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SMR.1587 - 5

SCHOOL AND WORKSHOP ON
QUANTUM ENTANGLEMENT, DECOHERENCE,
INFORMATION, AND
GEOMETRICAL PHASES IN COMPLEX SYSTEMS
(1 November - 12 November 2004)

Quantum Dynamics of Geometric Phases in Molecular Systems

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Quantum Dynamics of Geometric Phases in Molecular Systems

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69120 Heidelberg

MAIN PARTS

1. Origin of geometric phases in molecules (QD)
2. Examples and counter-examples
   (H_3, Na_3)

Introduction

Schrödinger equation for coupled electronic and nuclear motions:

$$H = H_{el} + T_N;$$

$$H_{el} = T_e + V(r,Q)$$

$$H_{el}\,\phi_n(r,Q) = V_n(Q)\,\phi_n(r,Q)$$

$$H\,\Psi(r,Q) = E\,\Psi(r,Q)$$

$$\Psi(r,Q) = \sum_n \chi_n(Q)\,\phi_n(r,Q)$$

$$[T_N + V_n(Q) - E]\,\chi_n(Q) = \sum_m \hat{\Lambda}_{nm}\chi_m(Q)$$

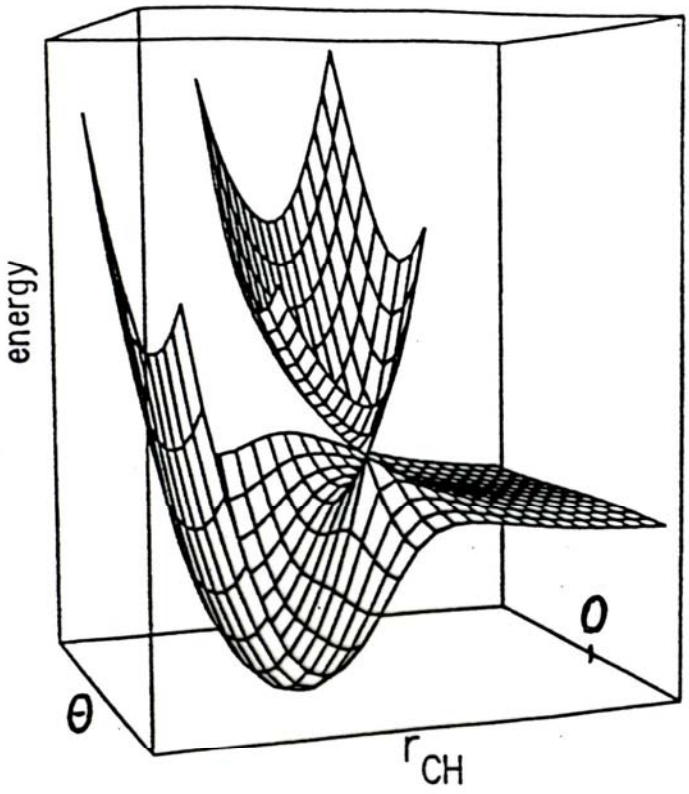
$$\hat{\Lambda}_{nm} = \sum \frac{\hbar^2}{M_i}\int d^{3N}r\,\phi_n^*\left(\frac{\partial\phi_m}{\partial Q_i}\right)\frac{\partial}{\partial Q_i} - \int d^{3N}r\,\phi_n^*\left(T_N\phi_m\right)$$

$$\int d^{3N}r\,\phi_n^*\left(\frac{\partial\phi_m}{\partial Q_i}\right) = \frac{\int d^{3N}r\,\phi_n^*(r,Q)\left(\frac{\partial H_{el}}{\partial Q_i}\right)\phi_m(r,Q)}{V_m(Q) - V_n(Q)} \longrightarrow \infty$$

for

$V_m(Q) \to V_n(Q)$

Divergent nonadiabatic couplings at conical intersections



codimension 2

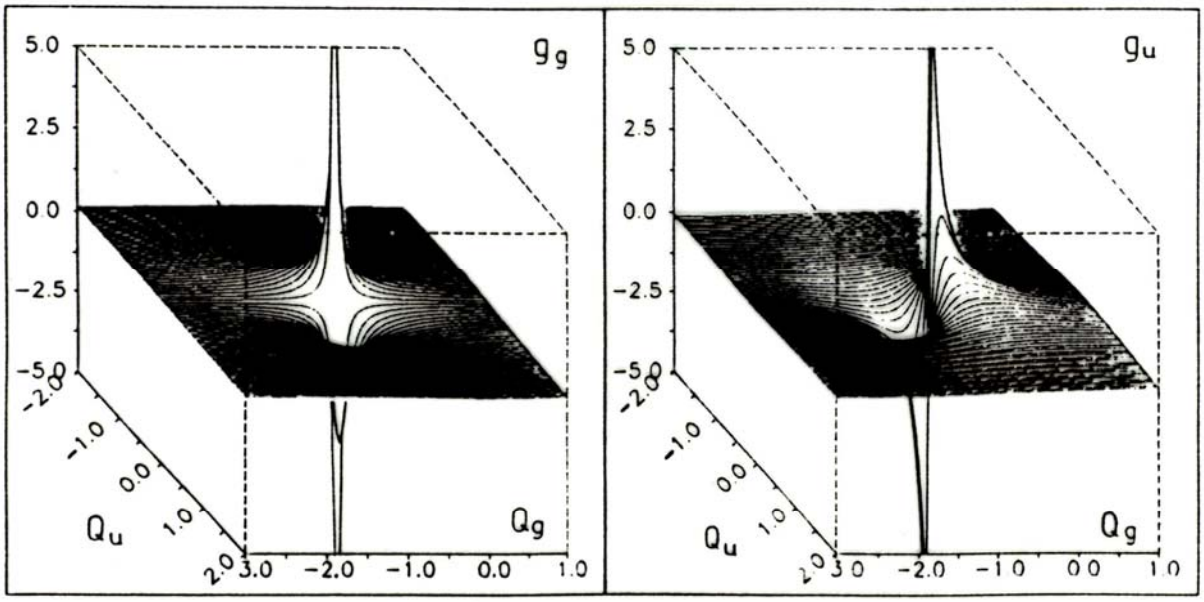
Derivative coupl.

$$\int d^{3N}r\ \phi_n^*\left(\frac{\partial \phi_m}{\partial Q_i}\right) =$$

$$= \frac{\int d^{3N}r\ \phi_n^*\left(\frac{\partial H_{el}}{\partial Q_i}\right)\phi_m}{V_m(Q) - V_n(Q)}$$

$\longrightarrow \infty$

for $V_n(Q) \rightarrow V_m(Q)$



Gives rise to femtosecond internal conversion processes

"funnels"

Sign change (geometric phase) at conical intersections

$$\phi = c_1\varphi_1 + c_2\varphi_2,$$

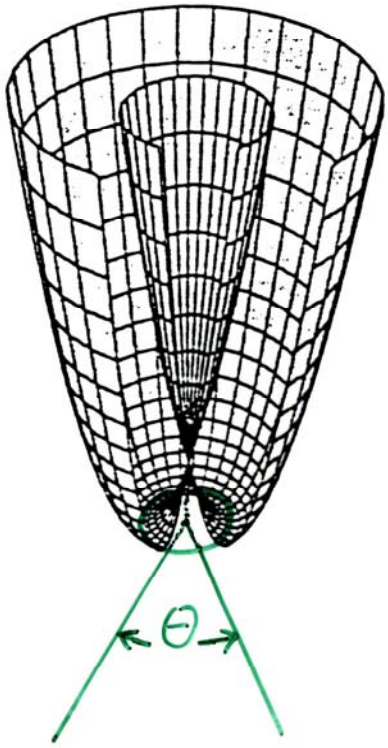
$$\begin{bmatrix} H_{11}-E, & H_{12} \\ H_{21}, & H_{22}-E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0,$$

$$\begin{bmatrix} W+(m+k)x-E, & ly \\ ly, & W+(m-k)x-E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0,$$

$$E = W + mx \pm \sqrt{(k^2x^2 + l^2y^2)},$$

$$kx = \varrho \cos\theta, \; ly = \varrho \sin\theta,$$

$$c_1 = \sin\tfrac{1}{2}\theta, \qquad c_2 = -\cos\tfrac{1}{2}\theta,$$



$\theta \rightarrow \theta + 360^\circ$

$c_1 \rightarrow -c_1$

$c_2 \rightarrow -c_2$

Adiabatic electronic wave function changes sign when encircling the locus of degeneracy in a closed loop (Herzberg & Longuet-Higgins, 1963).

Equivalently: geometric phase (Berry 1984).

Sign change has its counterpart in dynamics, e.g. half-odd integer quantization of vibronic angular momentum. LHOPS '59

Time evolution of wavepackets ?

The Jahn-Teller Theorem

Jahn and Teller (1937)

Molecules in an orbitally degenerate state are unstable w.r.t. an asymmetric distortion unless the degeneracy is accidental or all nuclei lie on a straight line.

Twofold degeneracy:

Tetragonal systems: $(E)^2 = A_1 + B_1 + B_2$

$E \otimes b$ Jahn-Teller Effect

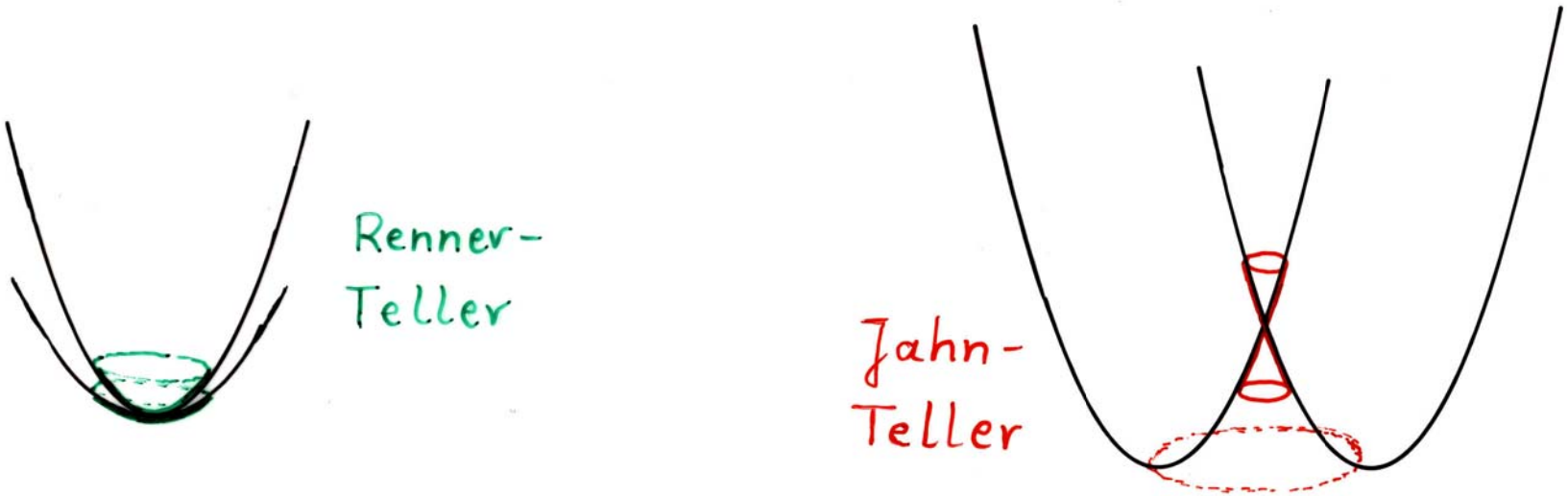
Trigonal systems: $(E)^2 = A_1 + E$

$E \otimes e$ Jahn-Teller Effect

There always exists a suitable nontotally symmetric vibrational mode (couples in 1st order).

Schematic Comparison

Teller ← 1934 → ***Landau***



'Rotational' degree of freedom

Glancing intersection

no GP

Conical intersection

GP exists

The linear E ⊗ e Jahn-Teller Effect

$$\mathscr{H}_{\text{dia}} = \mathscr{H}_0 \mathbf{1} + k \begin{pmatrix} Q_x & Q_y \\ Q_y & -Q_x \end{pmatrix}$$

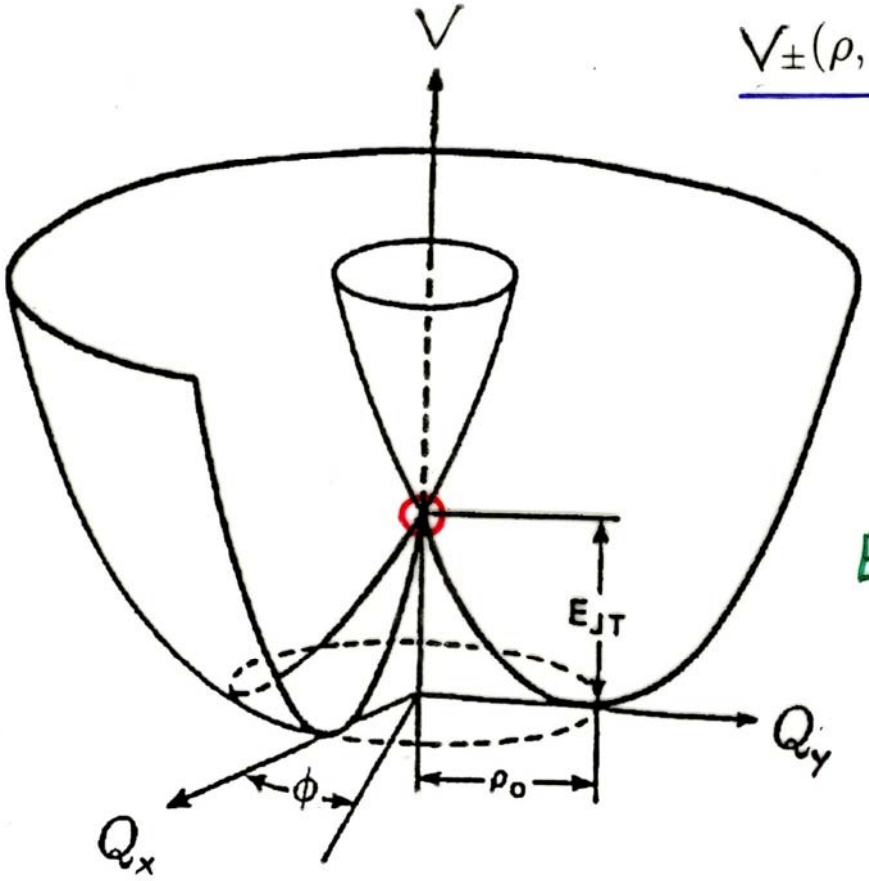
$$\mathscr{H}_0 = \hat{T}_N + W_0 = \hat{T}_N + \frac{\omega}{2}(Q_x^2 + Q_y^2)$$

$\llcorner g^2$

→ ***Adiabatic potential energy surfaces***

"Mexican hat"

$$V_{\pm}(\rho, \phi) = \frac{1}{2}\omega\rho^2 \pm |k|\rho.$$



$$E_{JT} = \frac{k^2}{2\omega} \equiv D\omega$$

$$g_0 = \frac{|k|}{\omega}$$

Nonadiabaticity above c.i.

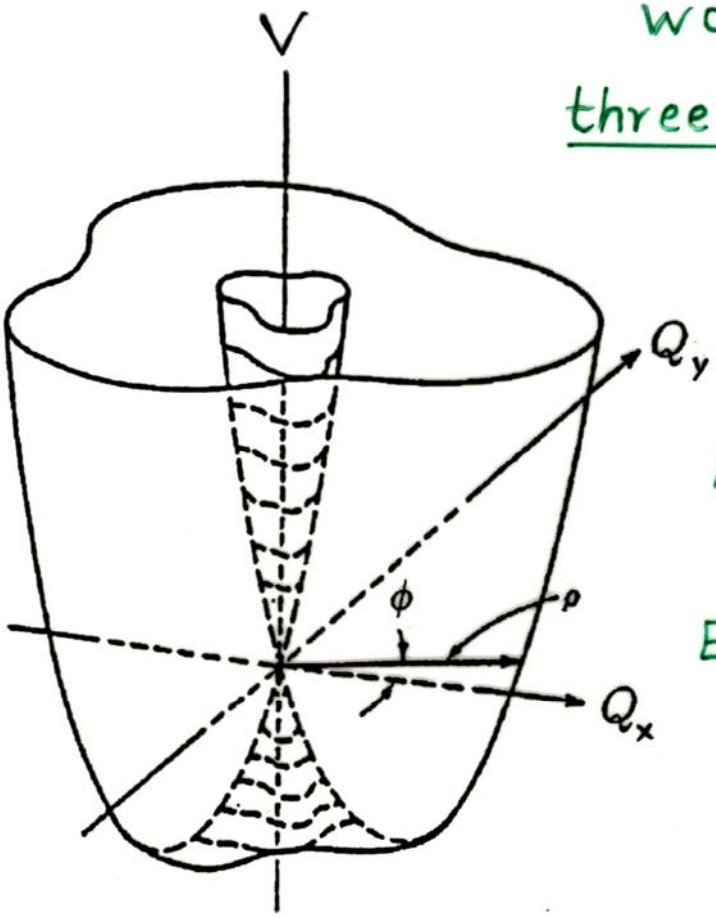
⇒ distinguish $D > 1$ and $D \lesssim 1$

The quadratic E ⊗ e Jahn-Teller Effect

$$\mathscr{H}_{\text{dia}} = \mathscr{H}_0 1 + k \begin{pmatrix} Q_x & Q_y \\ Q_y & -Q_x \end{pmatrix} - \frac{g}{2} \begin{pmatrix} Q_y^2 - Q_x^2 & 2Q_xQ_y \\ 2Q_xQ_y & -(Q_y^2 - Q_x^2) \end{pmatrix}$$

$$\mathscr{H}_0 = \hat{T}_N + W_0 = \hat{T}_N + \frac{\omega}{2}(Q_x^2 + Q_y^2)$$

→ ***Adiabatic potential energy surfaces***



"warping"

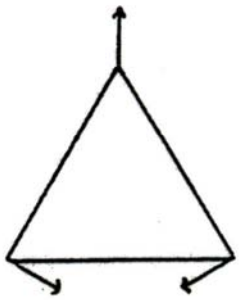
threefold symmetry

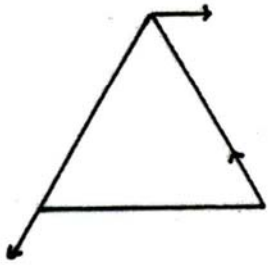
$$E_{JT} = \frac{k^2}{2(\omega - |g|)}$$

$$E_{barr} = \frac{2|g| E_{JT}}{(\omega + |g|)}$$

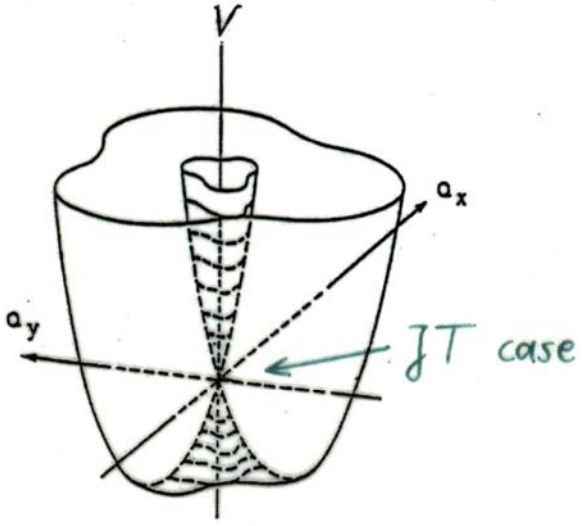
Lifting of (artificial) degeneracies of vib. levels

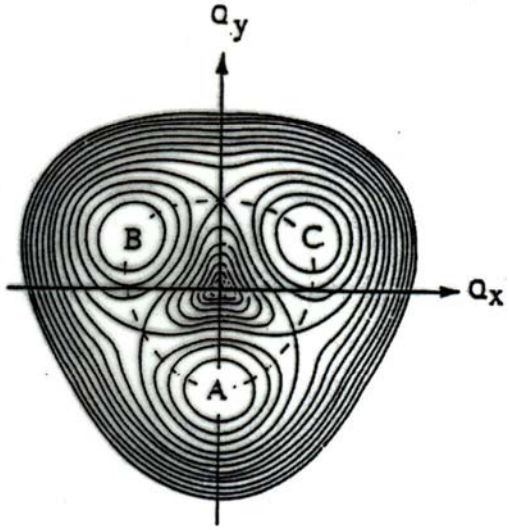
Coordinates and JT surfaces for X_3 molecules

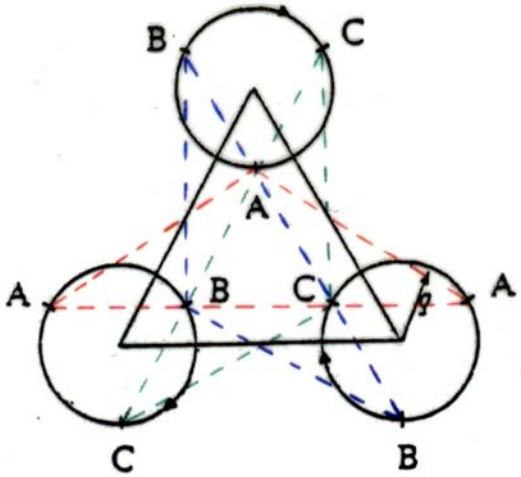




$C_{2v} \leftarrow Q_y$ $\qquad$ $Q_x \rightarrow C_s$







Quantum dynamics of geometric phases

Remember:

In molecular systems the 'slow' variables are not external parameters, but are themselves to be quantized $\Rightarrow$ observable effects

Free pseudorotation: half-odd integer quantum numbers

Warped p.e.s.: inverted tunneling splitting (energy levels; 1D picture)

Wave-functions:

Sign change leads to *destructive interference* of portions of the wave-packet encircling the conical intersection on *opposite sides;*
Anomalous symmetry — Kendrik et al (1995), Schön & Köppel (1995)

2D picture (radial + pseudorotational motion; more realistic):
Different *global shape* of the wave-function!
Schön & Köppel (1994, 1995)
– " – (1998, with s.o. coupling)

Geometric phase effects for lower Mexican hat surface (cylindrical symmetry; g=0)

H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, R. A. Sack, Proc. Roy. Soc. A (London) ***244*** *(1958) 1*

Sign change $\phi(2\pi) = -\phi(0) \Rightarrow \chi(2\pi) = -\chi(0)$
(total wave function $\Psi = \phi\,\chi$ must be single-valued)

⇒ half-odd integer vibrational angular momentum !

$$E_{pl} = (p - \tfrac{1}{2}) - \tfrac{1}{2}k^2 + \frac{l^2}{2k^2}. \qquad (\omega = 1) \qquad (6{\cdot}16)$$

TABLE 6. SELECTED LOW-ENERGY EIGENVALUES, COMPARED WITH APPROXIMATE VALUES FROM EQUATION (6·16)

$k^2 = 10$

	$l = \frac{1}{2}$	$l = \frac{3}{2}$
	−4·485	−4·370
	−3·477	−3·320
	−2·461	−2·242
	−1·425	−1·127
(6·16)	$-N$·487	$-N$·387
	−N.5 (ℓ=0)	

$k^2 = 20$

	$l = \frac{1}{2}$	$l = \frac{3}{2}$	$l = \frac{5}{2}$
	−9·493	−9·439	−9·334
	−8·492	−8·429	−8·306
	−7·490	−7·414	−7·270
	−6·488	−6·395	−6·224
	−5·484	−5·368	−5·165
(6·16)	$-N$·494	$-N$·444	$-N$·344
	−N.5 (ℓ=0)		

$k^2 = 30$

	$l = \frac{1}{2}$	$l = \frac{3}{2}$	$l = \frac{5}{2}$	$l = \frac{7}{2}$
	−14·496	−14·460	−14·391	−14·288
	−13·495	−13·456	−13·379	−13·266
	−12·494	−12·451	−12·365	−12·239
	−11·494	−11·444	−11·348	−11·208
	−10·493	−10·436	−10·327	−10·171
(6·16)	$-N$·496	$-N$·462	$-N$·396	$-N$·296
	−N.5 (ℓ=0)			

⇒ Eigenvalues with inclusion of GP effects fit coupled-surface results better than without GP !

Berry's Geometrical Phase and the Sequence of States in the Jahn-Teller Effect

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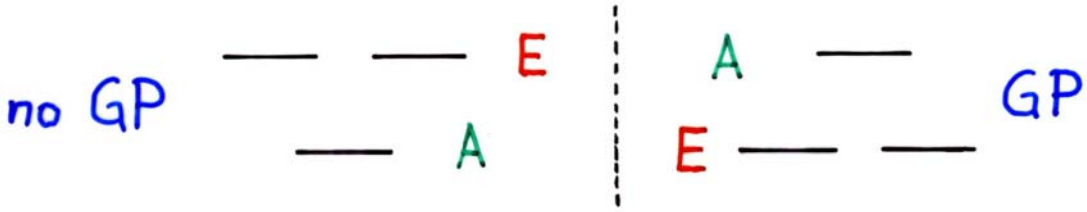
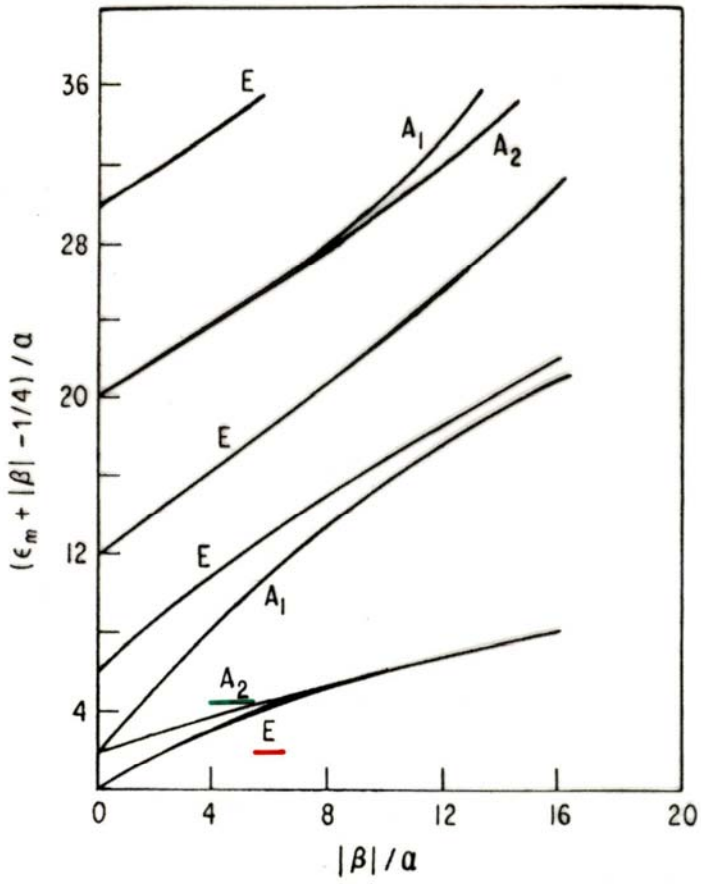
(Received 14 October 1986)

A proof is given for the Jahn-Teller problem of an orbital doublet ($E \otimes \varepsilon$) that the order of the lowest vibronic levels is fixed by the requirement that the vibrational part of the wave function change sign under 2π rotation in the vibrational coordinates. This sign change in turn is a consequence of the sign change in the electronic part of the wave function, a special case of Berry's geometrical phase. Experimental confirmation of this sign change and thus of Berry's phase is available from studies of Jahn-Teller defects in crystals that reveal the sequence of these lowest levels.

PACS numbers: 71.55.−i, 03.65.Bz, 33.10.Lb, 76.30.Fc





M. O'Brien, Proc. Roy. Soc. A 281 (1964) 323

Experimental verification: impurities in solids (paramagnetic ions: EPR spectra, phonon spectra) (e.g. Cu^{2+} : MgO).

Adiabatic approximation

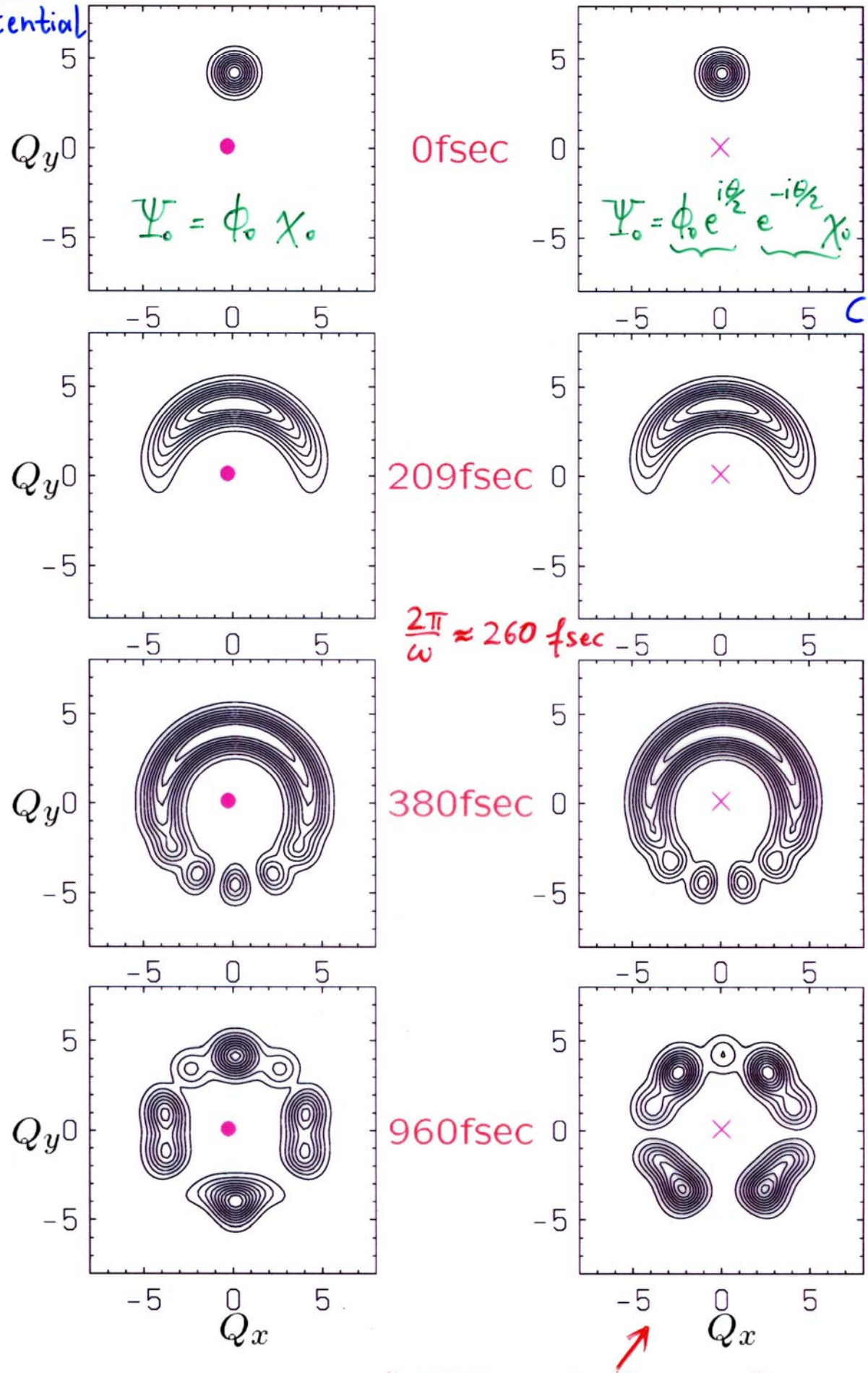
No vector-potential

PJT-case

JT-case

Vector-potential

$\frac{\partial}{\partial\theta} + \frac{i}{2}$



$\Psi_0 = \phi_0\,\chi_0$

$\Psi_0 = \phi_0\, e^{i\theta/2}\, e^{-i\theta/2}\,\chi_0$

⇑

Convenient for grid methods

$\frac{2\pi}{\omega} \approx 260$ fsec

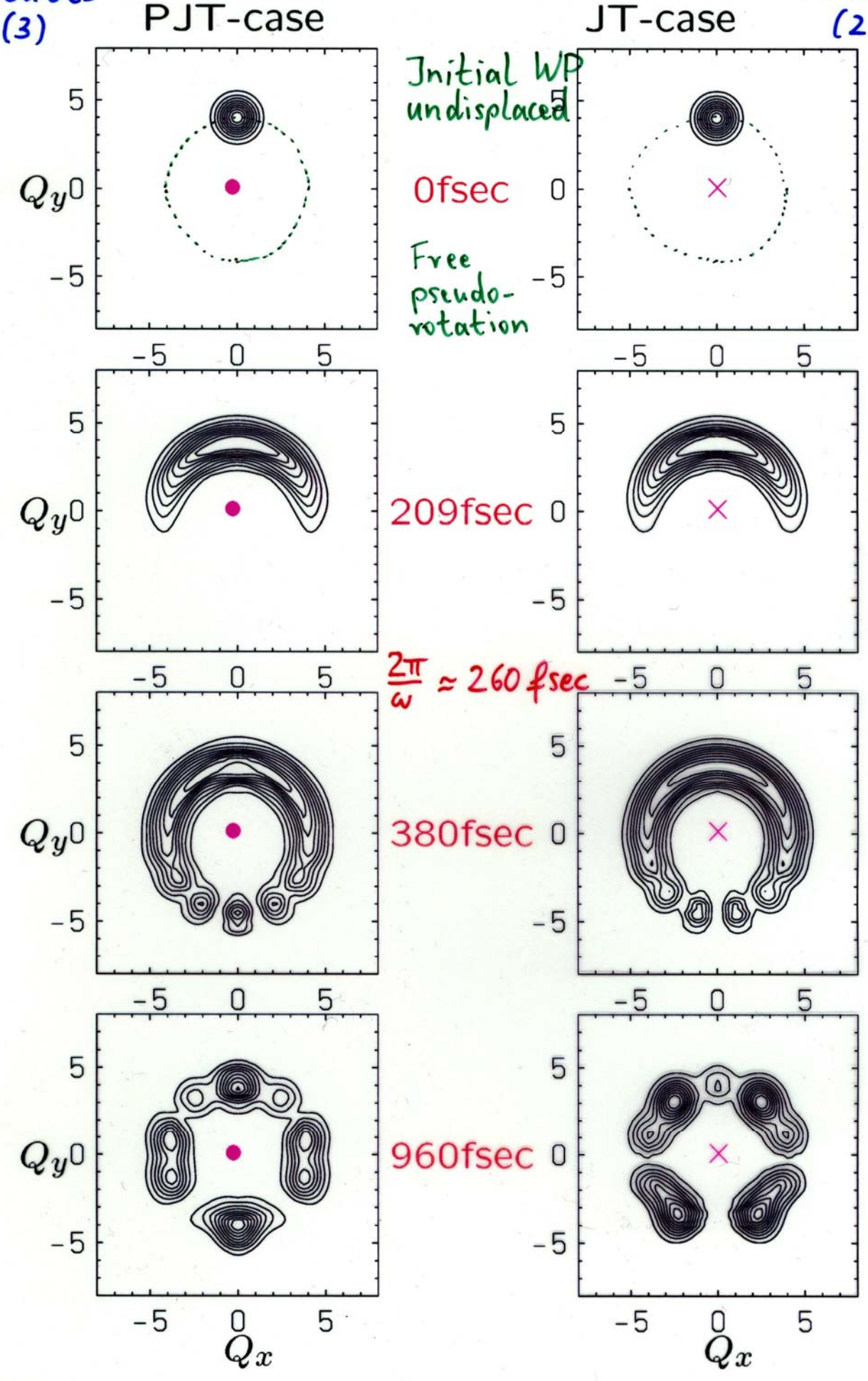
"Self-interference"

■

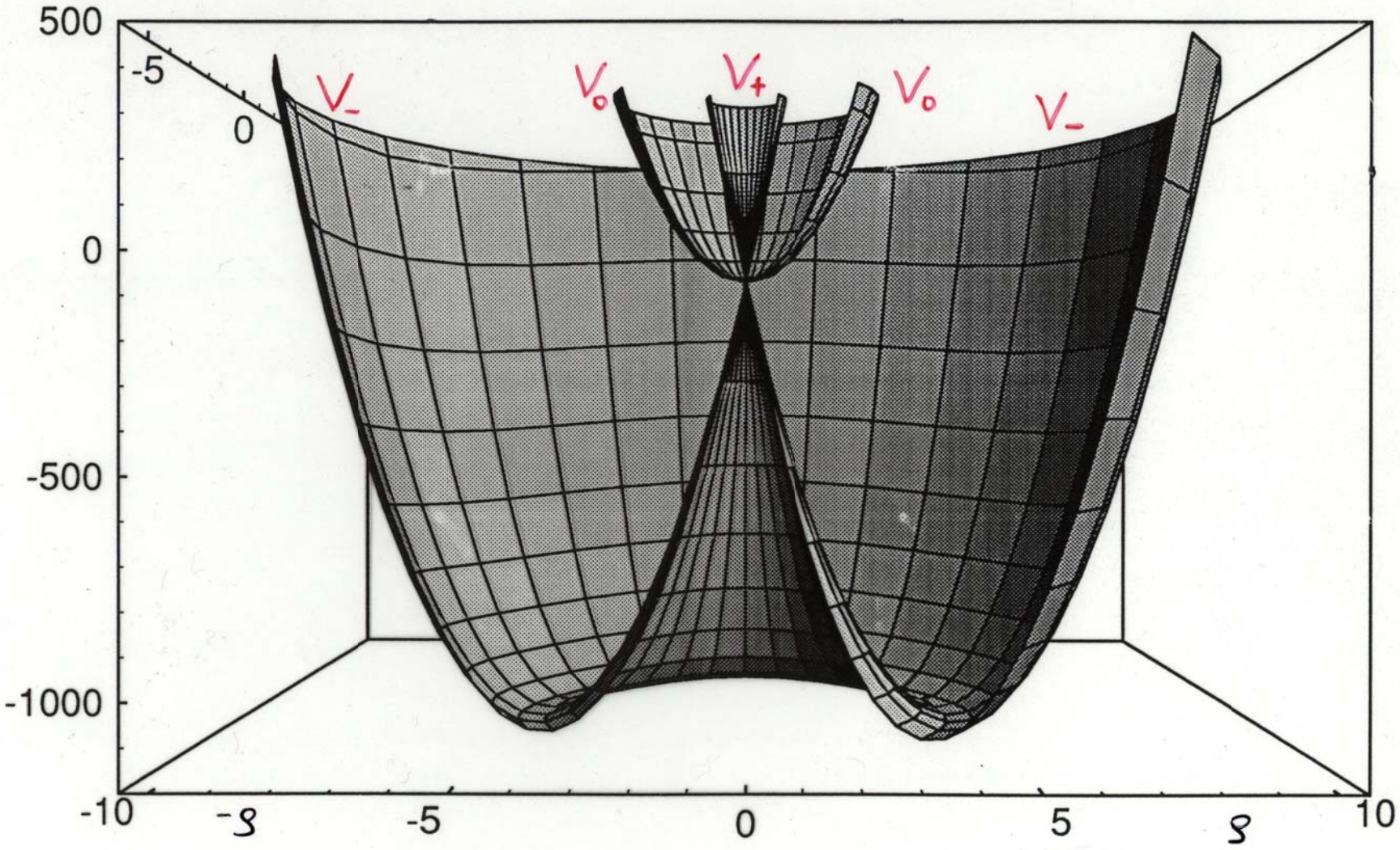
coupled states (3)

Diabatic calculation

coupled states (2)



TRIPLE INTERSECTION



(no GP)

$$V_{\pm}(\rho) = \frac{\omega}{2}\rho^2 \pm \sqrt{2}\,\lambda\,\rho$$

Identical to JT-surfaces ($\sqrt{2}\,\lambda \triangleq k$)

Linear (A + E) × e Pseudo-Jahn-Teller Effect

$$V^{PJT} = \begin{pmatrix} 0 & 0 & \lambda\rho\cos\theta \\ 0 & 0 & \lambda\rho\sin\theta \\ \lambda\rho\cos\theta & \lambda\rho\sin\theta & \Delta \end{pmatrix}$$

Δ: E − A energy gap

$$|-\rangle = \frac{1}{\sqrt{2}}\left(w_+ \cos\theta\ |1\rangle + w_+ \sin\theta\ |2\rangle - w_-\ |A\rangle \right) e^{is\theta}$$

$$w_\pm = \sqrt{1 \pm \frac{1}{\sqrt{1 + 8(\lambda\rho/\Delta)^2}}}$$

Real and single-valued.

$$\langle - | \nabla_R | - \rangle = i\, s\, (\nabla_R \theta)$$

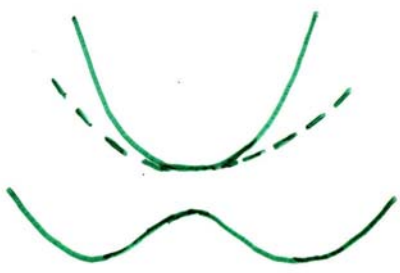
$$\boxed{\gamma_\pm(C) = -2\pi s = 0 \quad (s = 0)}$$

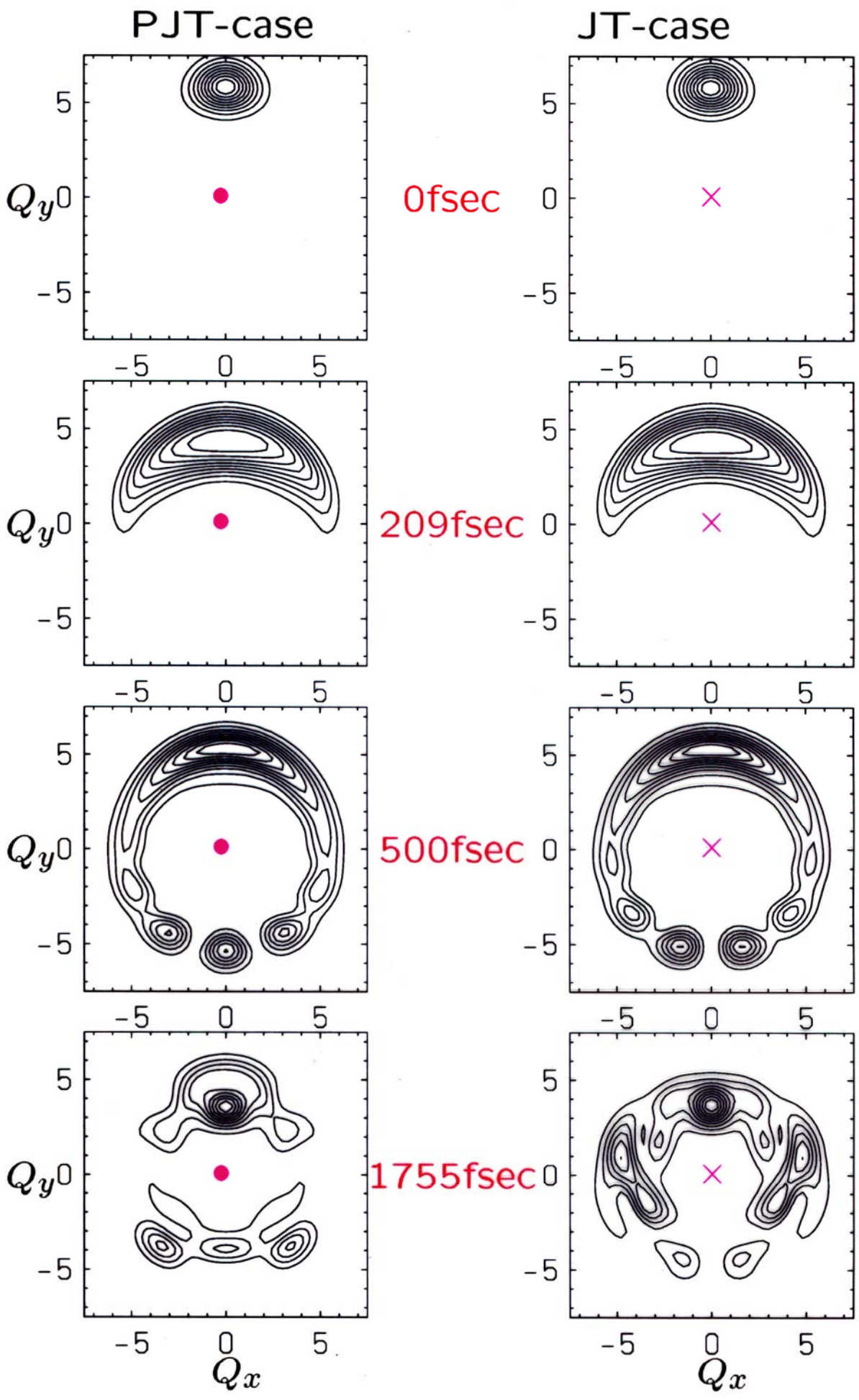
Meiswinkel & Köppel ('90)

Result independent of Δ !

$\Delta \neq 0$: glancing intersection.

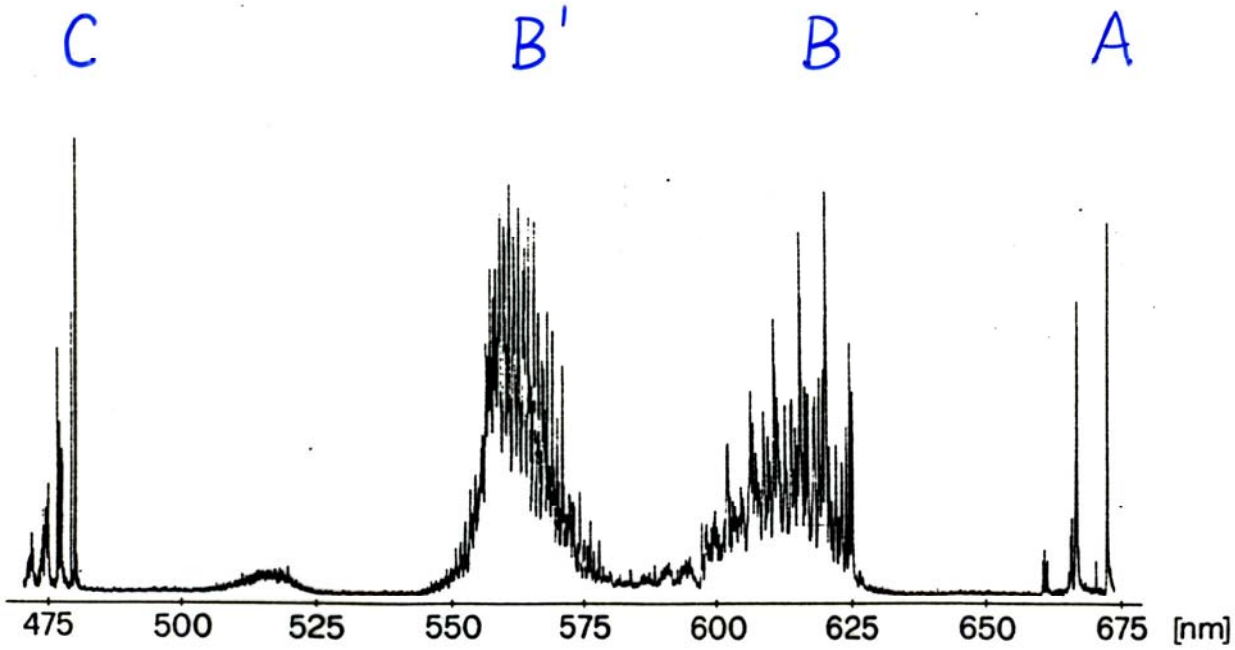
$\Delta = 0$: triple intersection.





J. Schön and H. Köppel, J. Chem. Phys. 103 ('95) 9292

The B system in the TPI spectrum of Na_3



VOLUME 56, NUMBER 24 PHYSICAL REVIEW LETTERS 16 JUNE 1986

Fractional Quantization of Molecular Pseudorotation in Na_3

Guy Delacrétaz,[1] Edward R. Grant,[2] Robert L. Whetten,[3] Ludger Wöste,[1] and Josef W. Zwanziger[2]

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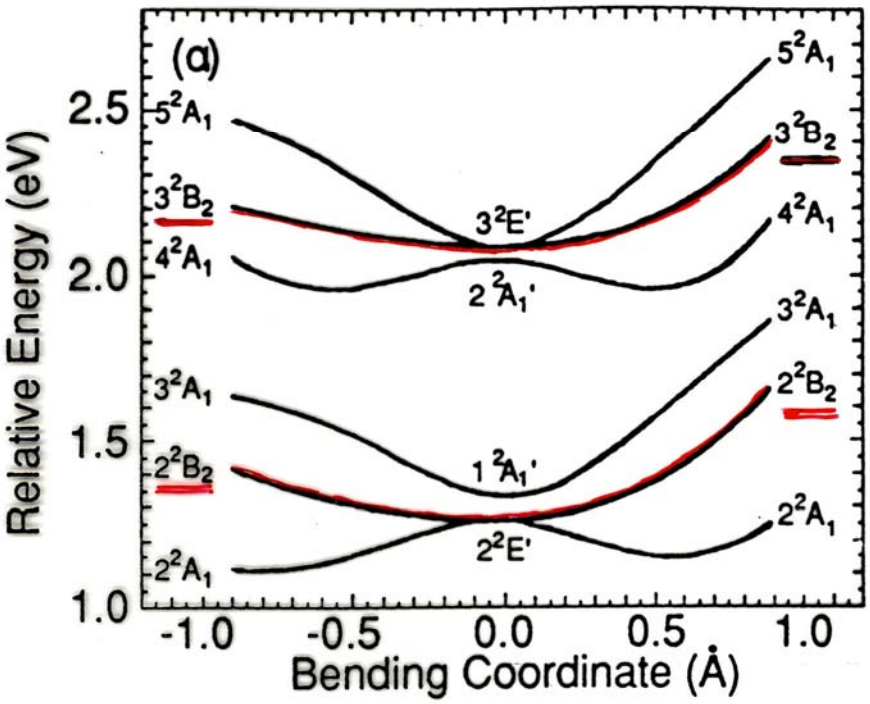
[2] *Department of Chemistry, Cornell University, Ithaca, New York 14853*
[3] *Department of Chemistry and Biochemistry, and Solid State Science Center, University of California, Los Angeles, Los Angeles, California 90024*

(Received 17 March 1986)

Fractional quantization of the adiabatic pseudorotation in an isolated molecule is reported. This result, concerning the large-amplitude pseudorotation in $2^2E'$ Na_3, constitutes the first direct verification of the adiabatic sign-change theorem, and also presents the most complete picture of the level structure and internuclear dynamics of a metal-atom cluster yet given.

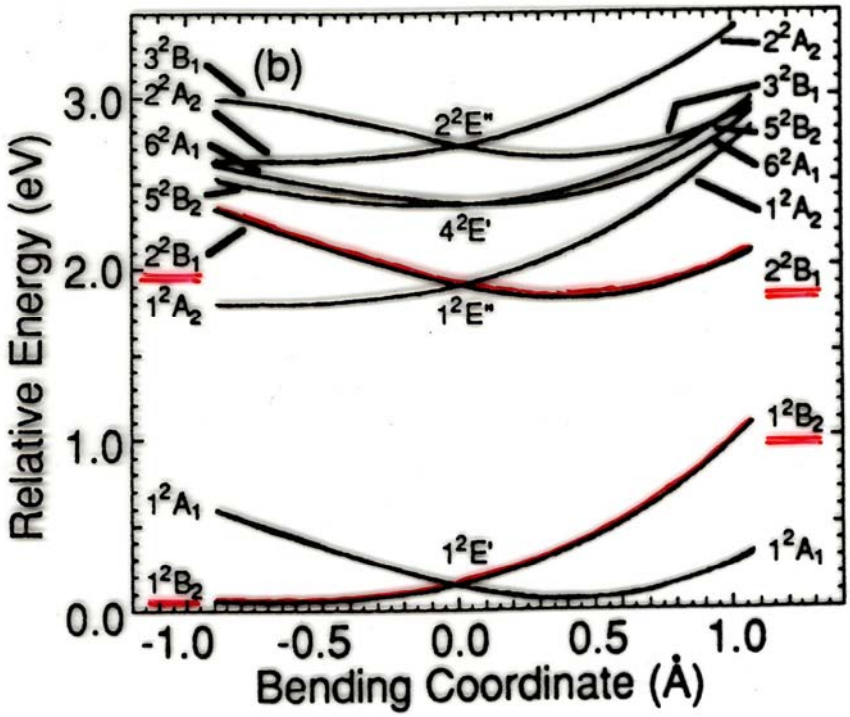
Later work (ab initio & analysis of spectrum): integer quantization

B

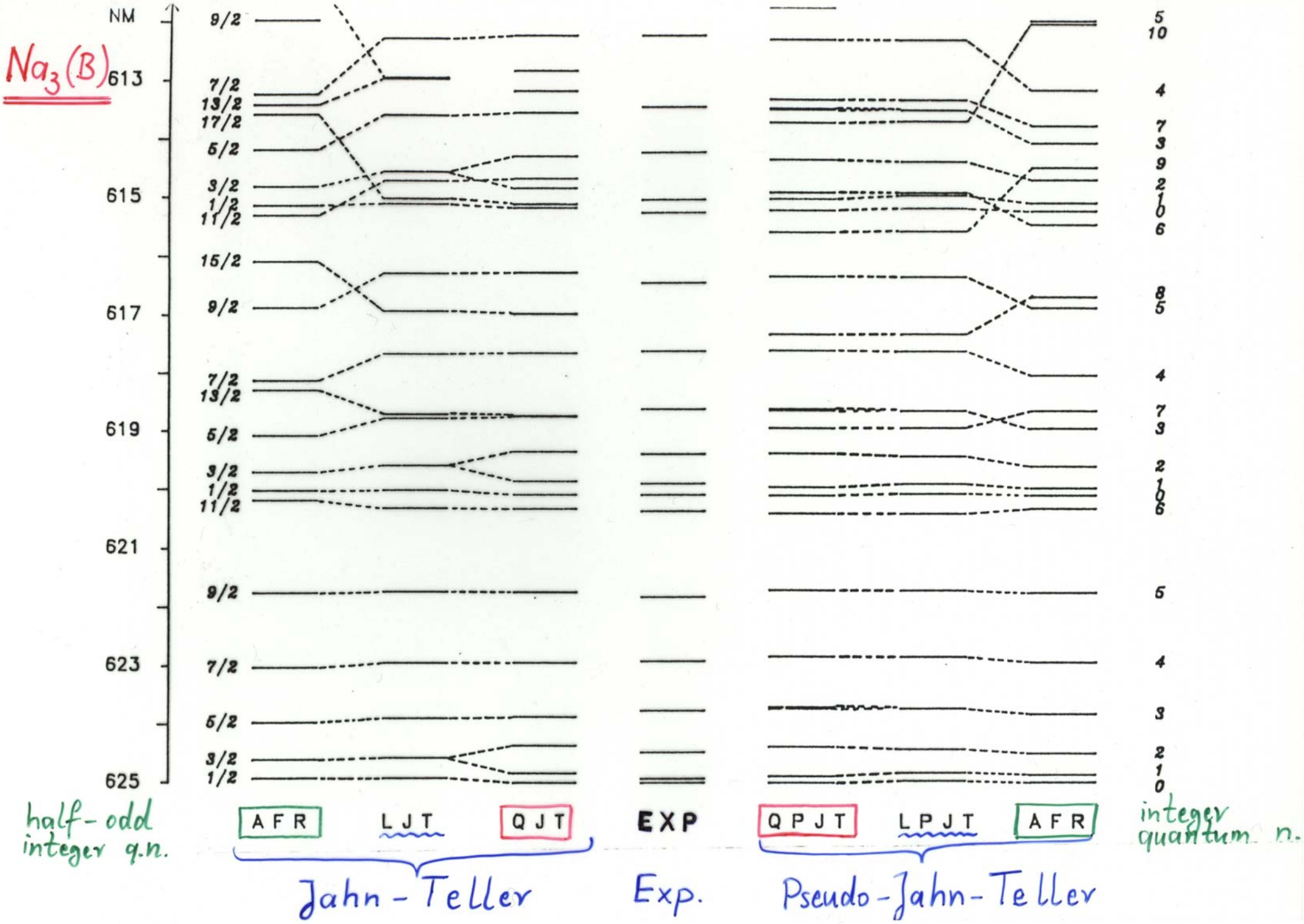


PJT - Verhalten

1988: Cocchini, Upton, and Andreoni: Sodium trimer, J. C. P. 88, 6068

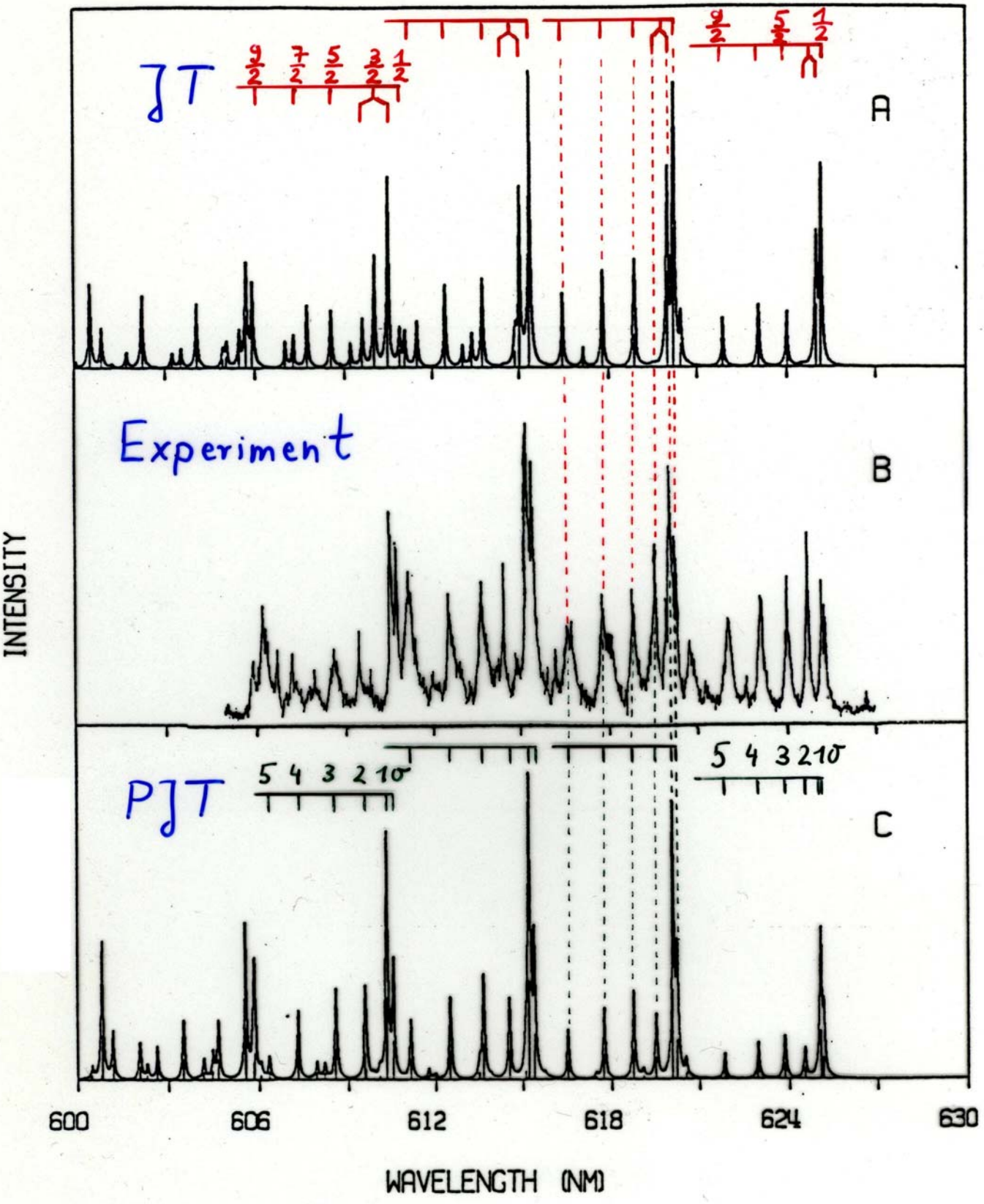


JT - Verhalten

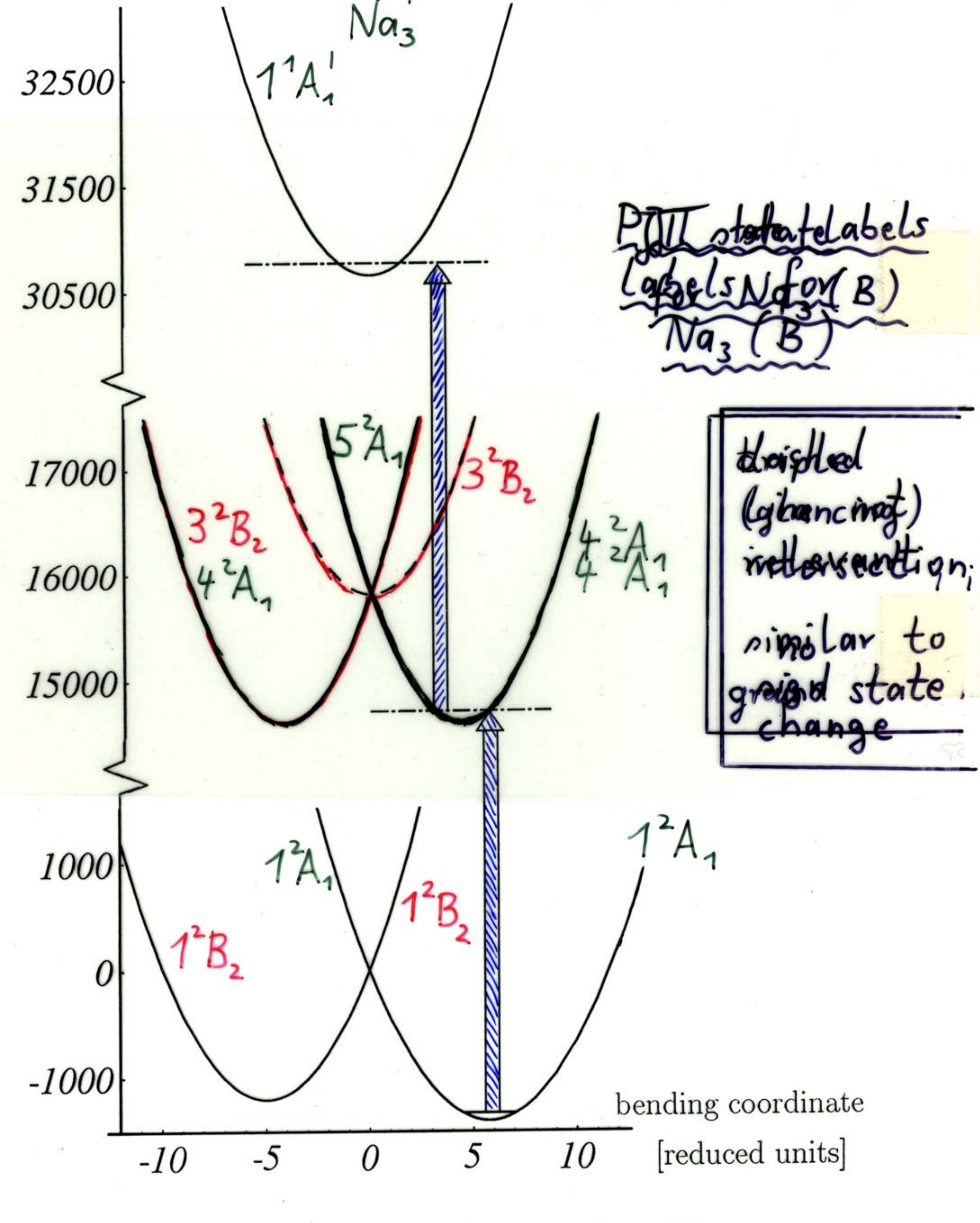

$Na_3(B)$
NM
613
615
617
619
621
623
625
9/2
7/2
13/2
17/2
5/2
3/2
1/2
11/2
15/2
9/2
7/2
13/2
5/2
3/2
1/2
11/2
9/2
7/2
5/2
3/2
1/2
5
10
4
7
3
9
2
1
0
6
8
5
4
7
3
2
1
0
6
5
4
3
2
1
0
half-odd integer q.n.
A F R
L J T
Q J T
EXP
Q P J T
L P J T
A F R
integer quantum n.
Jahn-Teller
Exp.
Pseudo-Jahn-Teller

R. Meiswinkel und H. Köppel, Chem. Phys. 144, 117 (1990)

— " — , Z. Phys. D 19, 63 (1991)

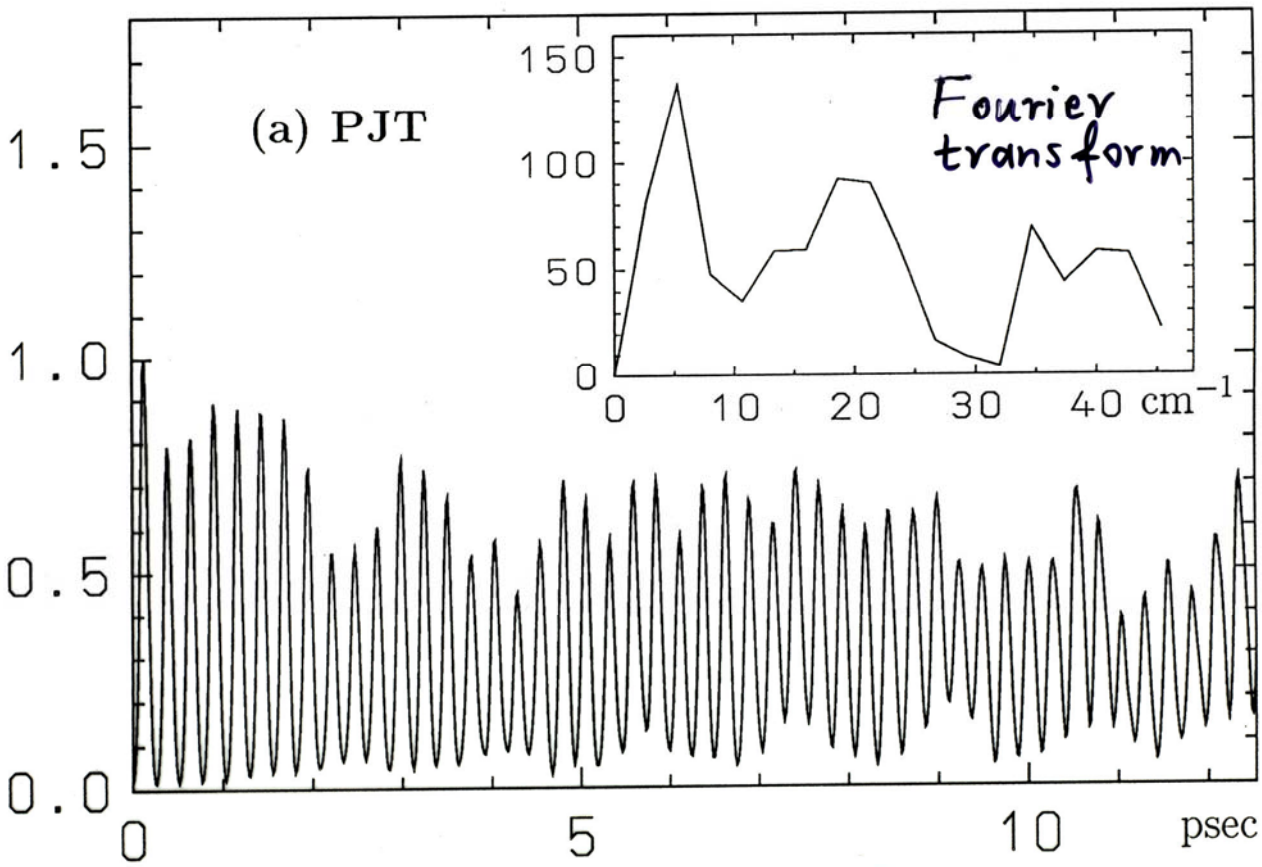


Na_3 / Na_3^+ potential curves and pump-probe pulses

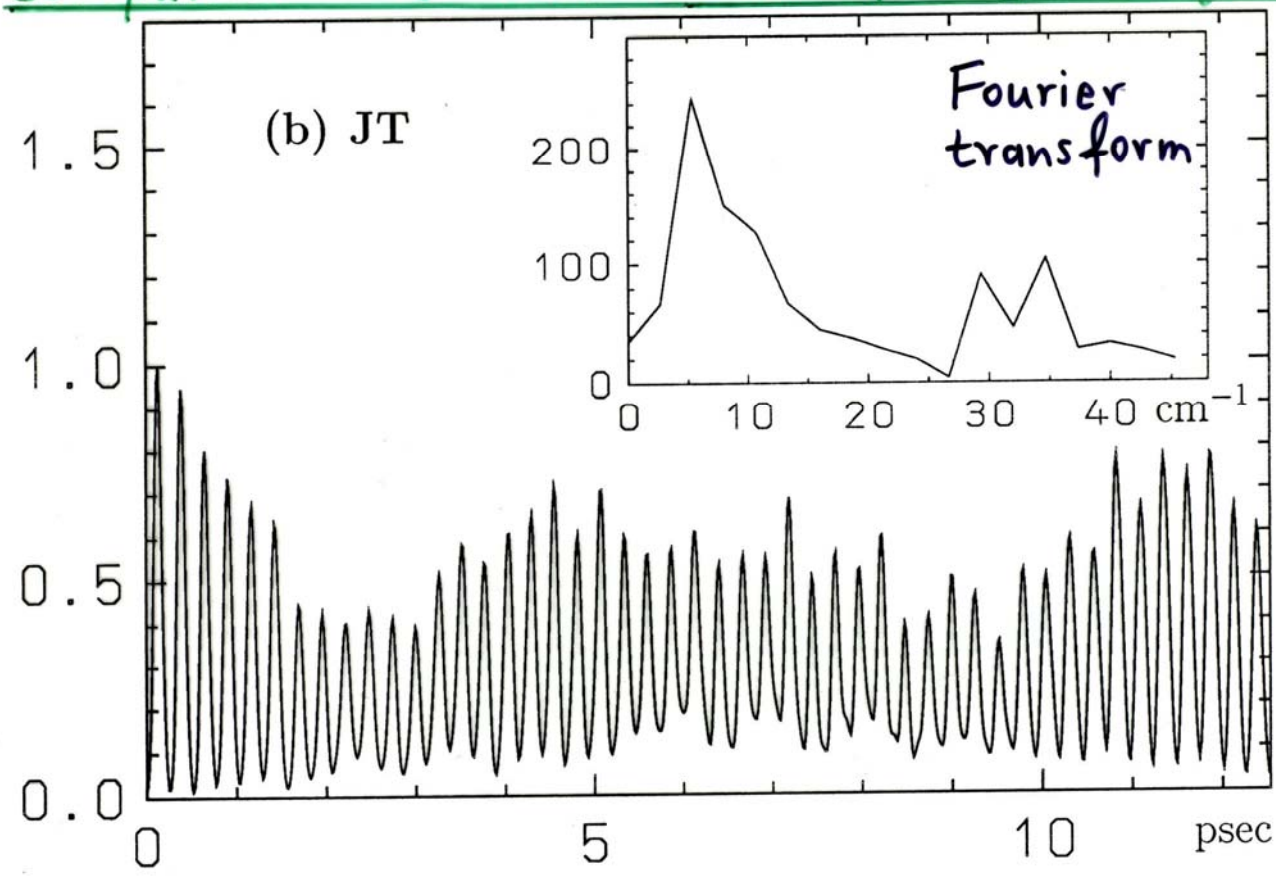


Experiment : $\Delta t = 60$ fs ; $\lambda = 623$ nm

J. Schön and H. Köppel, Chem. Phys. Lett. 231 ('94) 55



Comparison 2D calculation of Na_3 PP-signal



Experimental FT peaks at 9, 19 and 33 cm^{-1} (pseudorotation) & higher frequencies (vibrations)

Superposition of reactive and nonreactive scattering amplitudes in the presence of a conical intersection

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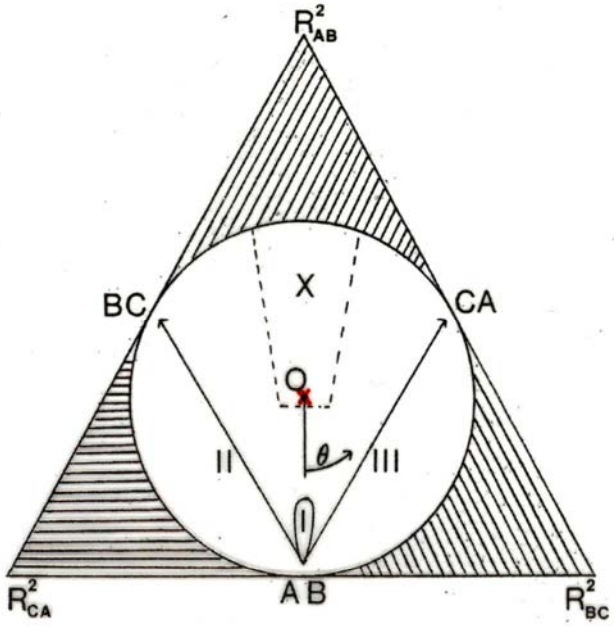
(Received 29 November 1979; accepted 14 January 1980)

J. Chem. Phys. 72 ('80) 3839

$$AB(v,j) + C \longrightarrow AC(v',j') + B$$



"Destructive interference upon encircling the intersection" (A = B)

The geometric phase effect shows up in chemical reactions

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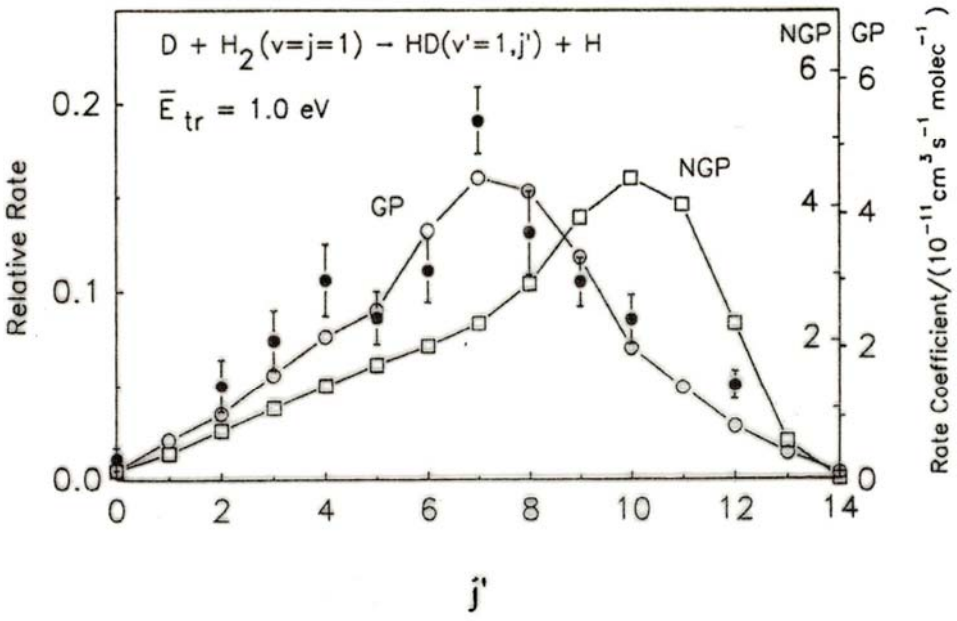
Received 18 February 1993; in final form 1 March 1993 Chem. Phys. Lett. 205('93) 577

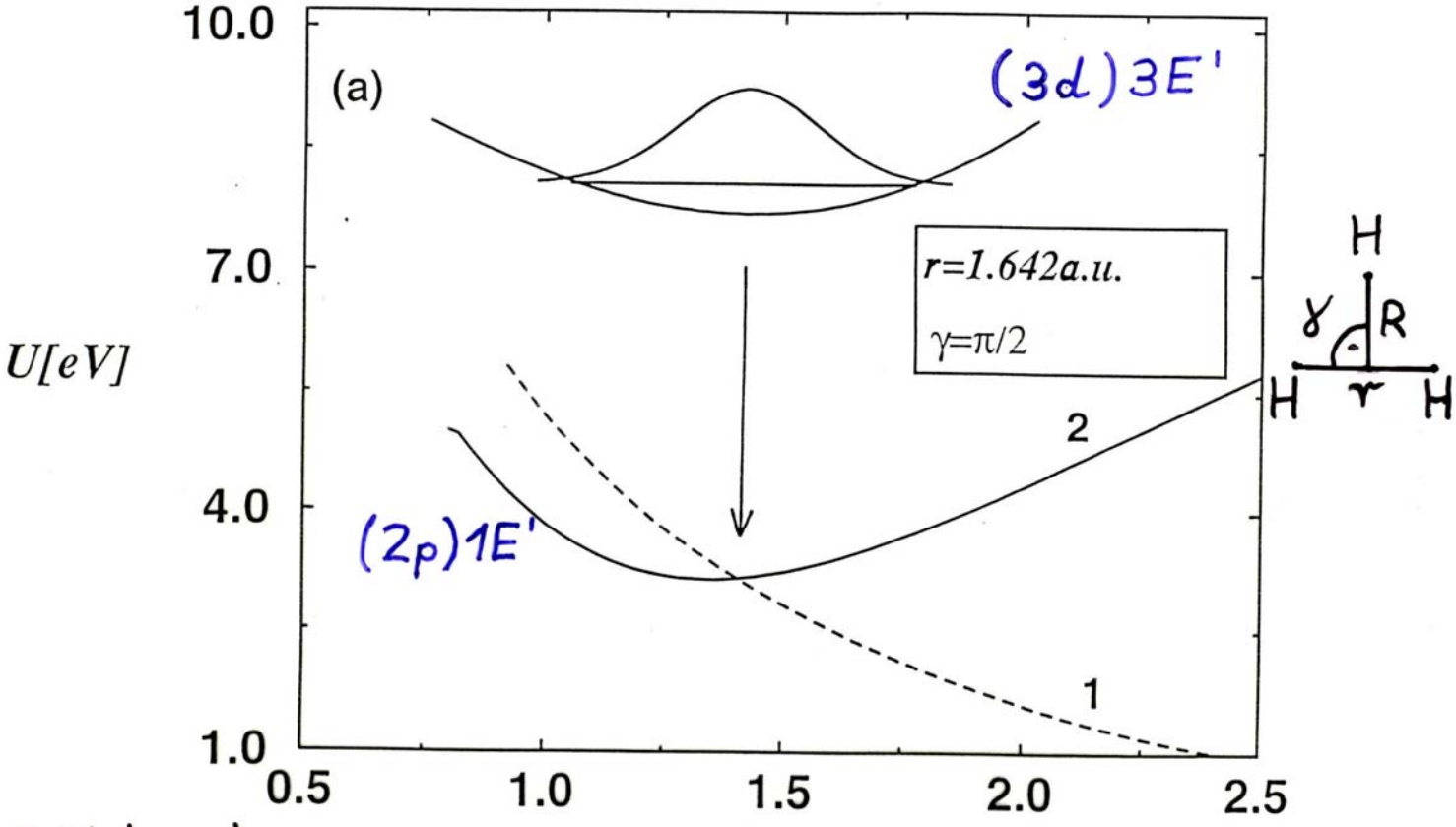
The persistent differences between the rotational state distribution measurements of Kliner, Adelman and Zare (J. Chem. Phys. 95 (1991) 1648) for the $D+H_2$ reaction and theory are shown to be almost entirely the result of the geometric phase effect. This effect is due to a conical intersection between the two lowest electronically adiabatic potential energy surfaces of this system. Using accurate quantum scattering calculations, we have identified it for the first time in a chemical reaction studied experimentally. Predictions of additional large dynamical effects are also made. This phase is apt to be important for many other systems displaying conical intersections.



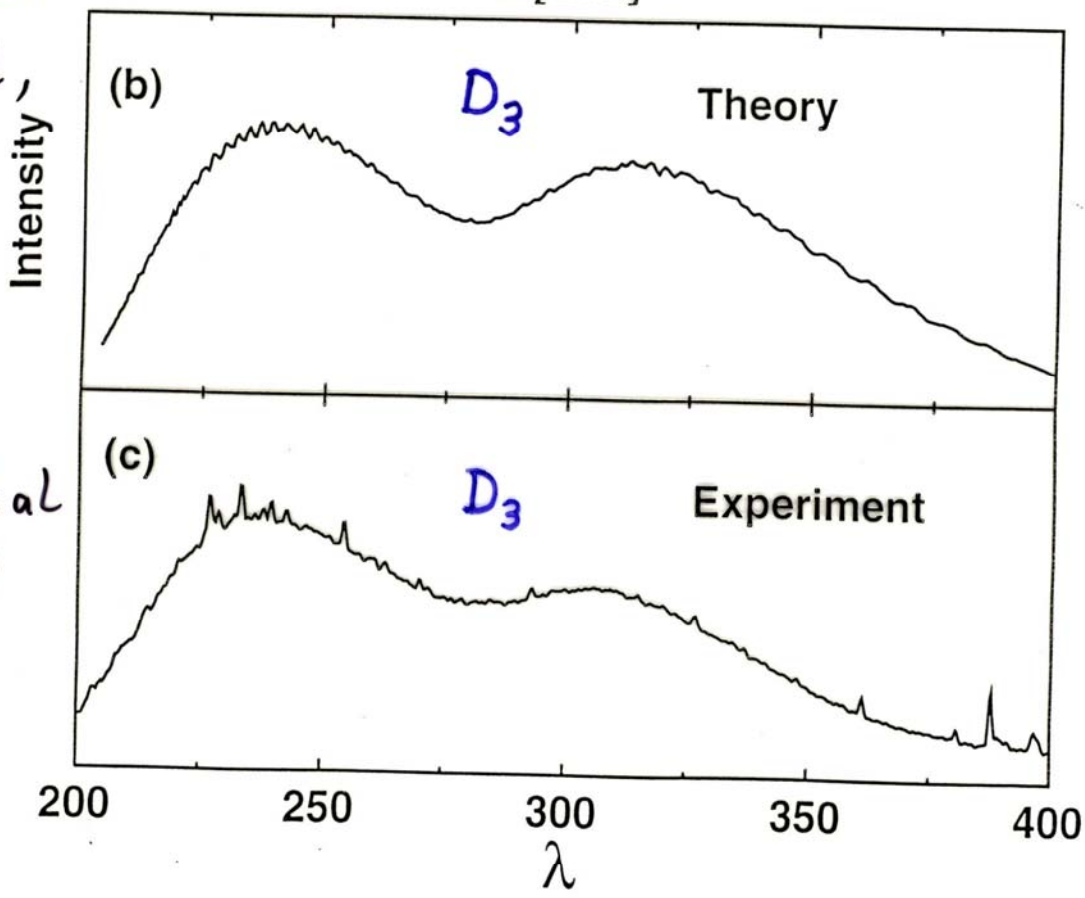
Later theoretical work (Kendrick) and experimental work (Wrede, Schnieder et al): no GP effect .

New theoretical work (Althorpe et al): Kendrick is right .

H_3/D_3: Rydberg Emission Spectrum



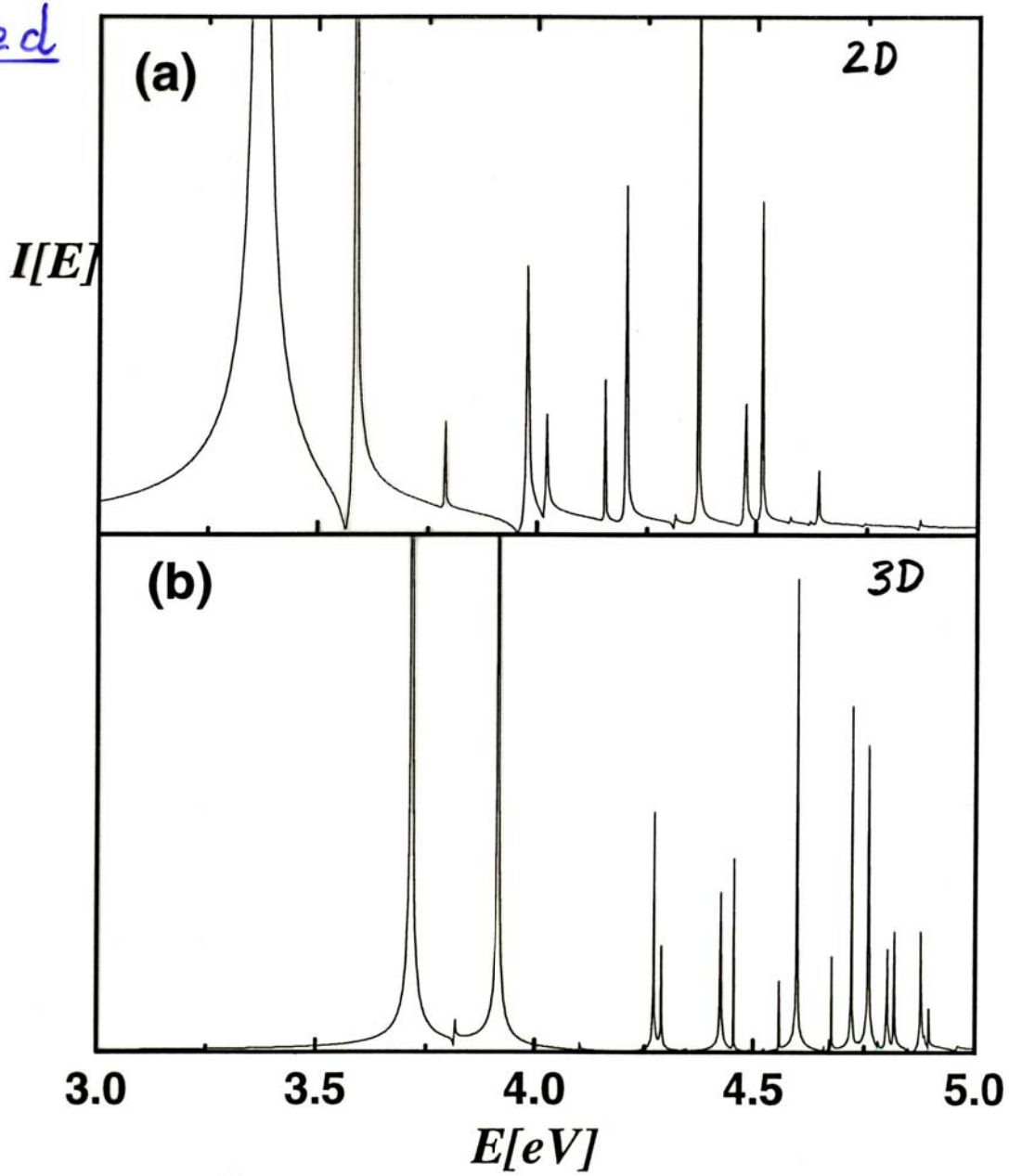
S. Mahapatra & H. Köppel, PRL 81, 3116 ('98)

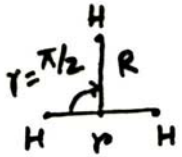


Figger et al ('94, '98)

FIG. 1. Mahapatra & Koeppel, J. Chem. Phys. 109, 1721 (1998)

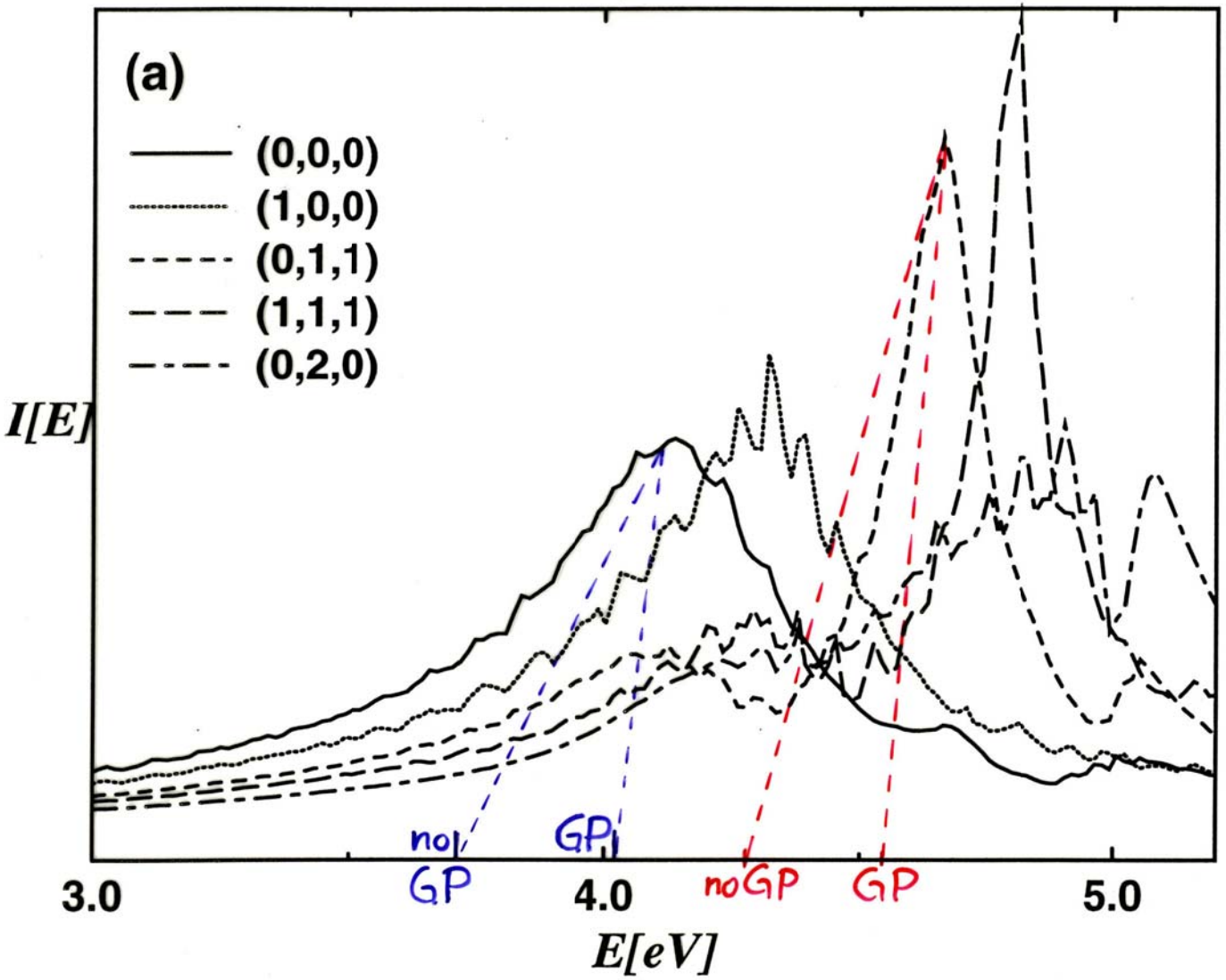
Uncoupled upper surface





Without GP

FIG. 7 Mahapatra & Koeppel, J. Chem. Phys. 109, 1721 (1998)



GP results from Lepetit et al (1990)

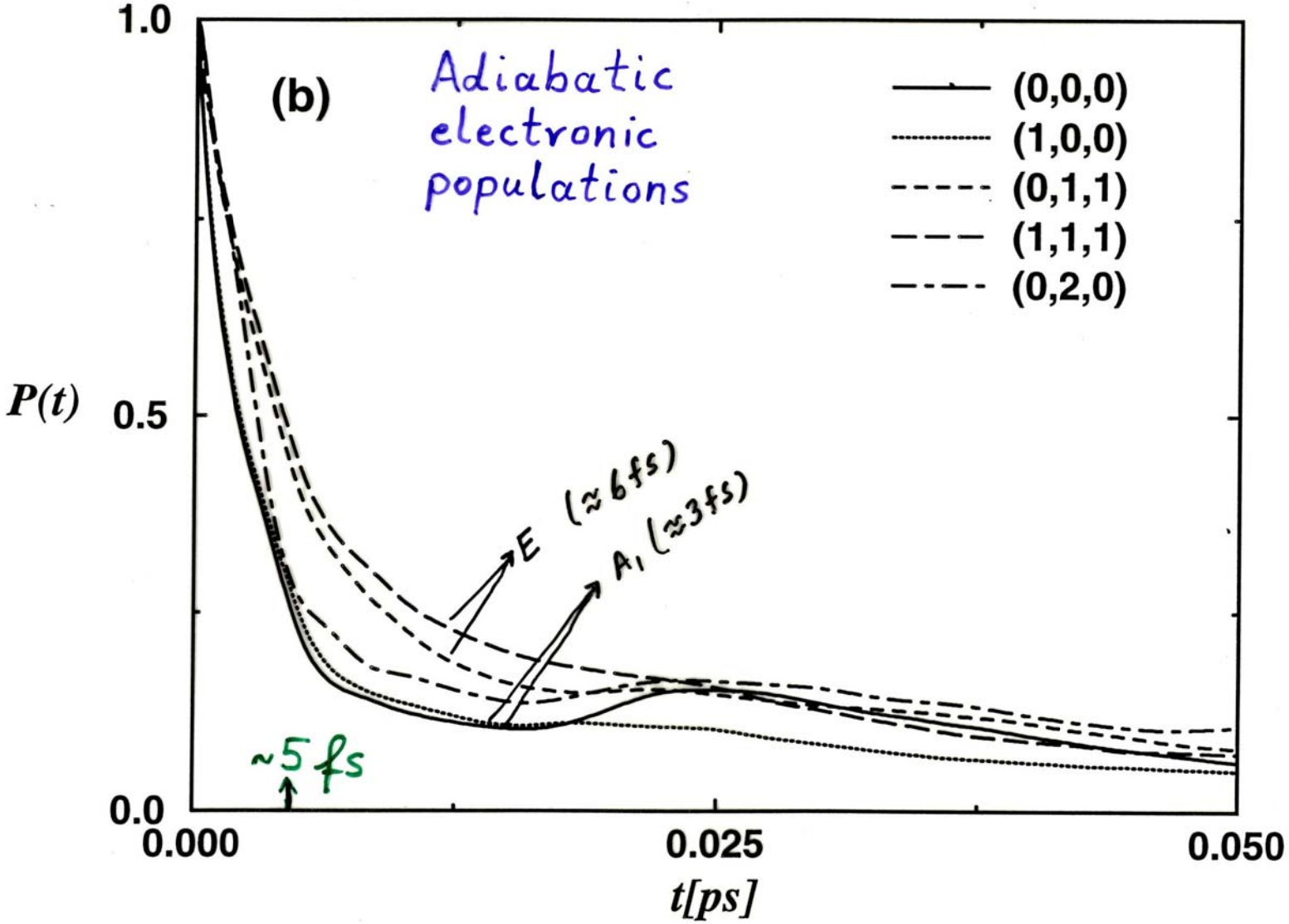
$P_-(t) = S \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} S^\dagger$

$P_+(t) = 1 - P_-(t)$

$P(t) \approx e^{-t/\tau}$

H_3

FIG. 7 (contd.) Mahapatra & Koeppel

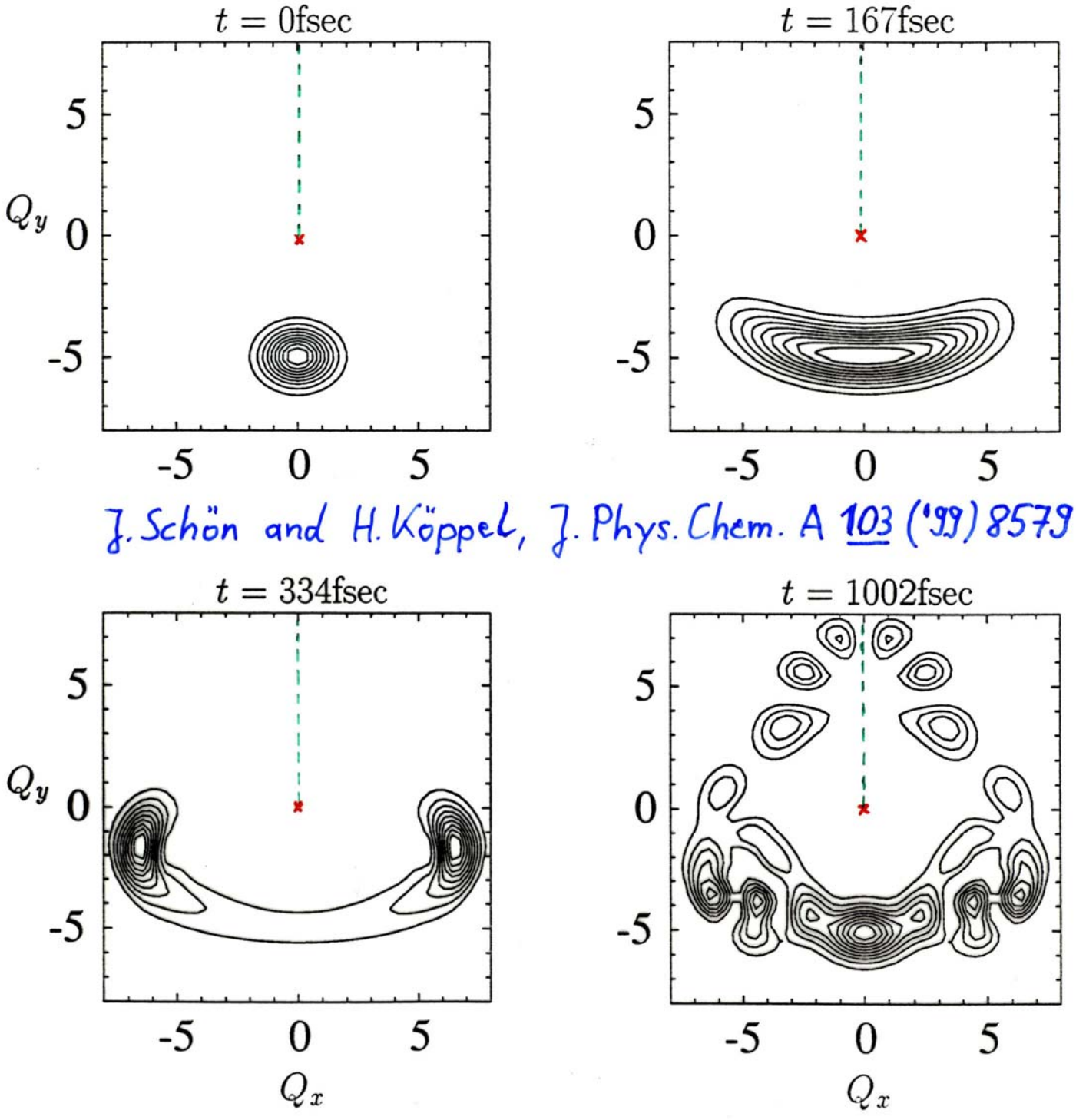


Extremely short timescale

Mode-specificity

Ground state dynamics:
Starting on saddle point

$Na_3(X)$

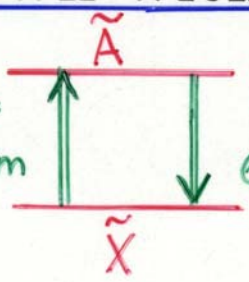


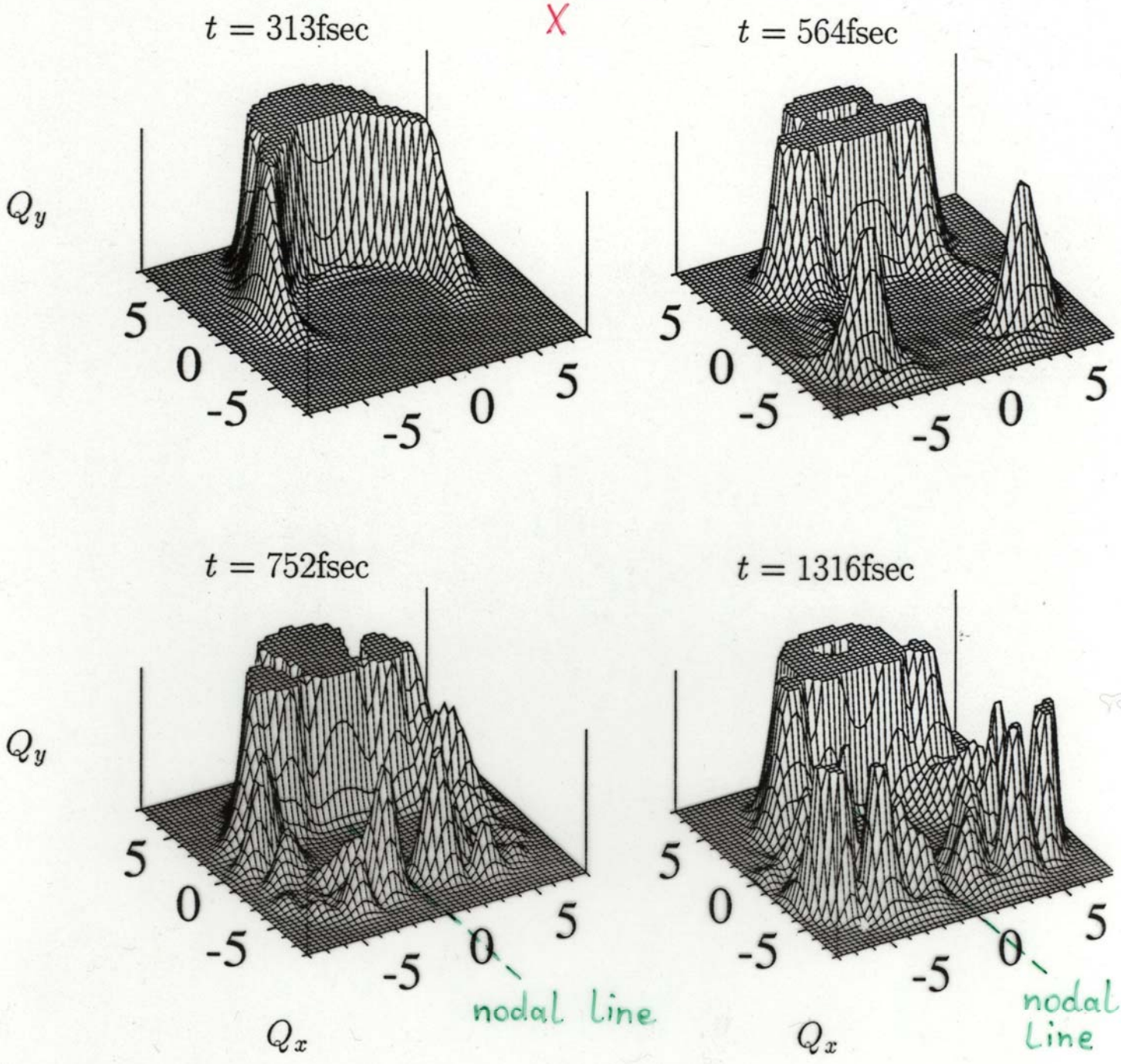
J. Schön and H. Köppel, J. Phys. Chem. A 103 ('99) 8579

Similar results on stationary states:
B. Kendrick, Phys. Rev. Lett. 79 ('97) 2431

Pump up and down with two pulses

$T_1 = T_2 = 60$ fs ; $\lambda_1 =$ 620nm $\lambda_2 =$ 623 nm ; $\Delta T = 245$ fs





$\lambda_2 > \lambda_1$ because of necessity to pump to saddle point (J. Schön & H. Köppel, to be published)

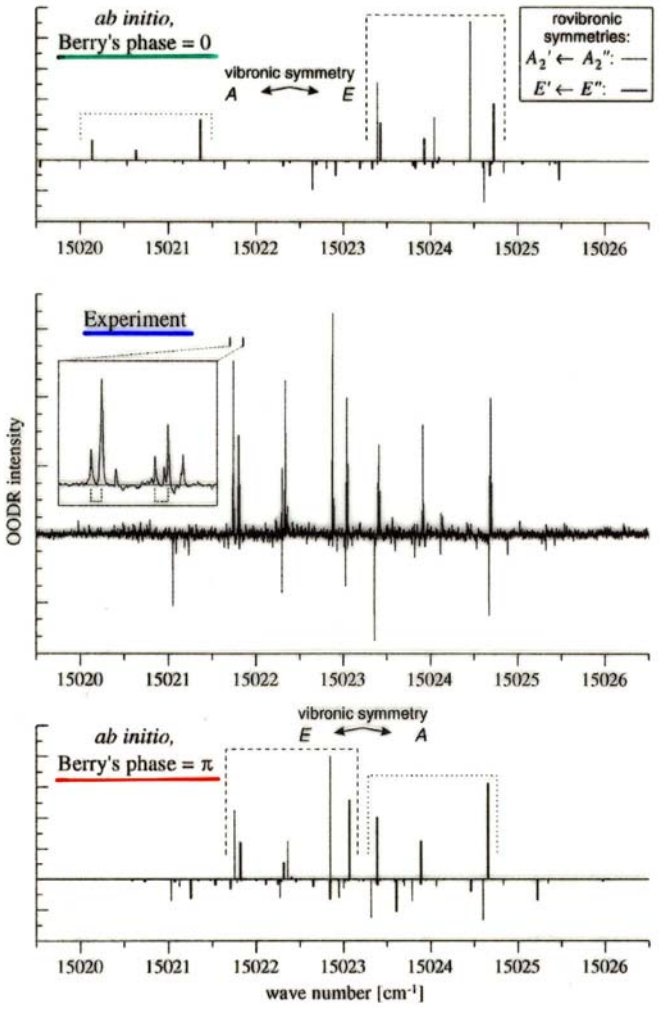
Unambiguous Proof for Berry's Phase in the Sodium Trimer: Analysis of the Transition $A^2E'' \leftarrow X^2E'$

H. von Busch, Vas Dev, H.-A. Eckel, S. Kasahara, J. Wang, and W. Demtröder
Fachbereich Physik, Universität Kaiserslautern, D-67653 Kaiserslautern, Germany

P. Sebald and W. Meyer
Fachbereich Chemie, Universität Kaiserslautern, D-67653 Kaiserslautern, Germany
(Received 29 June 1998)

Precise *ab initio* calculations of the rovibrational structures of the A^2E'' and X^2E' electronic states of Na_3 prompt a new vibrational assignment of the $A \leftarrow X$ transition and provide the basis for the rotational analysis of the vibrational band $A(v_s = 1, v_b = 0, v_a = 0) \leftarrow X(0,0,0)$ by means of high-resolution optical-optical double resonance. The calculations, which use the single-surface adiabatic approach, reproduce our experimental data only if, as required by theory, a geometric phase of π under pseudorotation around the equilateral configuration is imposed. We consider this the first verification of Berry's phase in high-resolution molecular spectroscopy. [S0031-9007(98)07707-2]

PACS numbers: 31.15.Ar, 33.15.Hp, 33.20.Kf, 33.40.+f



OODR - experim.

High-level MRCI calculations

Clearest example to date in molecular spectroscopy.

CONCLUSIONS

- Geometric phase effects represent a signature of conical intersections of potential energy surfaces which are relevant also below their minimum energy

- For higher energies masked by nonadiabatic effects; for very low energies 'quenched' by slow tunnelling

- Quantum dynamics of geometric phases: destructive self-interference

- Geometric phase effect not been established for H_3: averaged out for H + H_2 scattering; masked by nonadiabatic effects for Rydberg emission (*extremely short* life times of 5-7 fs)

- Geometric phase has been disproved for Na_3(B), been established for Na_3 (A) and predicted for Na_3(X)

- Much earlier work on impurities in solids

- Conceptual extensions: spin-orbit coupling; multiple conical intersections

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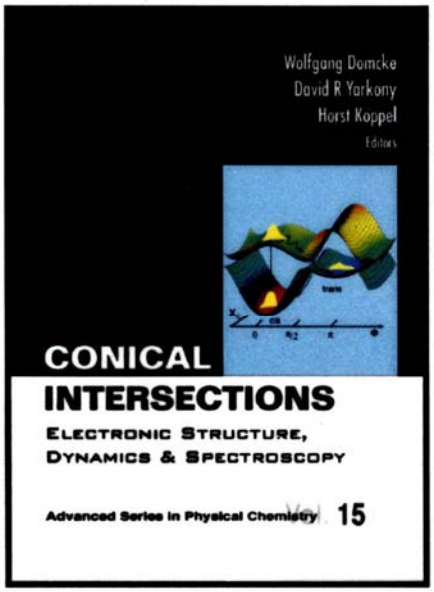
CONICAL INTERSECTIONS

Electronic Structure, Dynamics and Spectroscopy



edited by

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Technical University of Munich, Germany

David R Yarkony
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Horst Köppel
University of Heidelberg, Germany

It is widely recognized nowadays that conical intersections of molecular potential-energy surfaces play a key mechanistic role in the spectroscopy of polyatomic molecules, photochemistry and chemical kinetics. This invaluable book presents a systematic exposition of the current state of knowledge about conical intersections, which has been elaborated in research papers scattered throughout the chemical physics literature.

Section I of the book provides a comprehensive analysis of the electronic-structure aspects of conical intersections. Section II shows the importance of conical intersections in chemical reaction dynamics and gives an overview of the computational techniques employed to describe the dynamics at conical intersections. Finally, Section III deals with the role of conical intersections for researchers in the fields of molecular spectroscopy and laser control of chemical reaction dynamics.

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ACKNOWLEDGEMENTS

R. Meiswinkel ($Na_3(B)$)

J. Schön ($Na_3(X,B)$)

S. Mahapatra ($H_3(1E')$)

Deutsche Forschungsgemeinschaft
(financial support)