode linear Jahn-Teller problem ($g = 0$) as a function of the linear coupling parameter k. Vibrational energy and k are presented in reduced units in which the vibrational frequency is 1.

Lecture I

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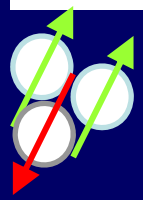
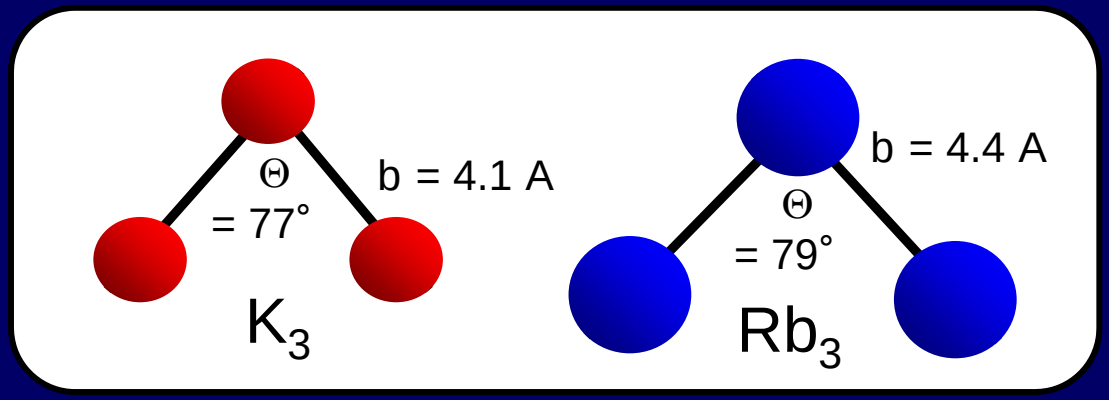
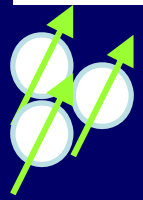
Homonuclear Alkali Trimers K_3 and Rb_3

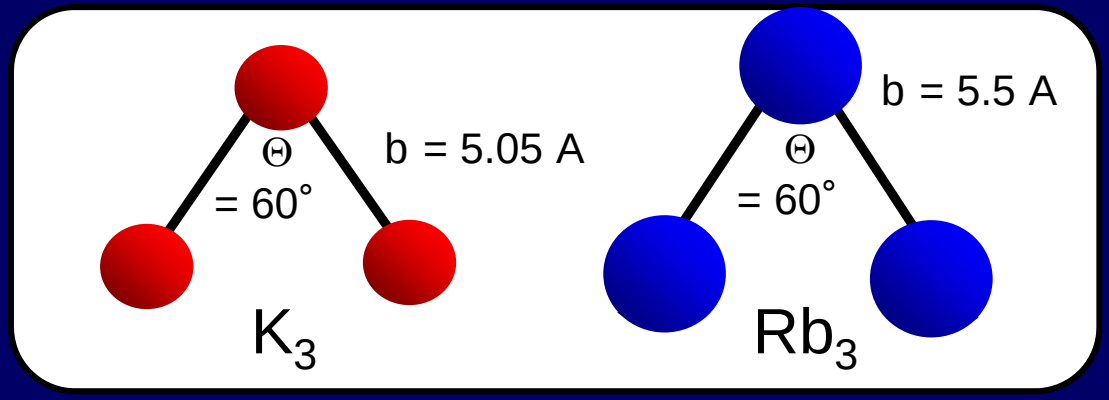
strongly bound
low-spin
$^2E´$ ground state





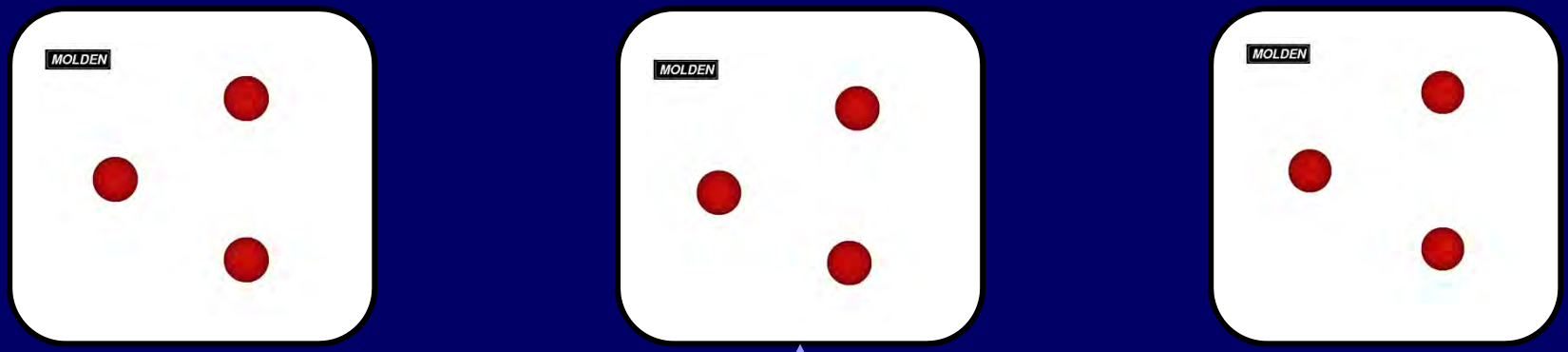
weak (van der Waals)
high-spin
$^4A_2´$ ground state



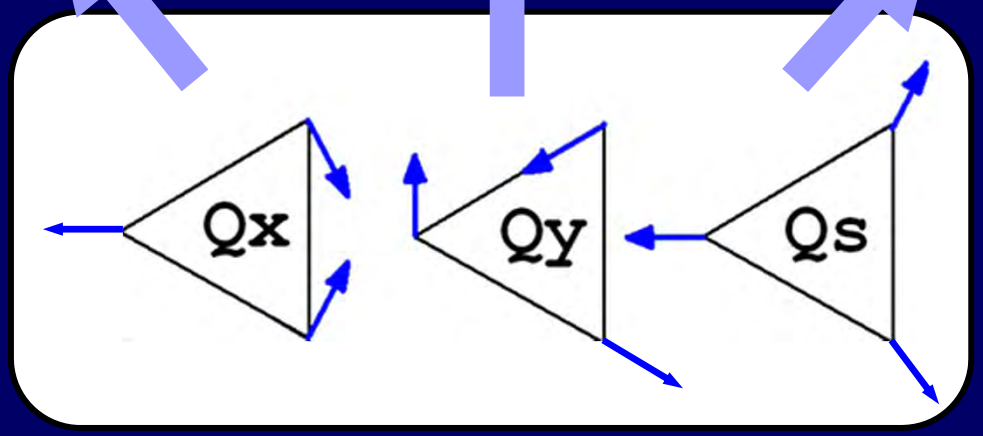


Geometry optimization at the RHF-CCSD(T) level of theory

Nuclear displacement coordinates

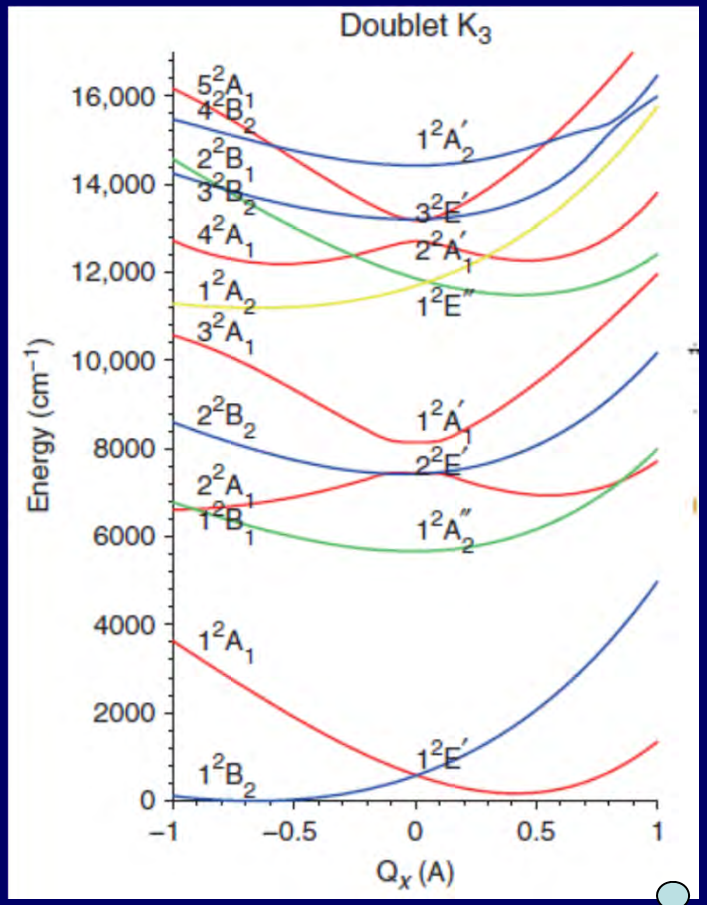


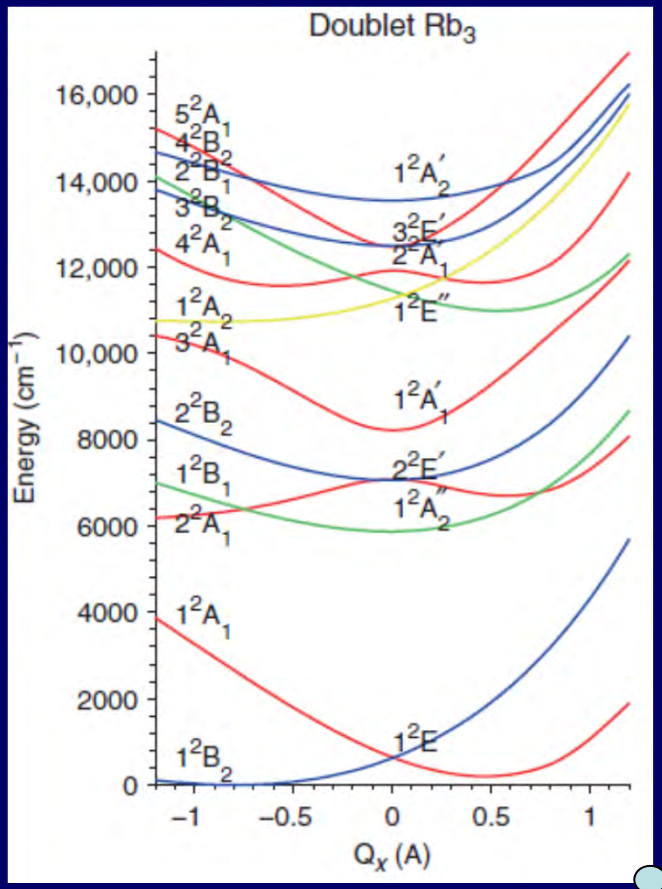
Q_x mode keeps C_{2v} symmetry !



Geometry optimization at the RHF-CCSD(T) level of theory

Introduction of normal coordinates





Geometry optimization at the RHF-CCSD(T) level of theory

Introduction of normal coordinates

Scan over Qx coordinate

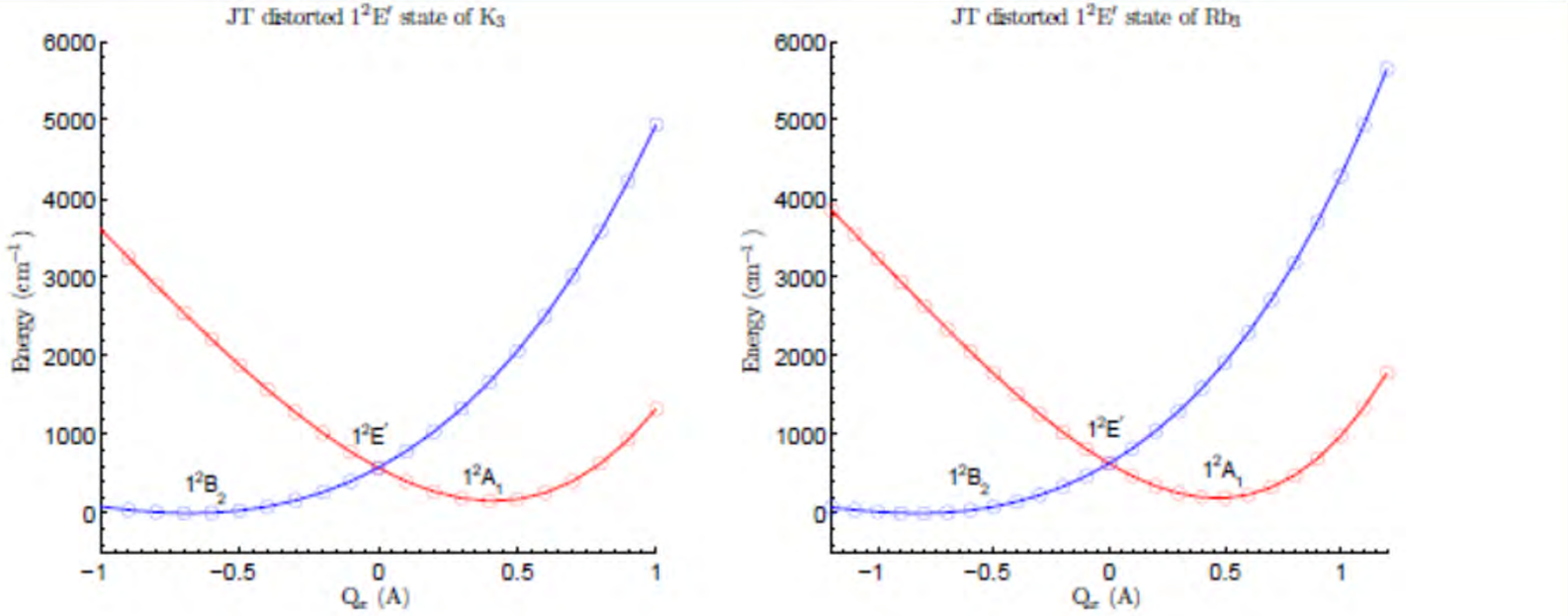
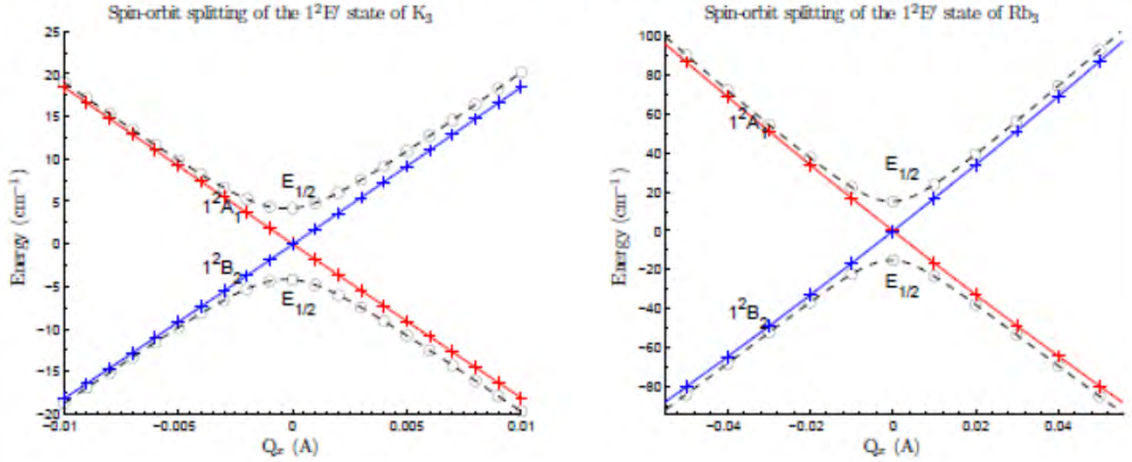


Figure 2: Potential energy curves for the $1^2E'$ ground states of K_3 and Rb_3, calculated at the RS2C level of theory. Energies are printed as functions of the Q_x coordinate, Q_y is set to zero. The double degeneracy of the $^2E'$ states at D_{3h} symmetry is nearly symmetrically lifted when lowering the symmetry to C_{2v}. The global minima of B_2 symmetry (blue) are reached at negative Q_x values, corresponding to obtuse distortions. The saddle points of the A_1 states (red) at positive Q_x values look like local minima in the one-dimensional scan. The zero of the energy is set to the global minimum.

A. W. Hauser, C. Callegari, P. Soldan, W. E. Ernst, Chem. Phys., in press

Permanent el. Dipole: Ground state K_3 0.3 D, Rb_3 0.27 D



Andreas W. Hauser

Lecture I

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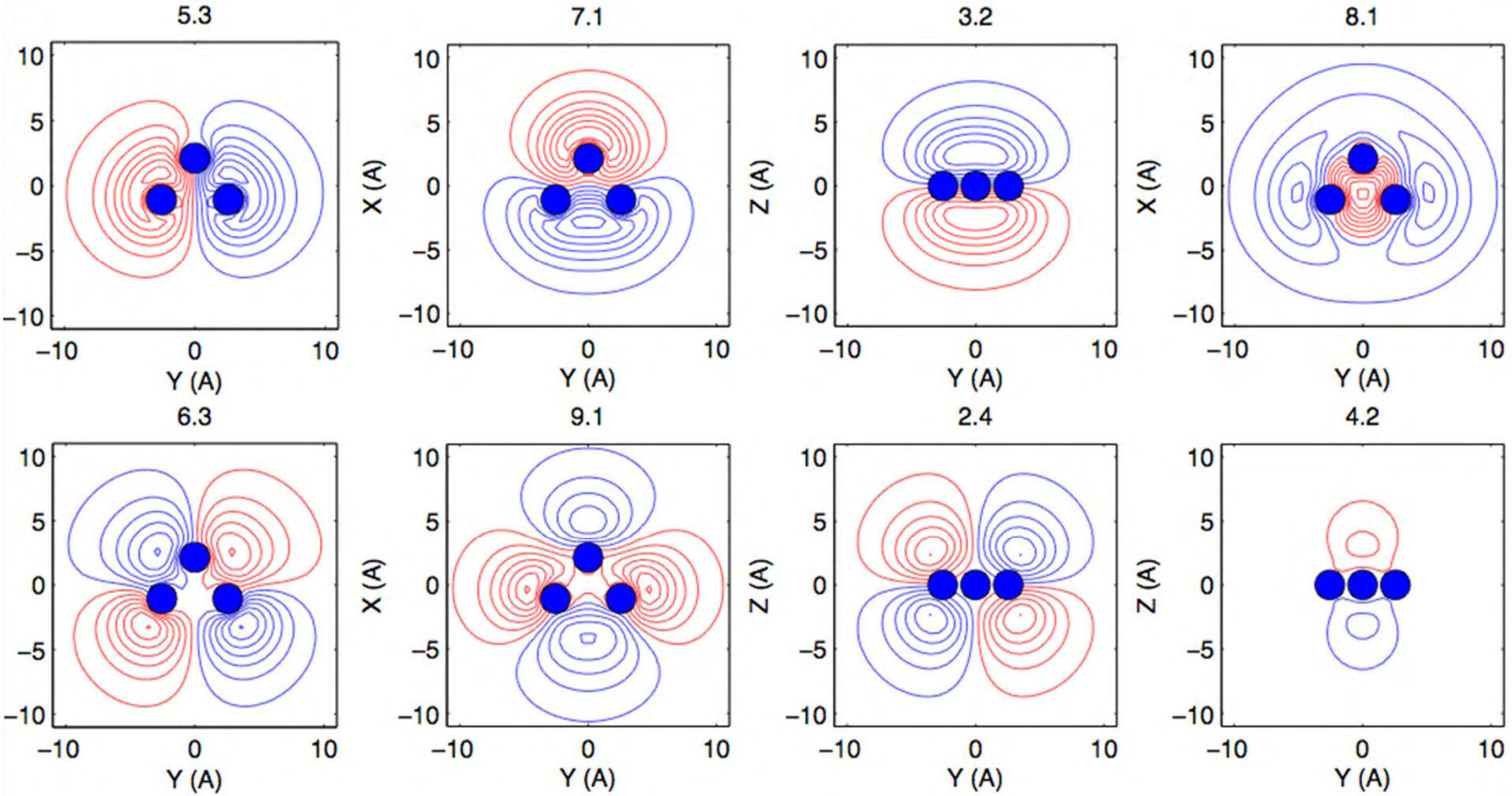
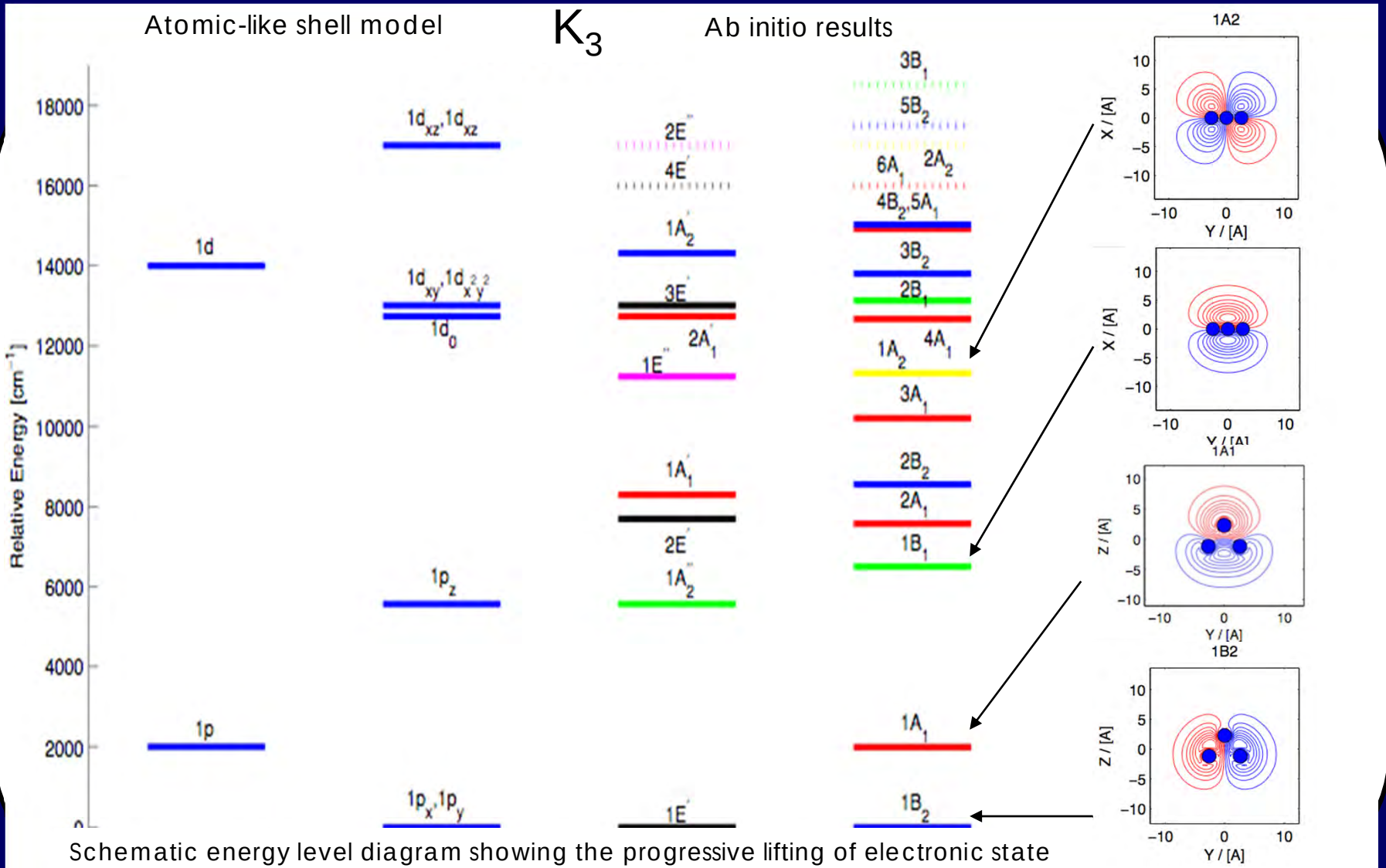
shell model for the doublet states

A common approximation: single-electron in effective spherical potential



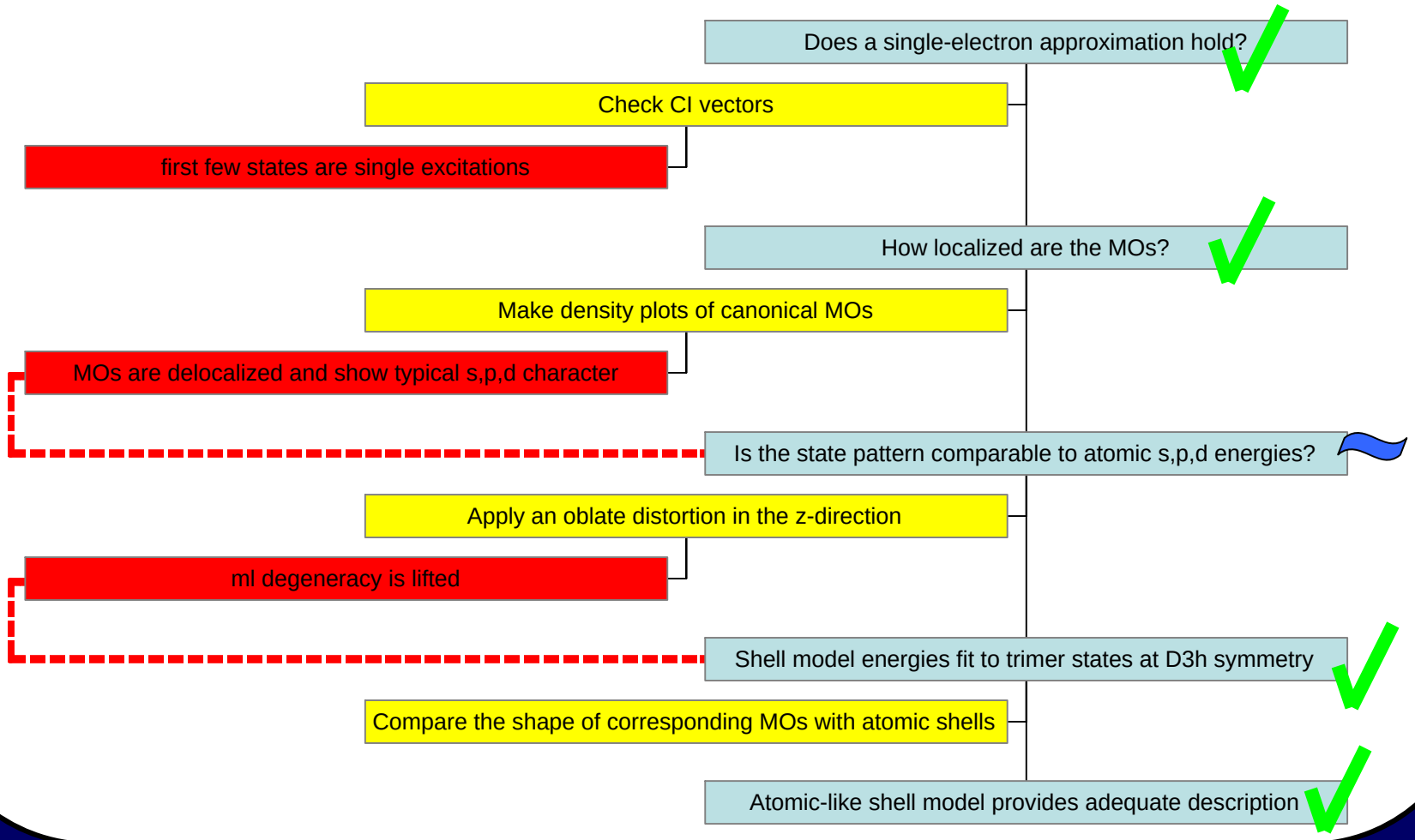
shell model for the doublet states



Schematic energy level diagram showing the progressive lifting of electronic state degeneracies as the applied MO theory becomes more sophisticated.

shell model for the doublet states

A common approximation: single-electron in effective spherical potential



Level Structure and Magnetic Properties from One-Electron Atoms to Clusters with Delocalized Electronic Orbitals: Shell Models for Alkali Trimers

by **A.W. Hauser, C. Callegari, W.E. Ernst**

in: P. Piecuch et al. (eds.), *Advances in the Theory of Atomic and Molecular Systems*, Progress in Theoretical Chemistry and Physics 20, DOI 10.1007/978-90-481-2985-0 30, Springer Science+Business Media B.V. 2009

Doublet states:
Electronic shell model,

See e.g. Cocchini, Upton, Andreoni, J. Chem. Phys. 1989

Quartet states:
Our model relating the electronic structure to the eigenstates of the harmonic oscillator, cf. single particle states in quantum dots
⇒ **Lecture II on Friday**

Lecture I

- introduction: metal clusters, jellium, shell structure, molecule?
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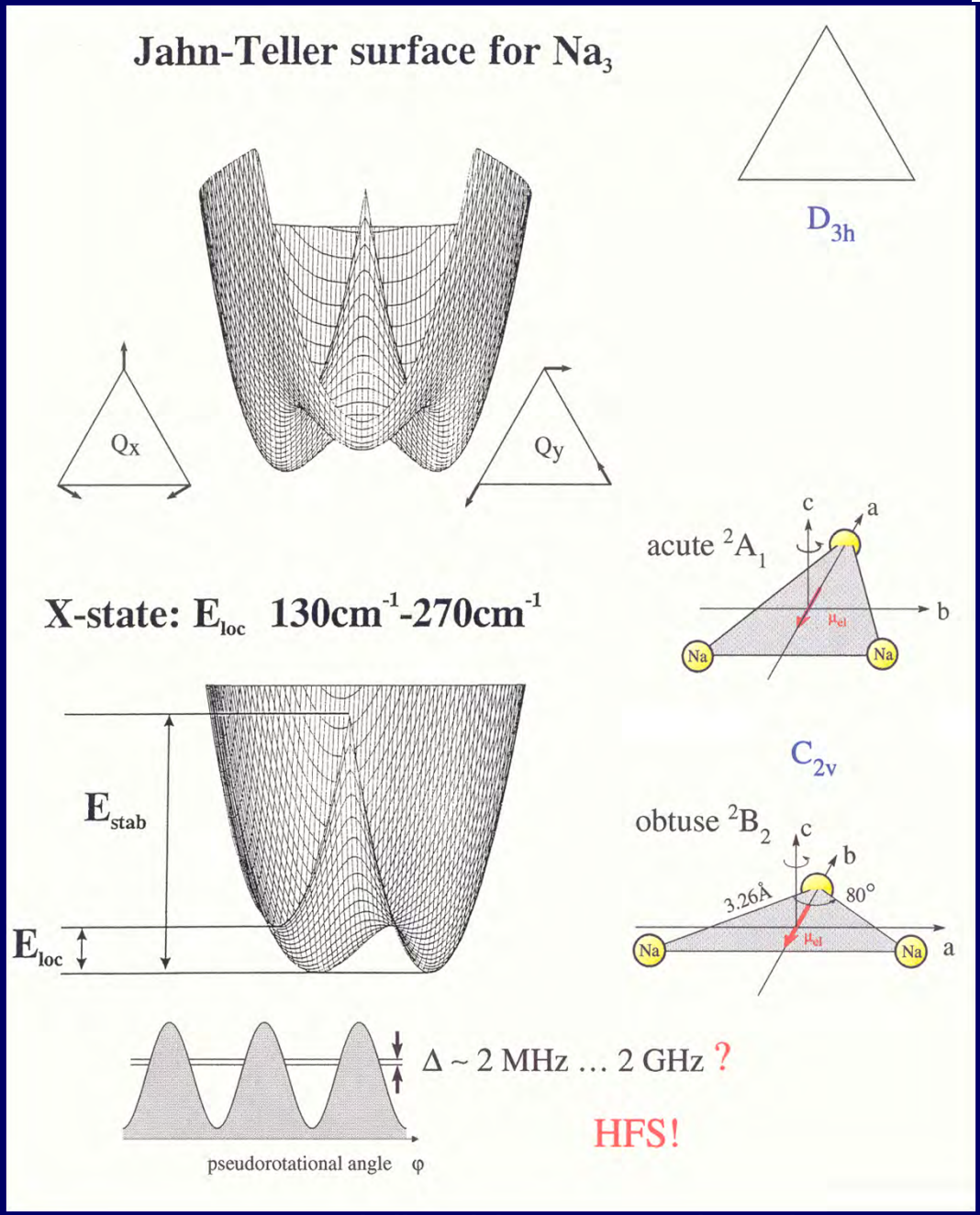
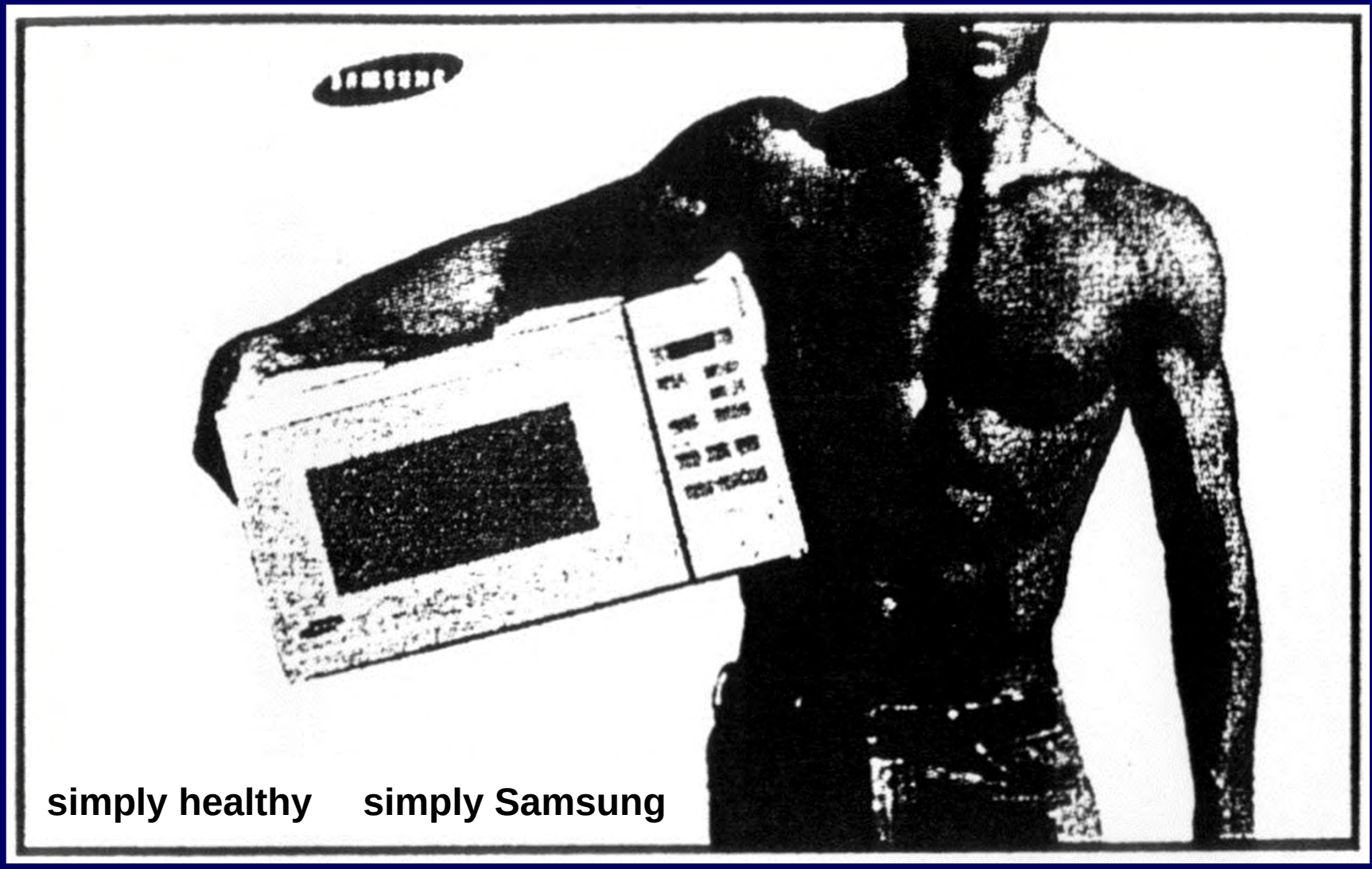
- *ab initio* K_3 and Rb_3 doublet states
- doublet state shell structure
- the ultimate resolution: electron spin density at the 3 nuclei

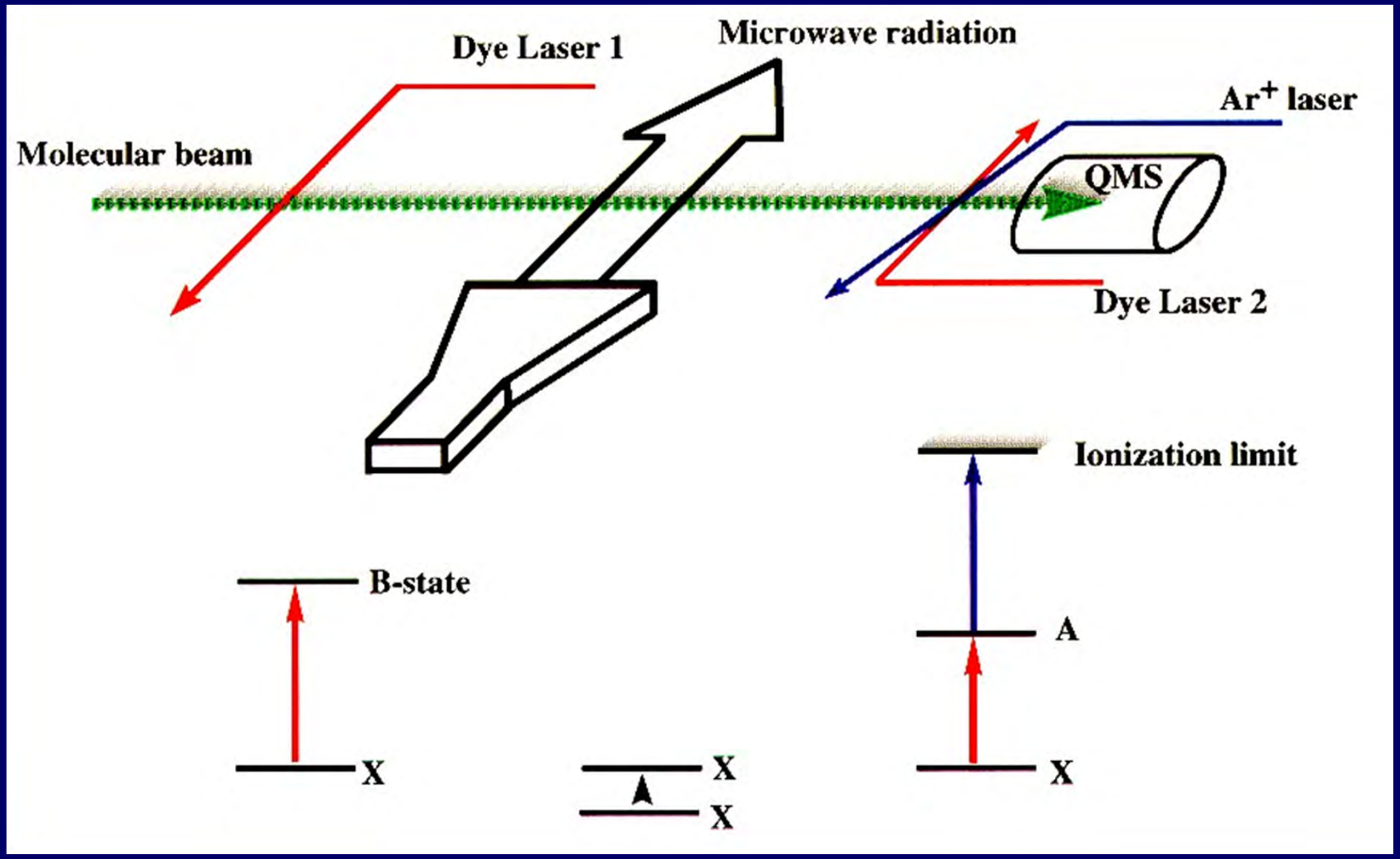
The 2 E‘ ground state





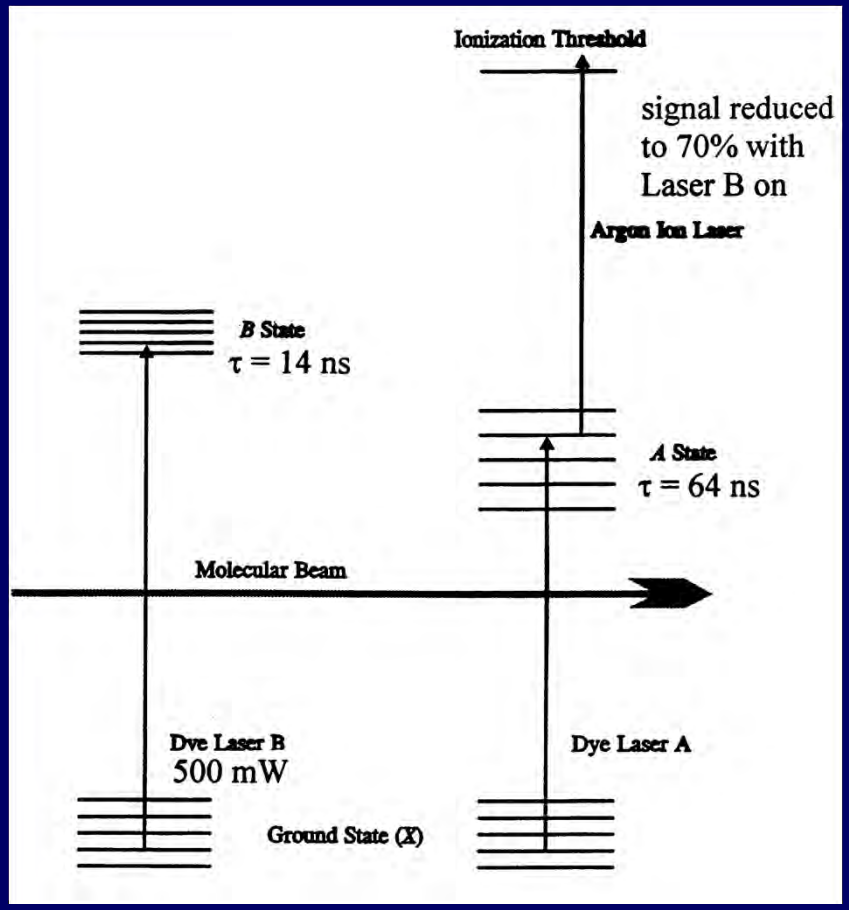
Microwave Man

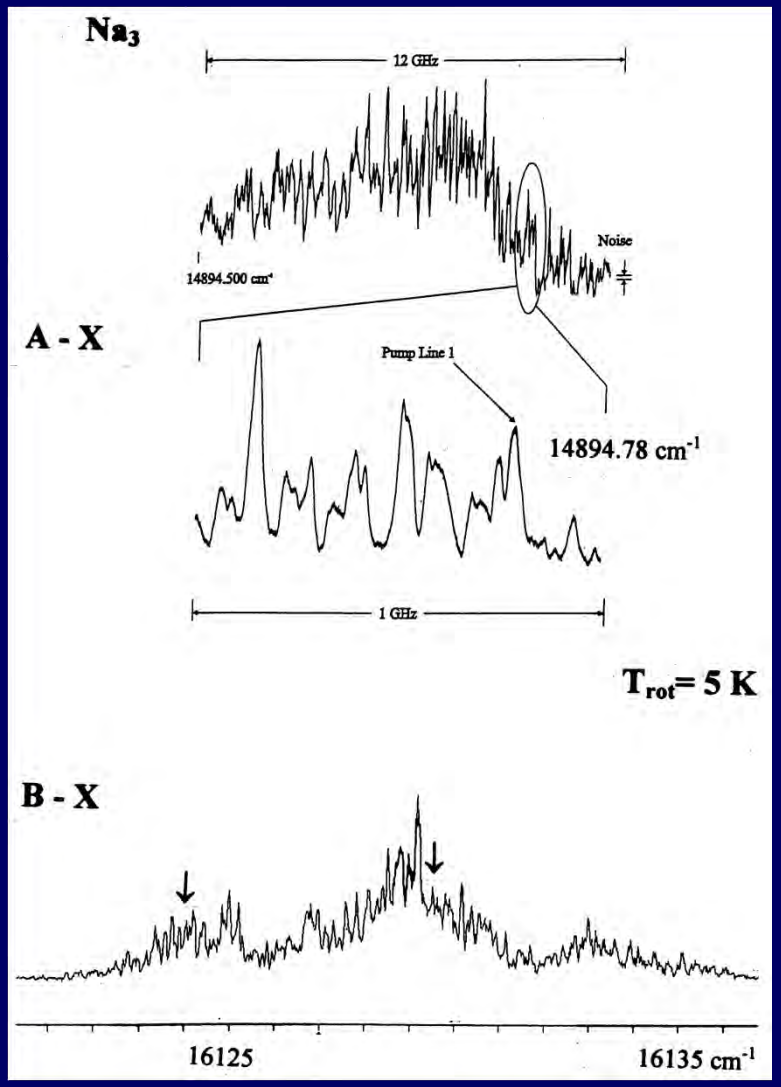
RTPI Detection of Microwave Absorption



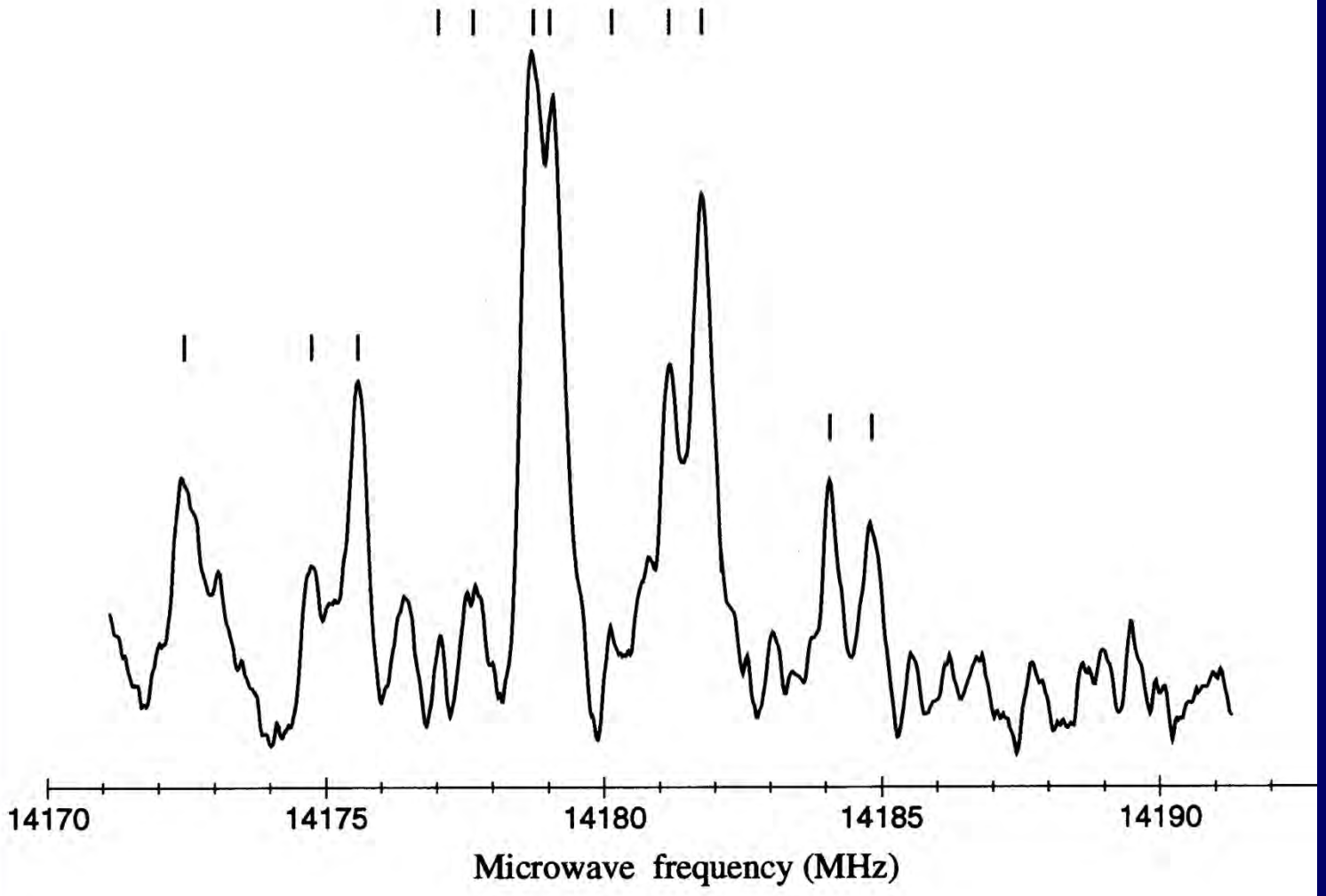
Idea from diatomic dipole measurements: W. E. Ernst, S. Kindt, and T. Törring, Phys. Rev. Lett. 51, 979-981 (1983),
For clusters: W. E. Ernst and J. Kändler, High Resolution Spectroscopy of Molecules and Small Clusters in Molecular Beams, in: Laser Spectroscopy IX, eds. M. S. Feld, J. E. Thomas, and A. Mooradian, 1989, 408-411

Optical Pumping and Probing





Hyperfine Structure of the 404 - 313 Rotational Transition
of the X-State of Na_3
(pumping A-14894.780, B-16123.945)



JOURNAL OF CHEMICAL PHYSICS VOLUME 117, NUMBER 15 p. 7102 - 7116 15 OCTOBER 2002

Hyperfine coupling and pseudorotational motion interaction in Na_3

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W. E. Ernst and O. Golonzka
Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802

(Received 12 February 2002; accepted 30 July 2002)

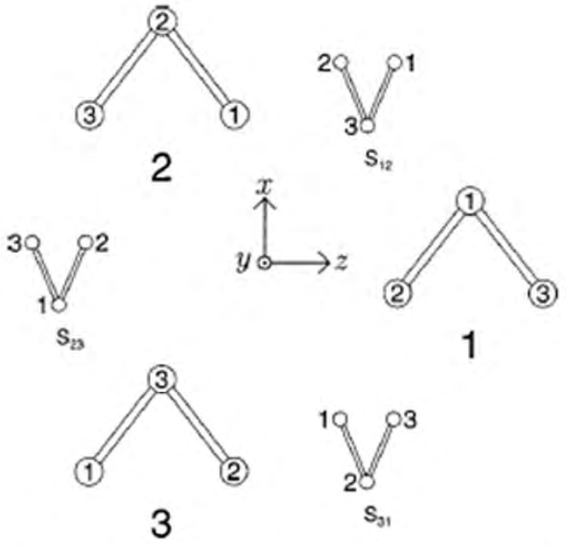


FIG. 4. The three nonsuperimposable configurations of Na_3 as chosen in this work in order to apply the IAM approach (Refs. 19 and 20) used in Sec. III A 2. Configurations 1, 2, and 3 correspond to vibrational wave functions centered at $\chi_p = 0$, $2\pi/3$, and $4\pi/3$, respectively. For these three configurations, atom numbering are indicated by the numbers 1, 2, or 3. All atoms are located in the xz-plane. The intermediate configurations labeled S_{12}, S_{23}, and S_{31} correspond to saddle points of the potential energy surface.

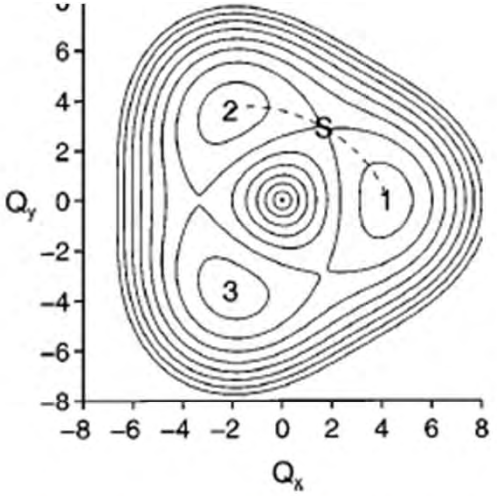
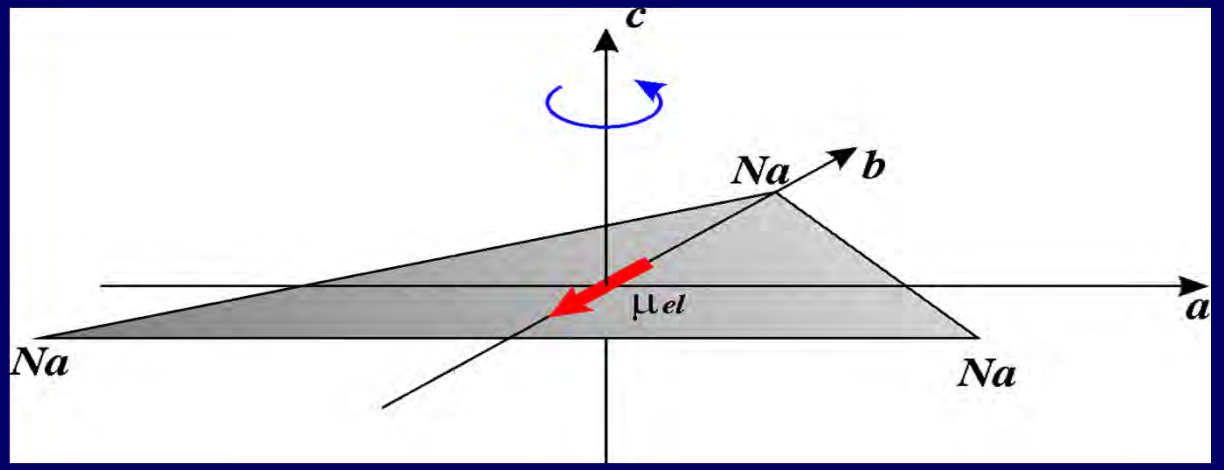


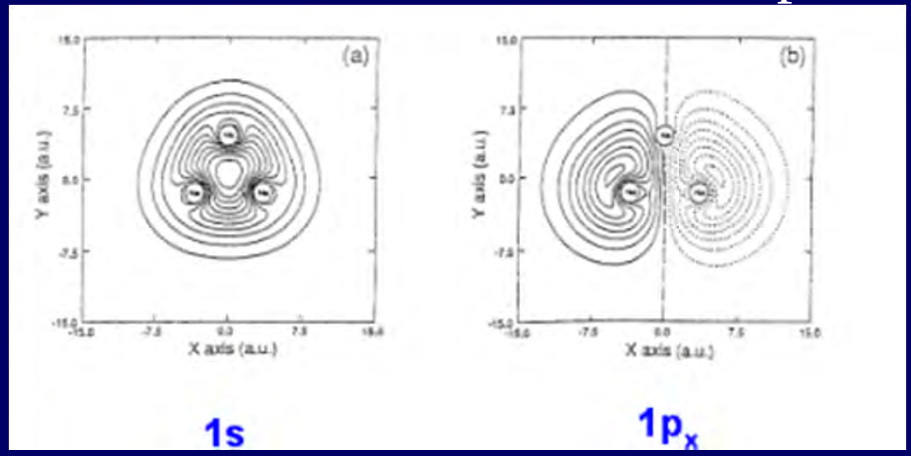
FIG. 5. The shape of the potential energy surface of Na_3 in its lower Jahn-Teller split E-type electronic state, as obtained by Cocchini *et al.* (Ref. 2). The surface is drawn as a function of the dimensionless Q_x and Q_y vibrational coordinates. Three minima numbered 1, 2, and 3, can be seen. The saddle point of interest for the pseudorotational motion is indicated by the letter S and is 130 cm^{-1} above the three minima. The point corresponding to $Q_x = Q_y = 0$ is the conical intersection point located 667 cm^{-1} above the minima. In the surface the dashed line indicates the tunneling path corresponding to the pseudorotational motion.

CONCLUSIONS



❶ Tunneling barrier > 200 cm^{-1} ❷ dipole moment $\mu_{el} \leq$ 0.05 D

❸ Magnetic hyperfine structure << atomic Na 3s hfs, and < 3p hfs



⇨ **delocalized electron orbital**
⇨ **shell model for metal clusters**

Oleg Golonzka
(Penn State U.
MIT
Intel Corp.)

Other Penn State PhD‘s:

Stefan Rakowsky
- pseudorotation

and

David Vituccio
- optical –optical double resonance

Funding from NSF and ACS-PRF

Summary from an intellectual point of view

Very detailed investigation of certain alkali trimer properties like

Painful experimental studies of rotational, fine and even hyperfine structure, in cases that seemed to be clear from more superficial considerations

yield

- an essentially different result for a fundamental question of a geometric phase in a molecular wavefunction

- the confirmation of the metallic character of a metal cluster of as few as 3 atoms

Lecture II (Friday)

alkali trimers on helium nanodroplets: van der Waals bound, high spin states