

The Jahn-Teller effect in CH_4^+ characterized by high-resolution photoelectron spectroscopy

H.J. Wörner, R. Van der Veen and F. Merkt, ETH Zürich, Switzerland

1. Introduction and motivation
2. PES of CH_4^+ and symmetry considerations
3. Tunneling calculations
4. Experimental assignment of rovibronic symmetries
5. Rotations in the ground state of CH_4^+ and comparison with experimental results
6. A two-dimensional model for large-amplitude motion

The methane cation: Introduction and motivation

One of the simplest organic cations

Spectroscopically uncharacterized (except ESR spectra in a matrix)

Highly fluxional molecule (like CH_5^+)

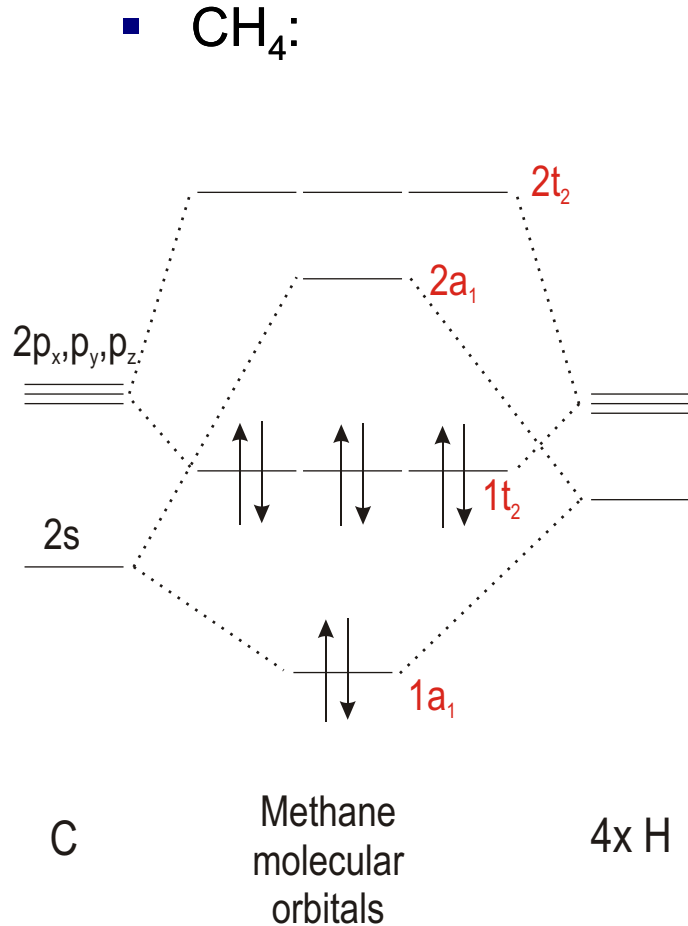
Model system for the T ($e+t_2$) Jahn-Teller effect

Test for ab initio theory (PES) and tunneling in high dimensionality

Ionization potential of methane is important in thermochemical cycles.

The Jahn-Teller effect in CH_4^+

■ CH_4 :



E

Jahn-Teller active modes

$T_2 \quad T_2 \quad A_1 + E + T_1 + T_2$

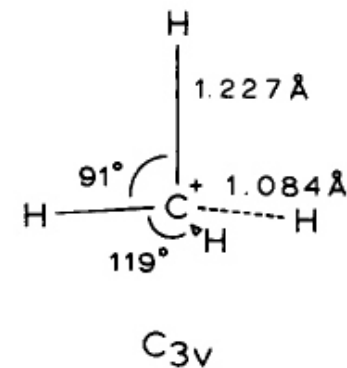
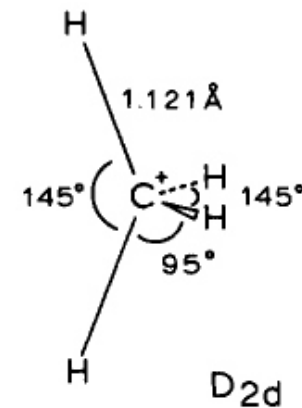
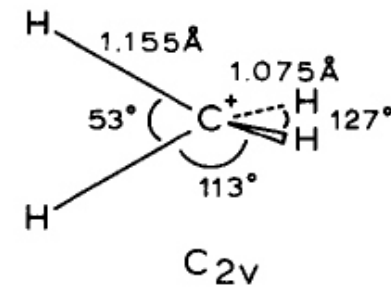
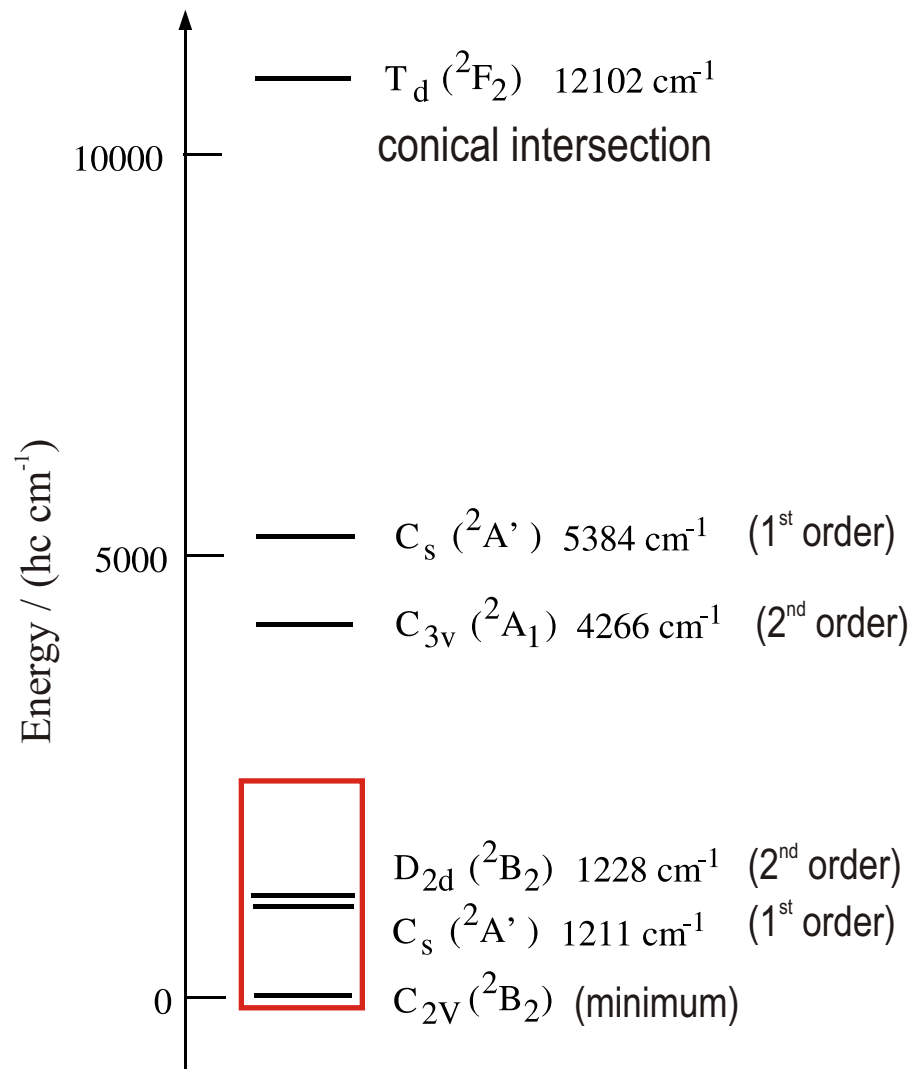
The Jahn-Teller problem is denoted

$T_2 \quad e+t_2+t_2$

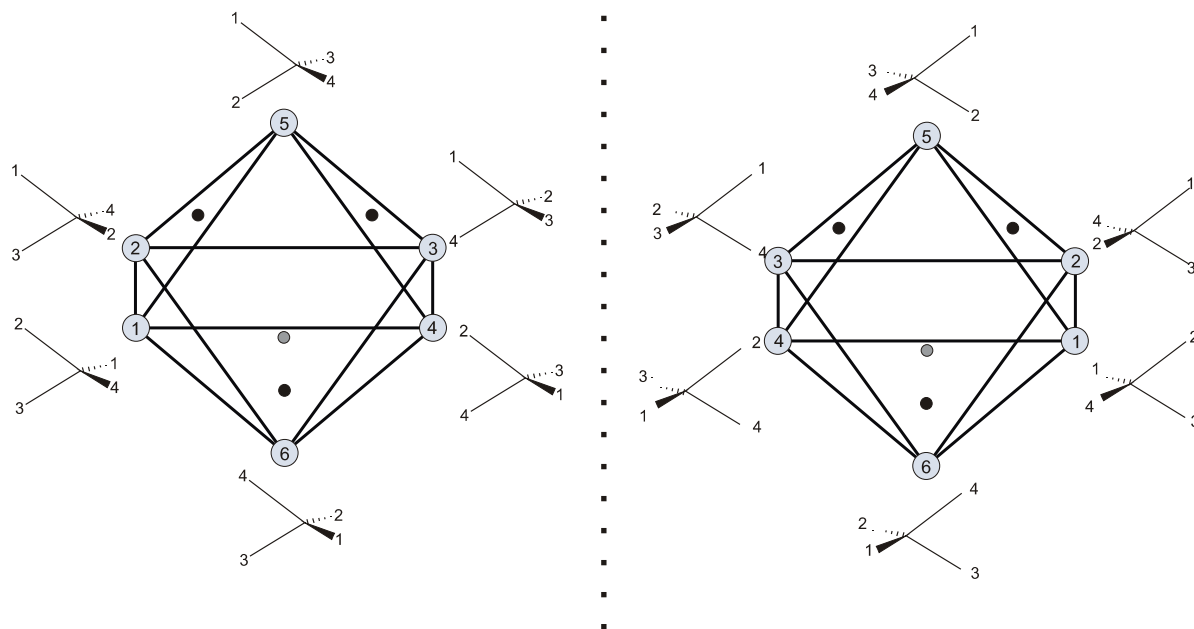
Possible equilibrium geometries in $T_2 \quad e+t_2$:

D_{2d} or C_{3v} in linear coupling

C_{2v} with quadratic coupling

The potential energy surface of CH_4^+ 

Topology of the potential energy surface



What is the molecular symmetry group?

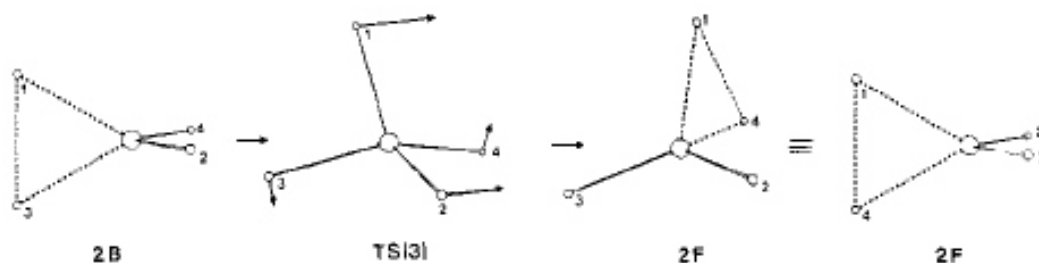
$$\text{CNPI} : G_{48} = S_4 \quad C_i$$

$$S_4 : E, (123), (12)(34), (12), (1432)$$

$$G_{48} : E, (123), (12)(34), \text{~~(12)~~, ~~(1432)~~, ~~(12)^*~~, ~~(123)^*~~, ~~(12)(34)^*~~, ~~(12)^*~~, ~~(1432)^*~~}$$

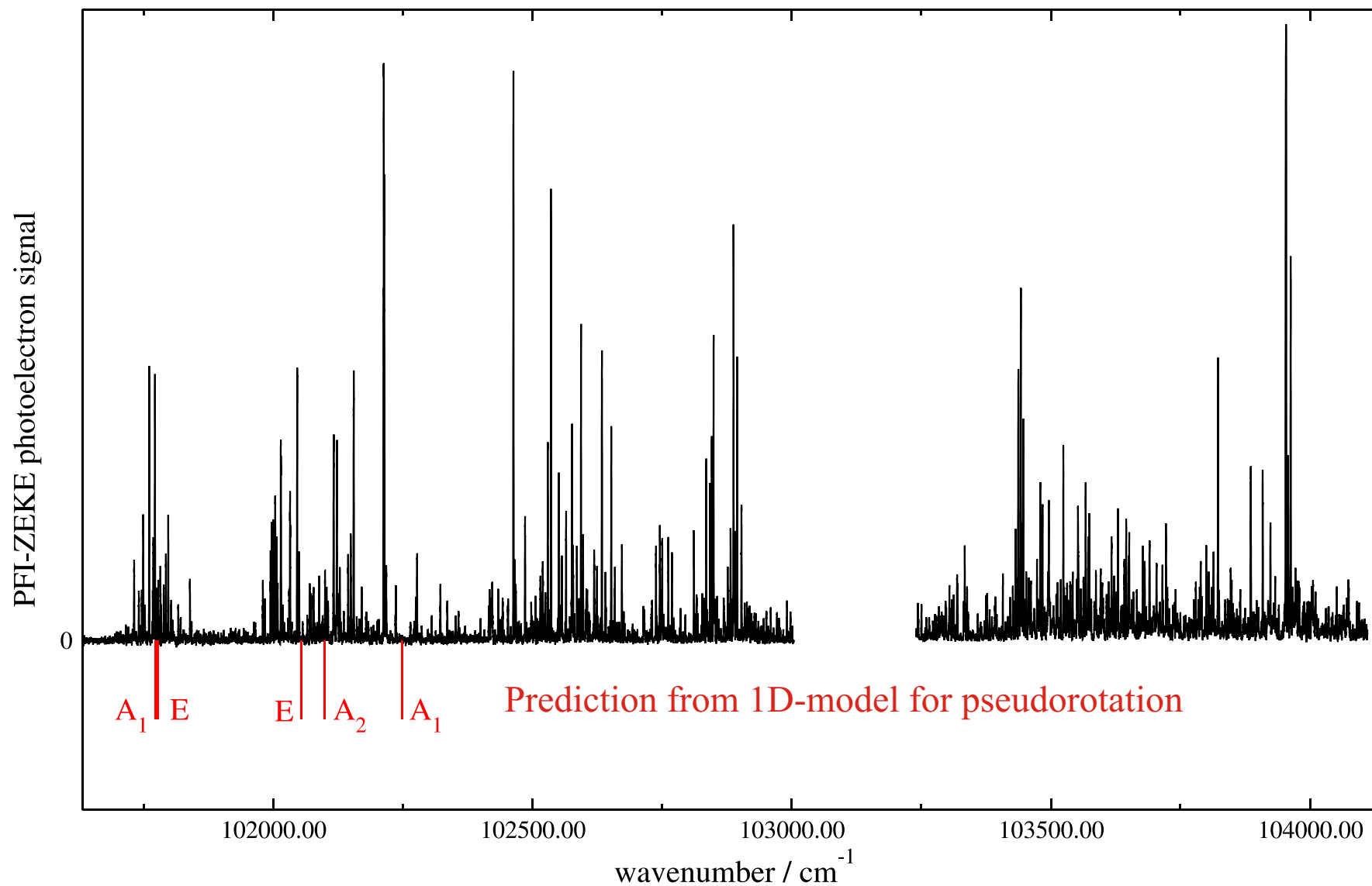
For non-interconverting enantiomers
the MS group is $T_d(M)$

Minimum energy interconversion pathway

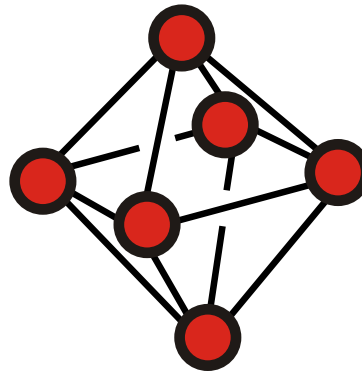


M.N. Paddon-Row, D.J. Fox, J.A. Pople, K.N. Houk and D.W. Pratt, JACS, 107, 7696 (1985)

PFI-ZEKE-PE spectrum of methane



Vibronic calculations: a tunneling treatment



Basis set:

$$\begin{aligned} \psi_n(r, Q) &= \sum_{j=1}^9 \psi_{n,j}(r, Q) \phi_0(q_j^{(n)}) \quad n = 1-6 \\ |n\rangle &= \left| \psi_n \right\rangle \end{aligned}$$

secular equation:

$$\begin{aligned} H &= \langle \psi_n | H | \psi_n \rangle \\ E &= \langle \psi_n | E | \psi_n \rangle \\ \underline{\underline{Hc}} &= \underline{\underline{ESc}} \end{aligned}$$

The $T_2 \otimes (e + t_2)$ Problem

The Hamiltonian is expressed in the diabatic electronic basis $\{|\xi\rangle, |\eta\rangle, |\zeta\rangle\}$

$$H = -\frac{\hbar^2}{2m} \sum_{\bar{\Gamma}\bar{\gamma}} \frac{\partial^2}{\partial Q_{\bar{\Gamma}\bar{\gamma}}^2} \mathbf{C}_\alpha + \mathbf{U}(Q)$$

with

$$\mathbf{U}(Q) = \sum_{\Gamma\gamma} \left(\frac{1}{2} G_\Gamma Q_{\Gamma\gamma}^2 \mathbf{C}_\alpha + F_\Gamma Q_{\Gamma\gamma} \mathbf{C}_{\Gamma\gamma} \right), \quad \gamma \in \Gamma, \quad \Gamma = E, T_2 \quad .$$

\mathbf{C} : unit matrix, \mathbf{C} : Clebsch-Gordan matrices

F : linear coupling constant, G quadratic coupling constants and harmonic frequencies

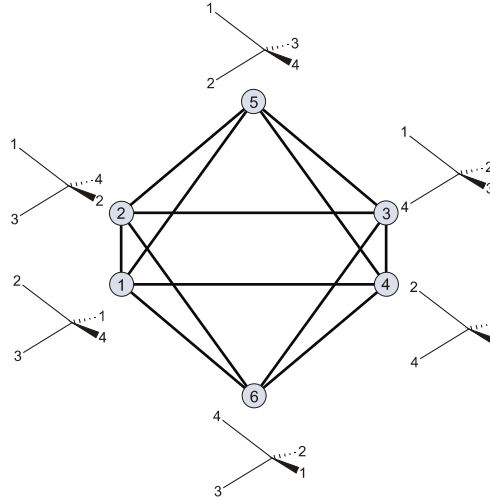
Diagonalization of the 3x3 Hamiltonian matrix:
adiabatic electronic wavefunction depending on Q

Matrix elements:

$$H_{nm} = \langle n|m \rangle \langle \chi_n | \mathbf{H} | \chi_m \rangle$$

$$S_{nm} = \langle n|m \rangle \langle \chi_n | \chi_m \rangle$$

Secular equation:



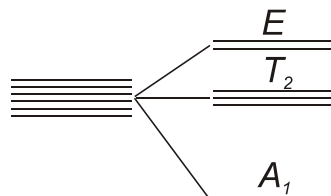
Min. n	$ n\rangle$
1	$\frac{1}{\sqrt{2}} (\xi\rangle + \eta\rangle)$
2	$\frac{1}{\sqrt{2}} (\xi\rangle + \zeta\rangle)$
3	$\frac{1}{\sqrt{2}} (- \xi\rangle + \eta\rangle)$
4	$\frac{1}{\sqrt{2}} (- \xi\rangle + \zeta\rangle)$
5	$\frac{1}{\sqrt{2}} (\eta\rangle - \zeta\rangle)$
6	$\frac{1}{\sqrt{2}} (\eta\rangle + \zeta\rangle)$

$$\begin{vmatrix} H_{11} - E & H_{12} - S_{12}E & 0 & H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E \\ H_{12} - S_{12}E & H_{11} - E & H_{12} - S_{12}E & 0 & H_{12} - S_{12}E & H_{12} - S_{12}E \\ 0 & H_{12} - S_{12}E & H_{11} - E & H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E \\ H_{12} - S_{12}E & 0 & H_{12} - S_{12}E & H_{11} - E & H_{12} - S_{12}E & H_{12} - S_{12}E \\ H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E & H_{11} - E & 0 \\ H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E & 0 & H_{11} - E \end{vmatrix} = 0$$

$$\begin{vmatrix} H_{11} - E & H_{12} - S_{12}E & 0 & -(H_{12} - S_{12}E) & H_{12} - S_{12}E & H_{12} - S_{12}E \\ H_{12} - S_{12}E & H_{11} - E & -(H_{12} - S_{12}E) & 0 & -(H_{12} - S_{12}E) & H_{12} - S_{12}E \\ 0 & -(H_{12} - S_{12}E) & H_{11} - E & H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E \\ -(H_{12} - S_{12}E) & 0 & H_{12} - S_{12}E & H_{11} - E & -(H_{12} - S_{12}E) & H_{12} - S_{12}E \\ H_{12} - S_{12}E & -(H_{12} - S_{12}E) & H_{12} - S_{12}E & -(H_{12} - S_{12}E) & H_{11} - E & 0 \\ H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E & 0 & H_{11} - E \end{vmatrix} = 0$$

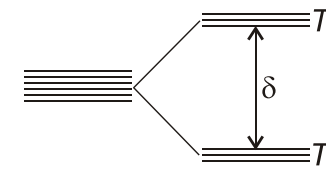
Eigenvalues:

$$E_{A_1} = \frac{H_{11} + 4H_{12}}{1 + 4S_{12}}, \quad E_{T_2} = H_{11}, \quad E_E = \frac{H_{11} - 2H_{12}}{1 - 2S_{12}}$$



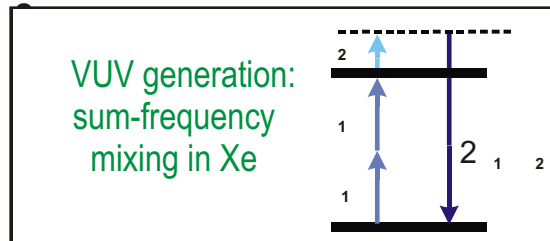
Without geometric phase

$$E_{T_1} = \frac{H_{11} + 2H_{12}}{1 + 2S_{12}}, \quad E_{T_2} = \frac{H_{11} - 2H_{12}}{1 - 2S_{12}}$$

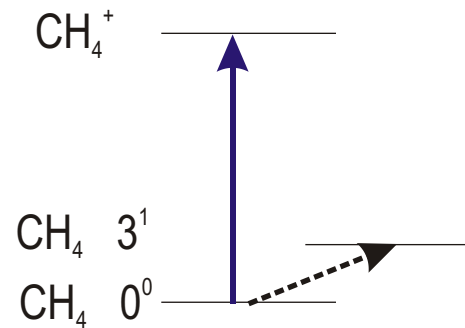


With geometric phase

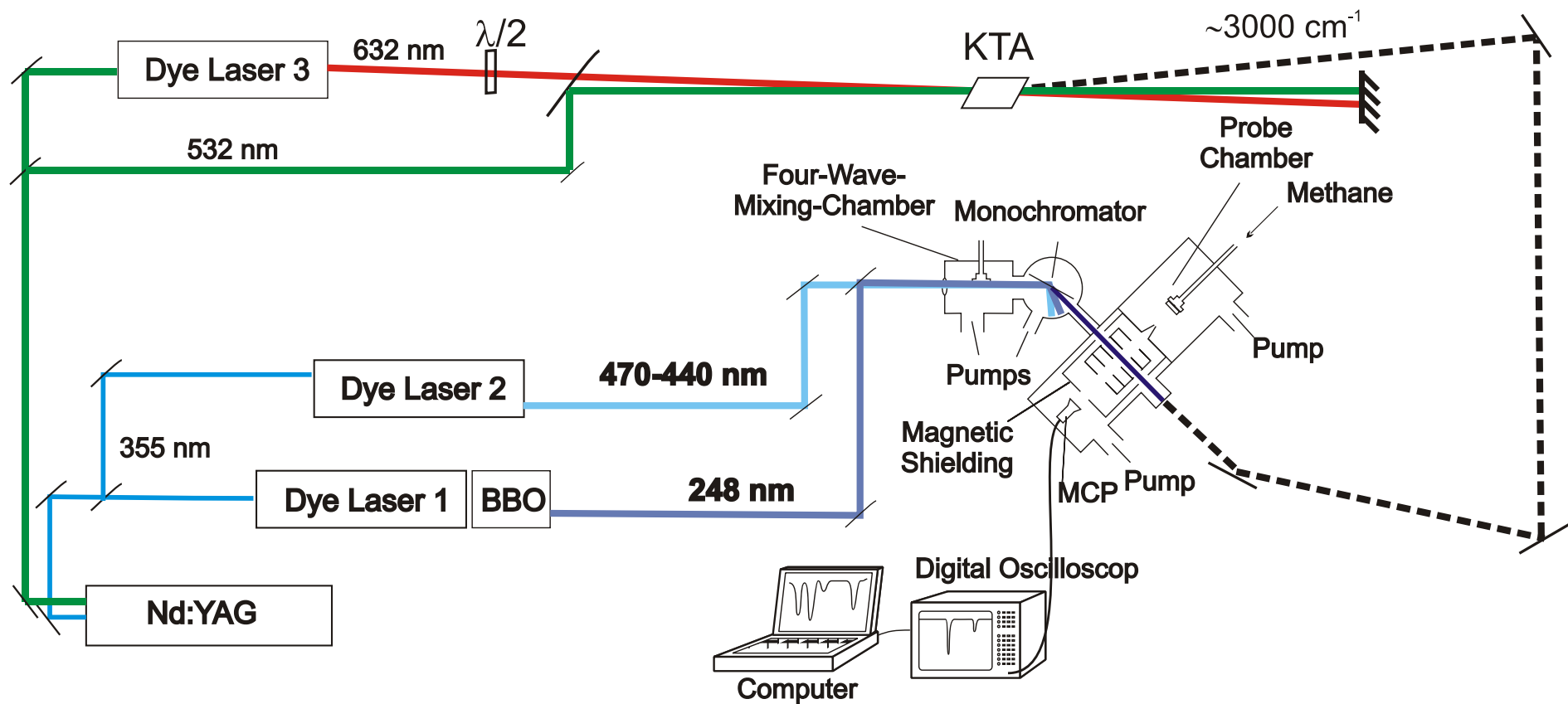
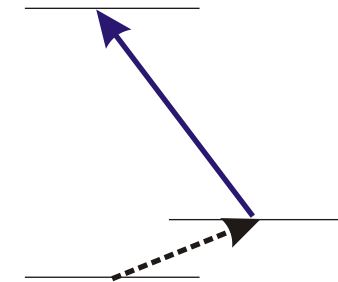
Experimental setup



“ZEKE-dip” spectroscopy



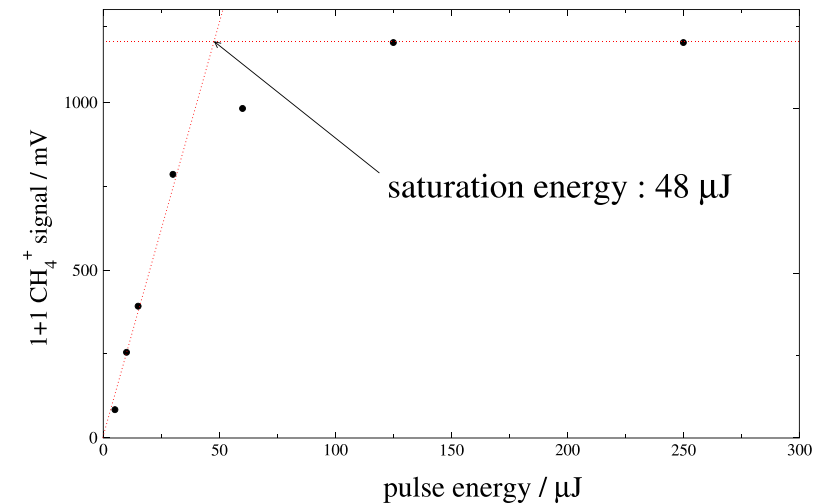
IR+VUV PFI-ZEKE-PE spectroscopy



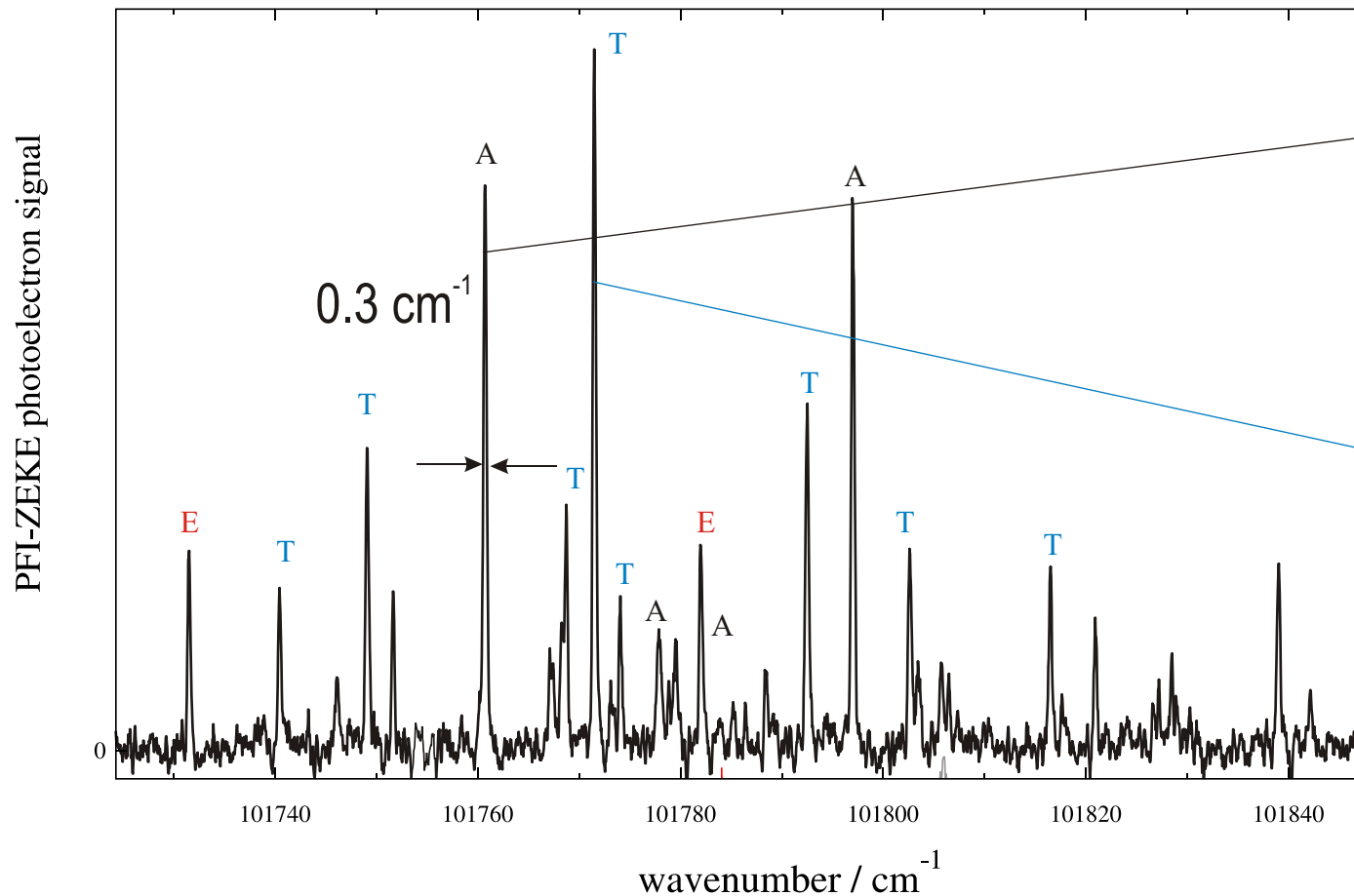
The figure illustrates the energy levels and transitions for the CH_4^+ ion. The left panel shows the energy levels for the 0^0 and 3^1 electronic states. The 0^0 state has four levels: A_1 (0), T_1 (1), E, T_2 (2), and A_2, T_1, T_2 (3). The 3^1 state has four levels: A_1, A_2 (0), E (1), T_1, T_2 (2), and $A_1, E, 2T_1, 2T_2$ (3). A red arrow labeled $R(1)$ indicates a transition from the 0^0 state to the 3^1 state. The right panel shows the energy levels for the 0^0 state of the CH_4^+ ion, with levels A_1 (0), T_1 (1), E (2), and T_1, T_2 (3). A table of symmetry labels and weights is provided:

ns spin	rve	weight
A_1	A_1, A_2	5
E	E	2
T_1	T_1, T_2	3

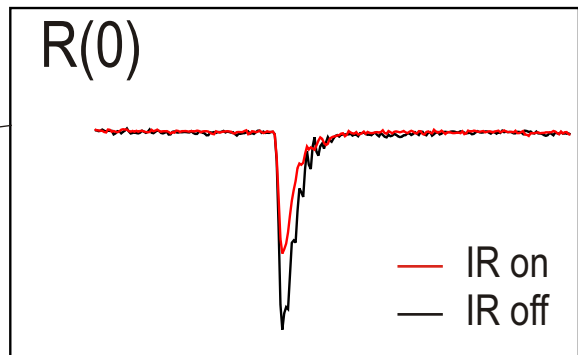
The right panel also shows a plot of the $+1 \text{ CH}_4^+$ signal (mV) versus the laser energy. The signal increases rapidly and then saturates at approximately 1000 mV. A red dotted line indicates the saturation energy, which is 48 μJ .



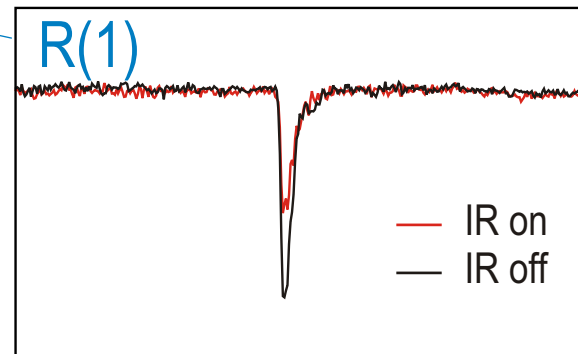
Results of the depletion ("ZEKE dip") experiments

PFI-ZEKE electrons
time-of-flight

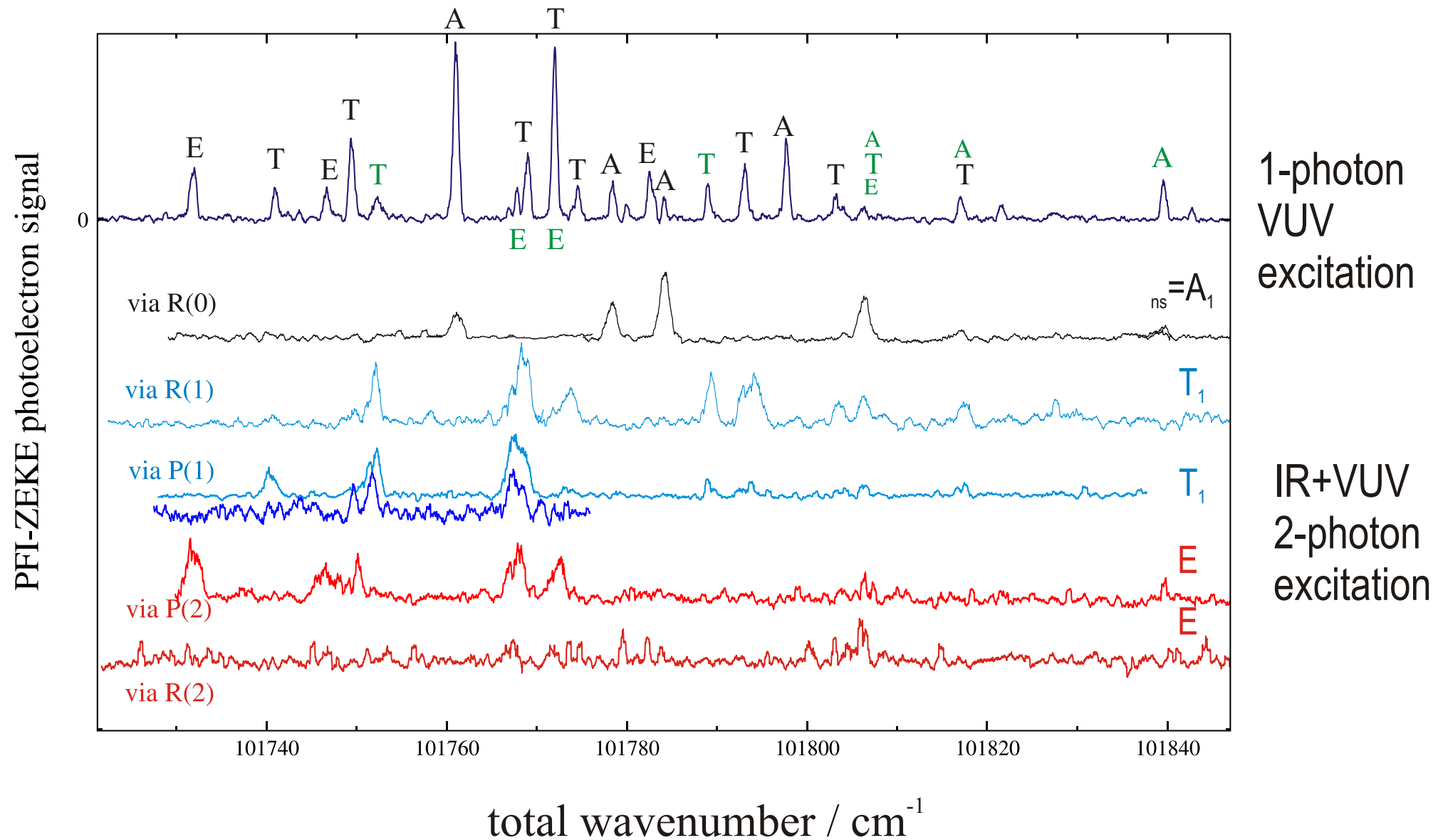
R(0)



R(1)

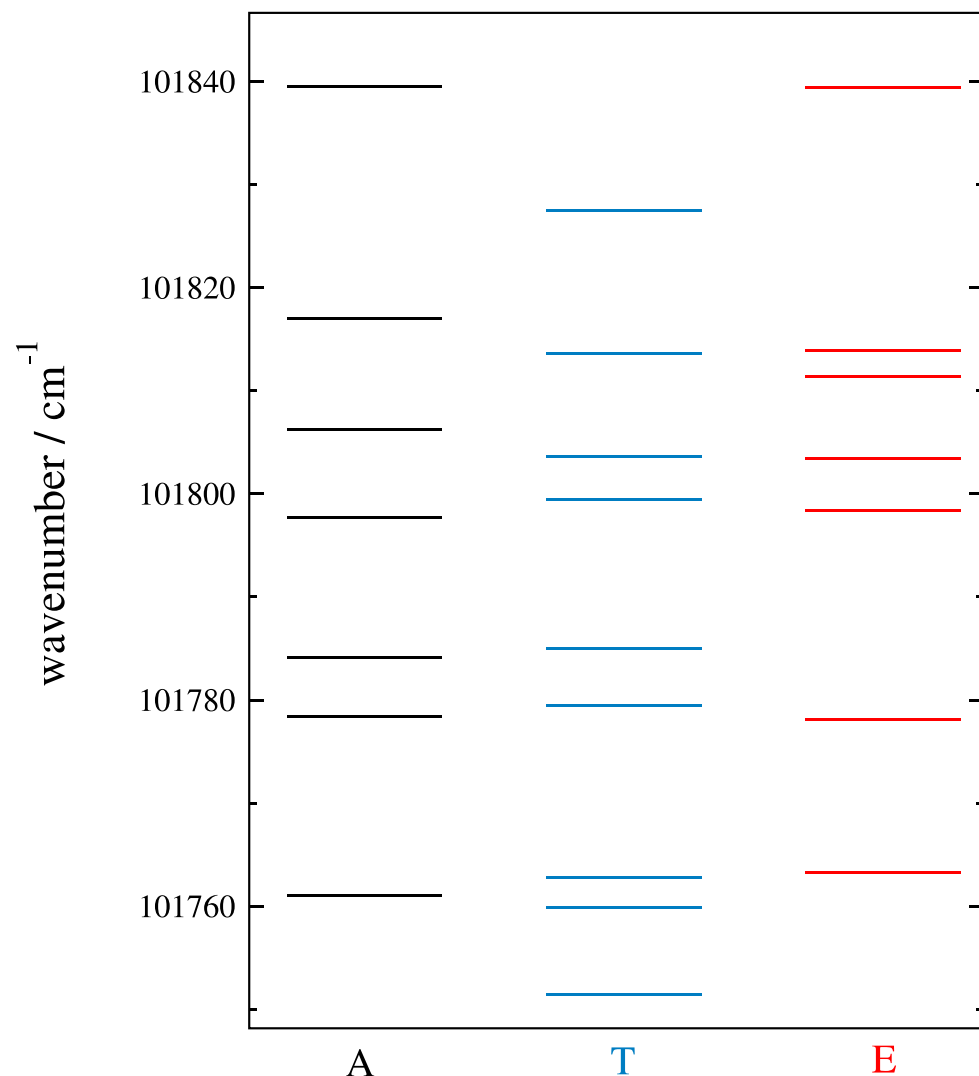

 $A_{\text{rve}}^+ = A_1 \text{ or } A_2, J''=0$
 $T_{\text{rve}}^+ = T_1 \text{ or } T_2, J''=1$
 $E_{\text{rve}}^+ = E, J''=2$

Results of the IR+VUV two-photon experiments



Experimental level scheme

(not field corrected)



Ionization energy of methane:

$$101753.0 \pm 1.0 \text{ cm}^{-1}$$

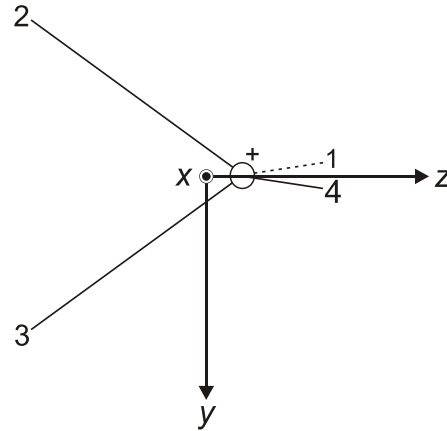
(Signorell et al.: $101773 \pm 35 \text{ cm}^{-1}$)

The rovibronic ground state has **T-symmetry** confirming our tunneling calculations including the geometric phase.

This level structure proves that CH_4^+ has a C_{2v} equilibrium geometry (incompatible with D_{2d} or C_{3v} geometries)

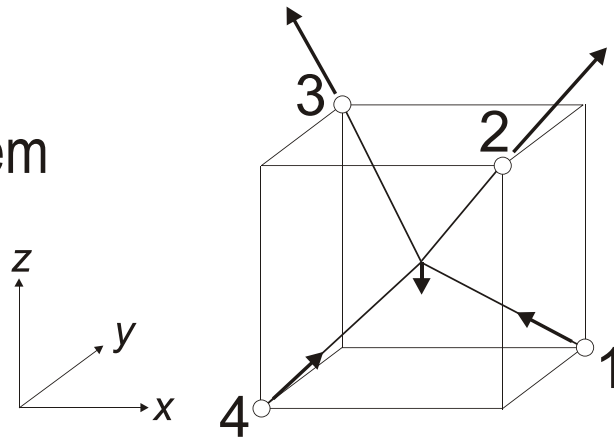
Rotation

Principal axis system
for one minimum



$$\frac{\hat{H}_{\text{As.Top}}}{hc} = C \hat{J}_x^2 + B \hat{J}_y^2 + A \hat{J}_z^2$$

Global axis system
for all minima



$$\begin{aligned} \frac{\hat{H}'_{\text{As.Top}}}{hc} &= \frac{1}{2}C (\hat{J}_x + \hat{J}_y)^2 + \frac{1}{2}B (-\hat{J}_x + \hat{J}_y)^2 + A \hat{J}_z^2 \\ &= \frac{1}{2}(C + B) (\hat{J}_x^2 + \hat{J}_y^2) + \frac{1}{2}(C - B) (\hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x) + A \hat{J}_z^2 \end{aligned}$$

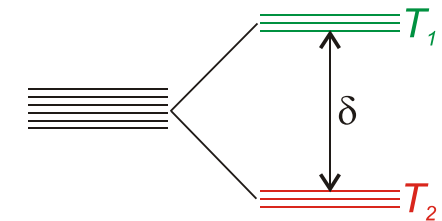
Rotation-tunneling: an effective rovibronic Hamiltonian

$$\mathbf{H}_{\text{rve}} = \mathbf{U}^T \mathbf{H}^{\text{rot}} \mathbf{U}$$

$$\mathbf{U} = \frac{1}{2} \left(\begin{array}{ccc|ccc} -1 & 0 & 1 & 0 & 1 & -1 \\ 0 & 1 & -1 & 1 & 0 & -1 \\ -1 & 0 & -1 & 0 & 1 & 1 \\ 0 & 1 & 1 & 1 & 0 & 1 \\ 1 & 1 & 0 & -1 & 1 & 0 \\ 1 & -1 & 0 & 1 & 1 & 0 \end{array} \right)$$

$\mathbf{T}_2 \qquad \mathbf{T}_1$

Min.	Type of distortion	Asymmetric top Hamiltonian
1	(23)/z-distortion	$\hat{H}_{11}^{\text{rot}}/hc = \frac{1}{2}(C+B) \left(\hat{J}_x^2 + \hat{J}_y^2 \right) + \frac{1}{2}(C-B) \left(\hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x \right) + A \hat{J}_z^2$
2	(13)/y-distortion	$\hat{H}_{22}^{\text{rot}}/hc = \frac{1}{2}(C+B) \left(\hat{J}_z^2 + \hat{J}_x^2 \right) + \frac{1}{2}(C-B) \left(\hat{J}_z \hat{J}_x + \hat{J}_x \hat{J}_z \right) + A \hat{J}_y^2$
3	(14)/-z-distortion	$\hat{H}_{33}^{\text{rot}}/hc = \frac{1}{2}(C+B) \left(\hat{J}_x^2 + \hat{J}_y^2 \right) - \frac{1}{2}(C-B) \left(\hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x \right) + A \hat{J}_z^2$
4	(24)/-y-distortion	$\hat{H}_{44}^{\text{rot}}/hc = \frac{1}{2}(C+B) \left(\hat{J}_z^2 + \hat{J}_x^2 \right) - \frac{1}{2}(C-B) \left(\hat{J}_z \hat{J}_x + \hat{J}_x \hat{J}_z \right) + A \hat{J}_y^2$
5	(12)/x-distortion	$\hat{H}_{55}^{\text{rot}}/hc = \frac{1}{2}(C+B) \left(\hat{J}_y^2 + \hat{J}_z^2 \right) + \frac{1}{2}(C-B) \left(\hat{J}_y \hat{J}_z + \hat{J}_z \hat{J}_y \right) + A \hat{J}_x^2$
6	(34)/-x-distortion	$\hat{H}_{66}^{\text{rot}}/hc = \frac{1}{2}(C+B) \left(\hat{J}_y^2 + \hat{J}_z^2 \right) - \frac{1}{2}(C-B) \left(\hat{J}_y \hat{J}_z + \hat{J}_z \hat{J}_y \right) + A \hat{J}_x^2$



\mathbf{H}_{rve} : add tunneling splitting to diagonal and diagonalize : rovibronic energies

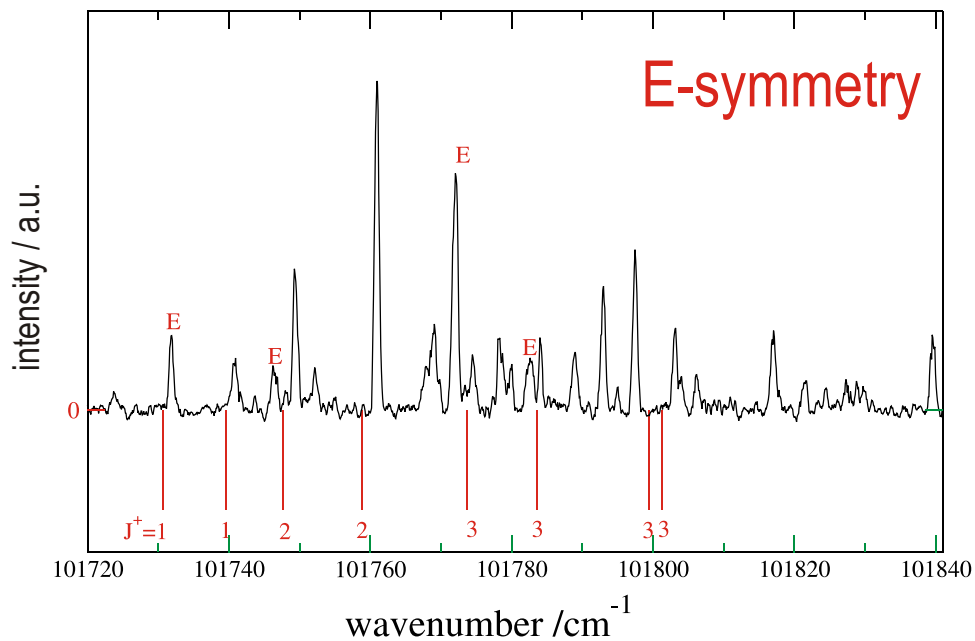
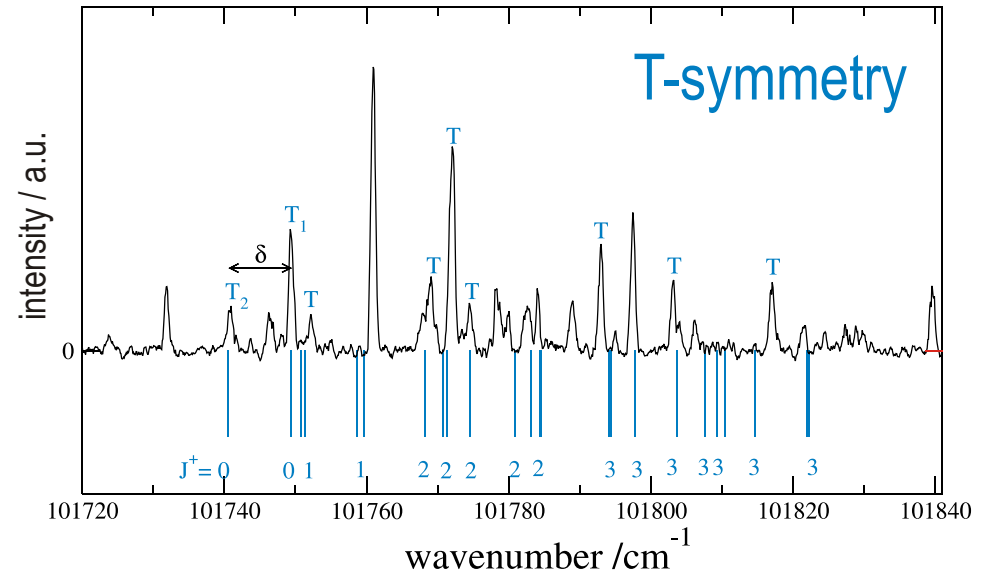
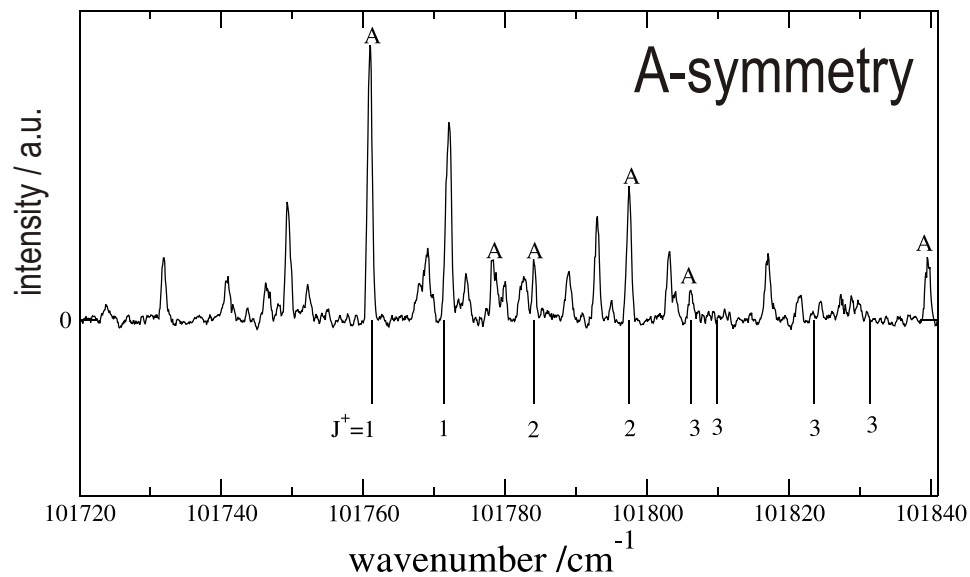
The diagram illustrates the evolution of energy levels for a system with two vibrational modes, A_1 and A_2 , under static distortion and free pseudo-rotation. The x-axis represents the transition from static distortion to free pseudo-rotation, with an arrow indicating 'Increasing tunneling splitting'.

Static distortion (C_{2v}): The energy levels are labeled on the left as B_1 , B_2 , A_1 , A_2 , B_1 , A_1 , A_2 , B_2 , B_1 , A_1 , A_2 , B_2 . The ground state is labeled $ev = B_2$.

Free pseudo-rotation (T_d): The energy levels are labeled on the right as $A_2 + E + 2T_1 + 2T_2$, $A_1 + E + T_1 + T_2$, T_1 , $A_1 + E + 2T_1 + 2T_2$, $A_2 + E + T_1 + T_2$, and T_2 . The ground state is labeled $ev = T_2$.

Transitions and Labels: Red lines connect the static distortion levels to the free pseudo-rotation levels. Labels along these lines include $T_1 + T_2$, $A_2 + E + T_1$, $A_2 + E + T_2$, $A_1 + E + T_1$, $A_1 + E + T_2$, and $T_1 + T_2$.

Comparison with theoretical predictions



Constants / cm⁻¹:

IE / hc	101753(1)
A	6.94
B	5.27
C	3.78
	8.5(1)

2D- model for pseudorotational motion: T (e+t₂) in linear coupling

$$H = H_0(e) + H_0(t_2) + \frac{k_E}{E\sqrt{E}} \begin{pmatrix} \frac{q}{2} & \frac{\sqrt{3}}{2}q & q & q \\ q & \frac{q}{2} & \frac{\sqrt{3}}{2}q & q \\ q & q & q & q \end{pmatrix} \quad \text{where}$$

$$\frac{k_T}{T\sqrt{T}} \frac{k_E}{E\sqrt{E}}$$

M.C.M. O'Brien, *Phys. Rev.* **187**, 407 (1969)

Mapping onto a sphere:

e-modes

$$q \quad \frac{q}{2}(3\cos^2 - 1)$$

$$q \quad q\frac{\sqrt{3}}{2}\sin^2 \cos 2$$

t₂-modes

$$q \quad q\frac{\sqrt{3}}{2}\sin 2 \sin$$

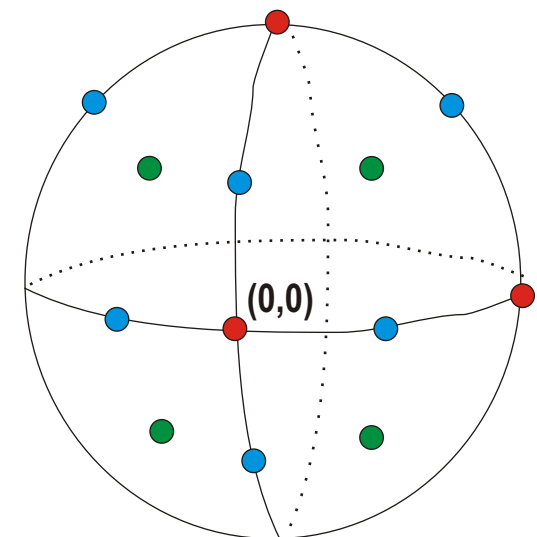
$$q \quad q\frac{\sqrt{3}}{2}\sin 2 \cos$$

$$q \quad q\frac{\sqrt{3}}{2}\sin^2 \sin 2$$

● D_{2d}

● C_{3v}

● C_{2v}

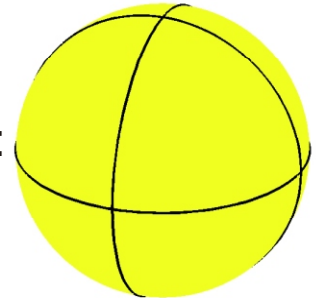


Pseudorotational motion

1. $\sigma^2 = 3/4$ and $\tau = e$

The sphere is an isoenergetic minimum subspace. The kinetic energy operator takes the simple form:

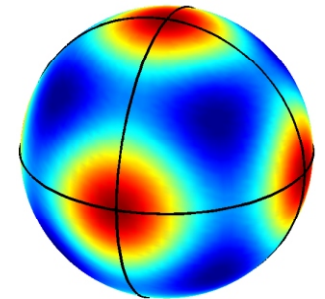
$$\hat{T} = \frac{\hbar^2}{2} \left(\frac{\partial^2}{\partial q^2} + \frac{\partial^2}{\partial q^2} + \frac{\partial^2}{\partial q^2} + \frac{\partial^2}{\partial q^2} + \frac{\partial^2}{\partial q^2} \right) = \frac{\hbar^2}{6q^2} \nabla^2,$$



2. $\sigma^2 = 3/4$ and/or $\tau = e$

The rotational symmetry is lost. The potential terms must be totally symmetric. Simplest form:

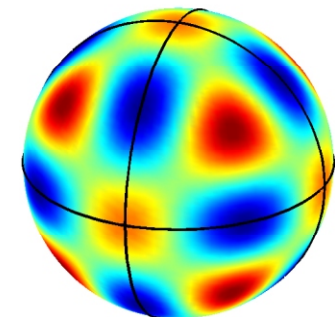
$$V_4(\theta, \phi) = Y_4^0 \sqrt{\frac{5}{14}} (Y_4^4 + Y_4^{-4})$$



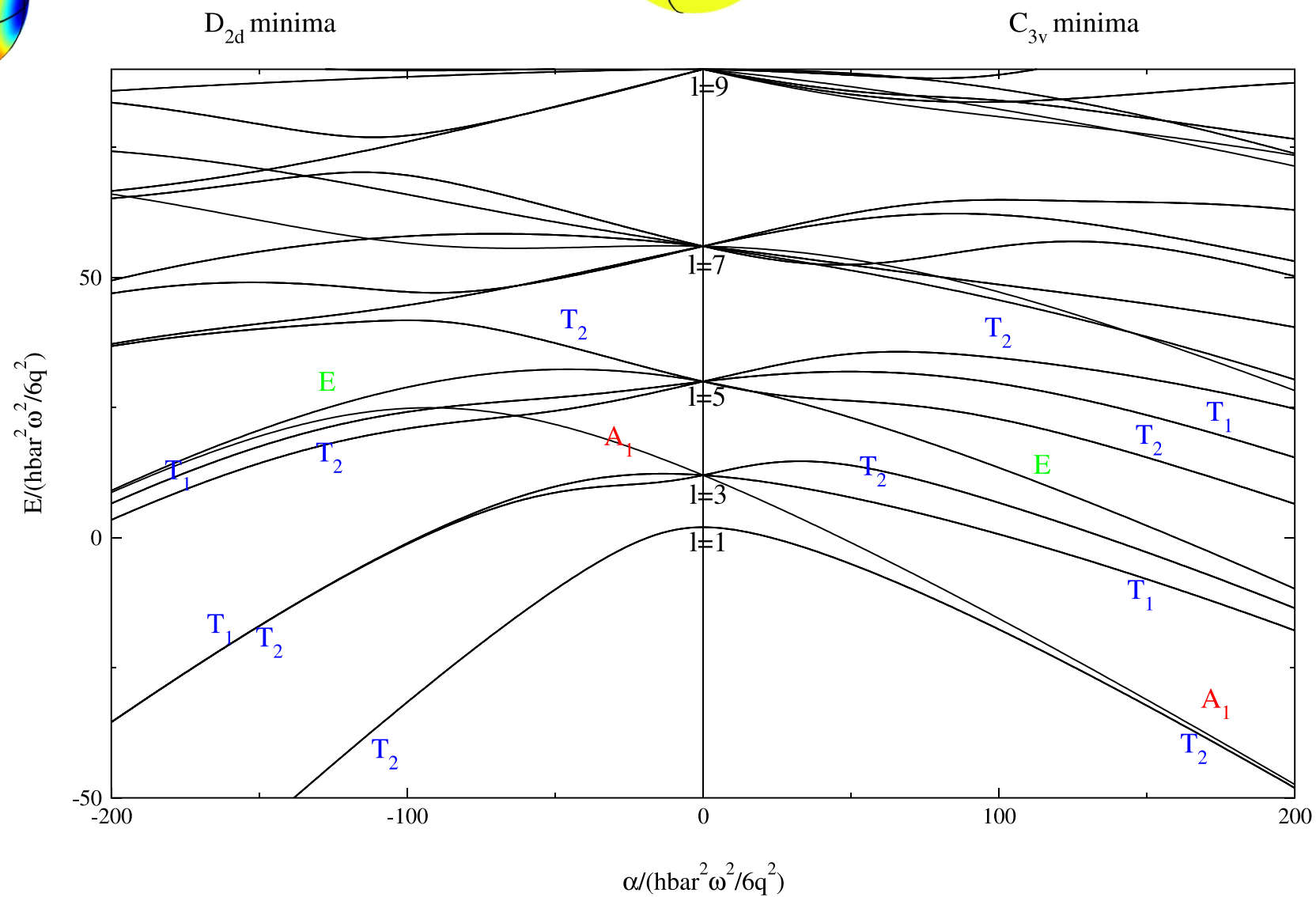
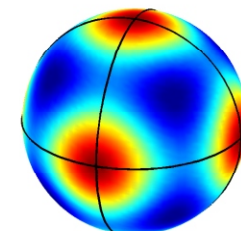
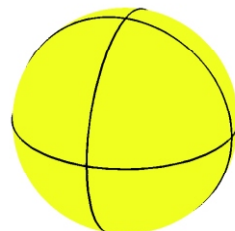
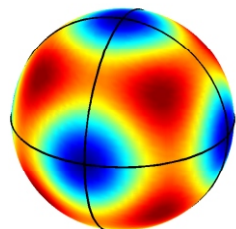
3. quadratic coupling

The lowest order term accounting for quadratic coupling is:

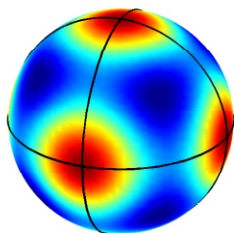
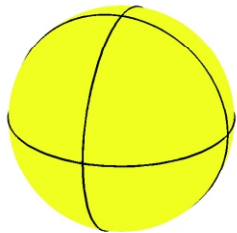
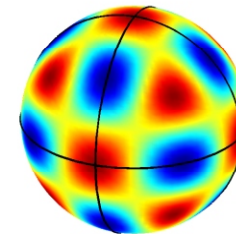
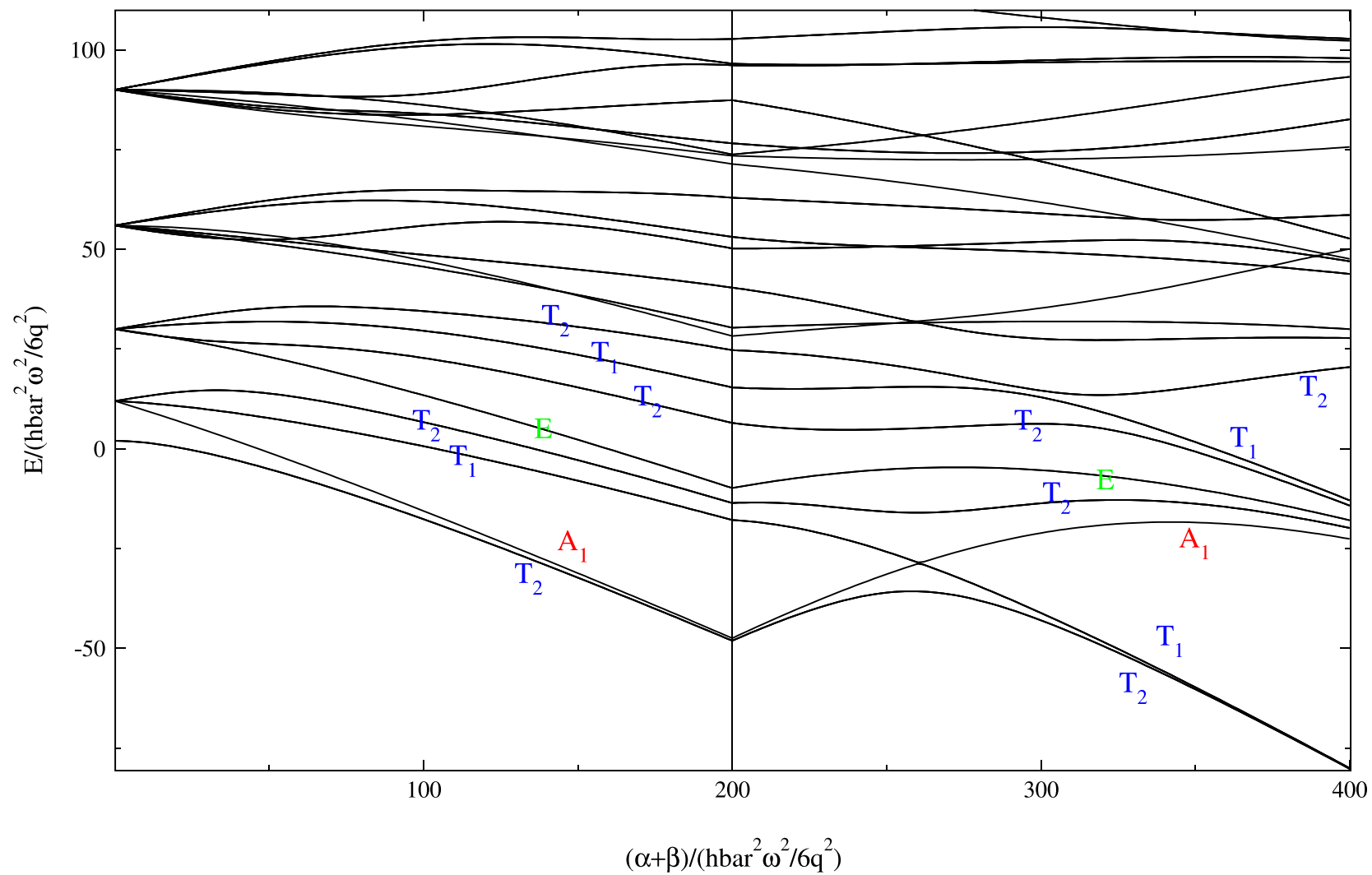
$$V_6(\theta, \phi) = Y_6^0 \sqrt{\frac{7}{2}} (Y_6^4 + Y_6^{-4})$$



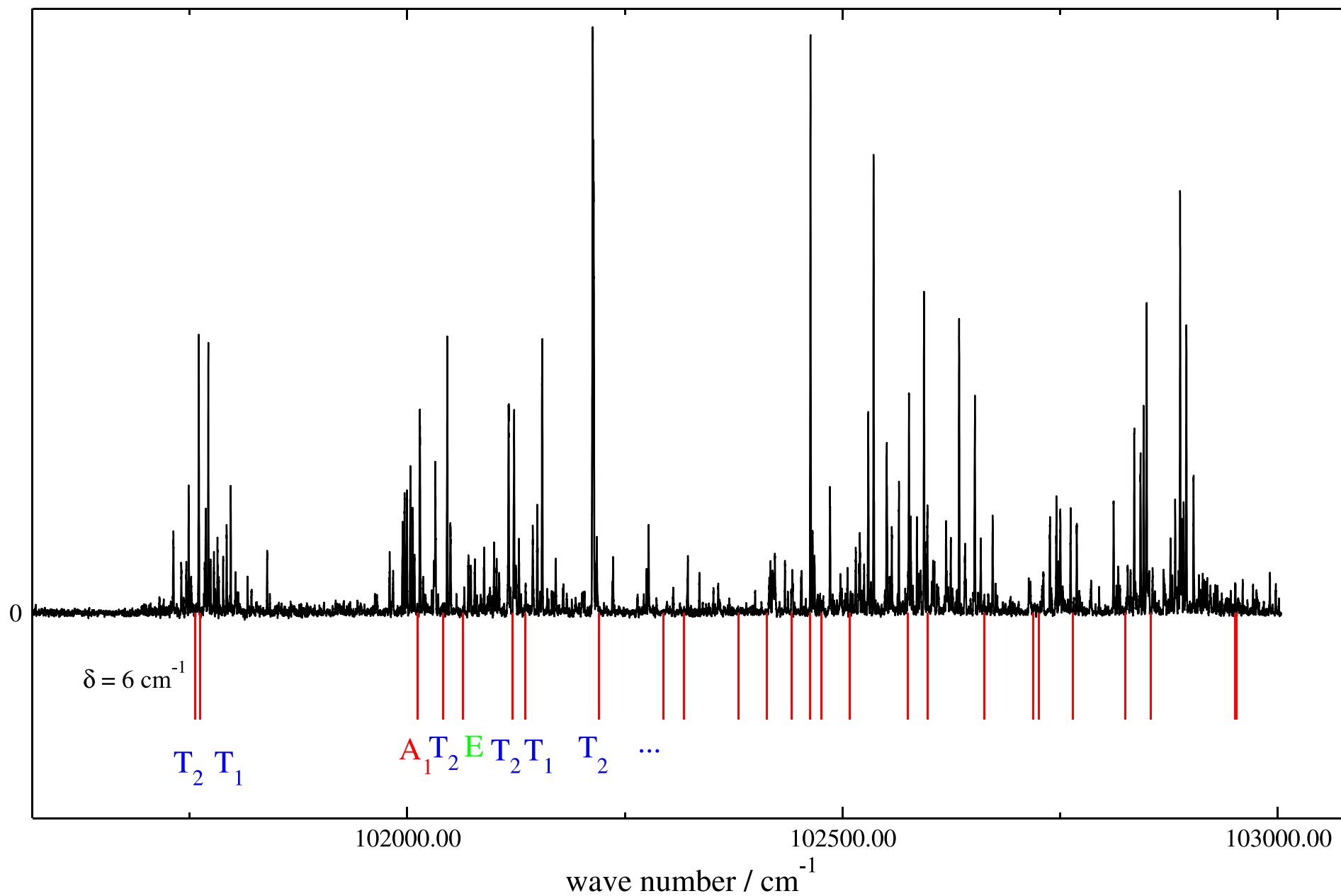
Linear coupling only



Linear + quadratic coupling

 C_{3v} minima C_{2v} minima

Two-dimensional vibronic calculation for the methane cation



Conclusions

Experiment

The symmetry (N^+ , $_{ve}$) of the lowest rovibronic levels of CH_4^+ has been determined experimentally.
The tunneling splitting in the rotationless ground state of the methane cation is determined to be $8.5(1) \text{ cm}^{-1}$.
The ionization potential of methane is determined to be $101753(1) \text{ cm}^{-1}$.

Rovibronic calculations with an effective Hamiltonian

The effect of the geometric phase on the rotational structure has been established for the first time.
This calculation enabled the complete assignment of the origin band of the PFI-ZEKE-PE spectrum.

2D vibronic calculations on a sphere

The Jahn-Teller vibronic problem in the ground state of CH_4^+ has been solved in 2 dimensions.
These calculations describe the large-amplitude motion of the hydrogen atoms in CH_4^+ .

Acknowledgments

Prof. Mark Child
Prof. Jon T. Hougen



Transformation to an adiabatic basis:

$$\begin{array}{rcccccc}
 x' & \cos & \cos & \cos & \sin & \sin & x \\
 y' & & \sin & & \cos & 0 & y \\
 z' & \sin & \cos & \sin & \sin & \cos & z
 \end{array}$$

$$|z'\rangle = \sin \cos |x\rangle + \sin \sin |y\rangle + \cos |z\rangle$$

Properties under inversion: q's remain unchanged, electronic ket changes sign

$$\hat{T}_{vib}(\mathbf{r}, \mathbf{q}) = E_{vib}(\mathbf{r}, \mathbf{q}) - Y_l^m(\mathbf{r}, \mathbf{q}) \left| z' \right\rangle_{vib}$$

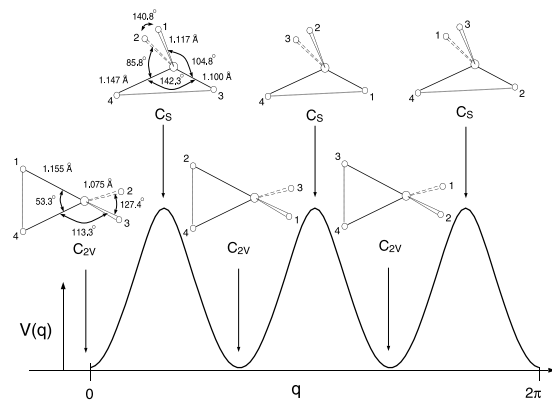
ψ_{ve} should be single-valued in parameter space.

Since ψ_{el} changes sign upon inversion ψ_{vib} must also change sign.

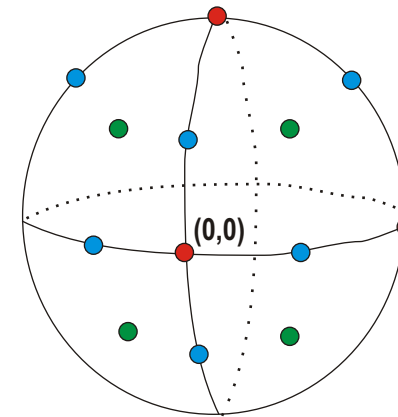
--> Only odd values of l are allowed

Comparison with one-dimensional model:

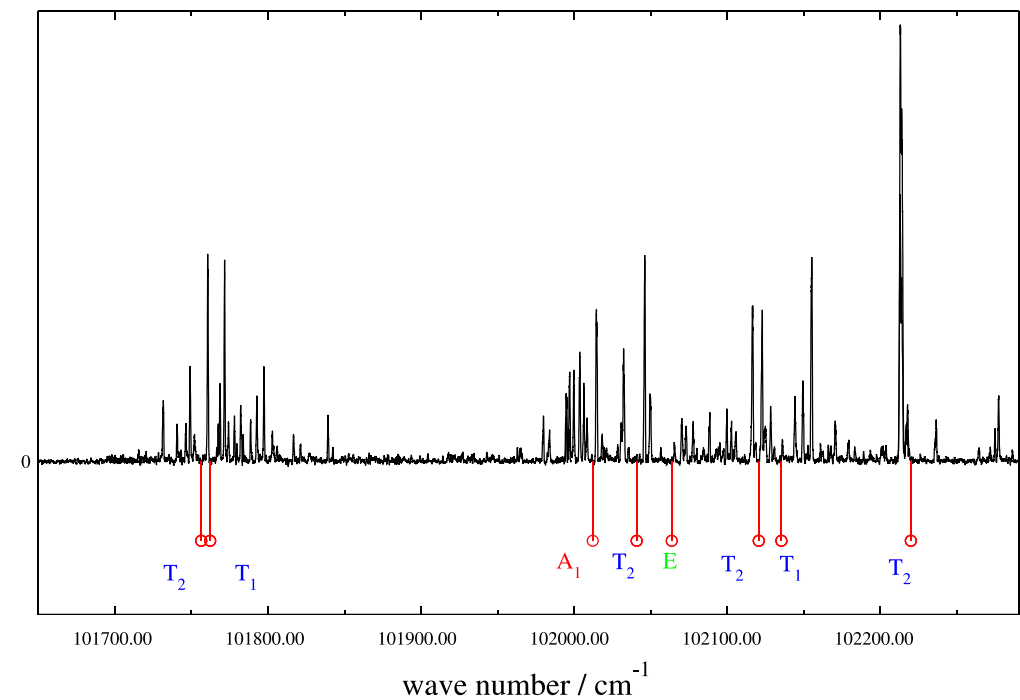
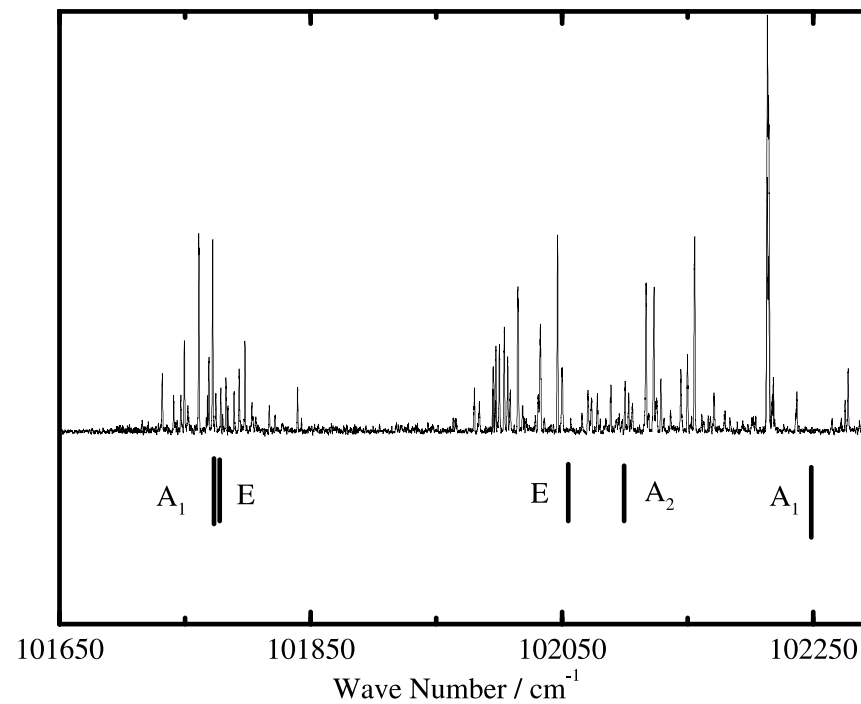
1D



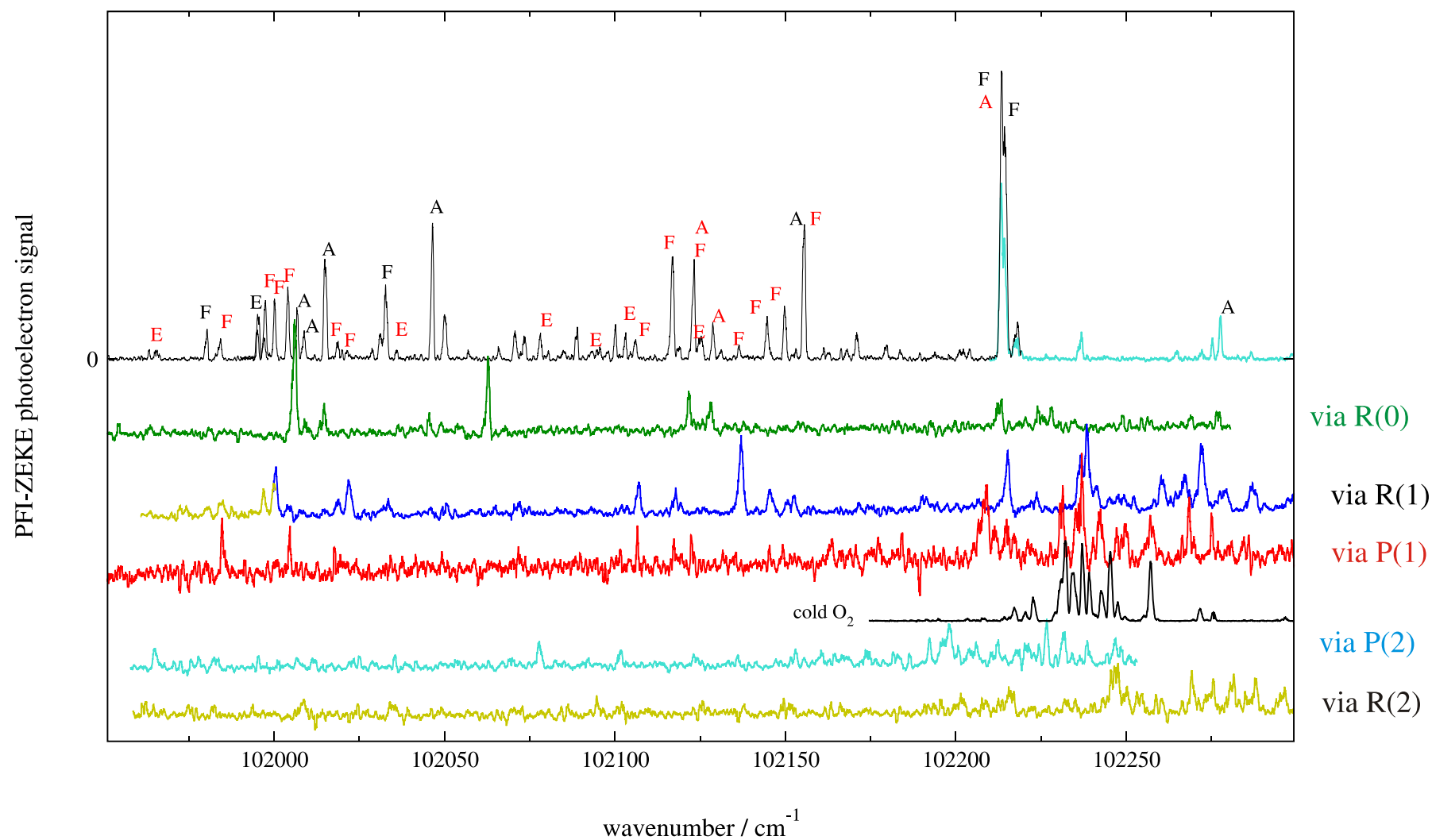
2D



Electron Signal (arb. units)



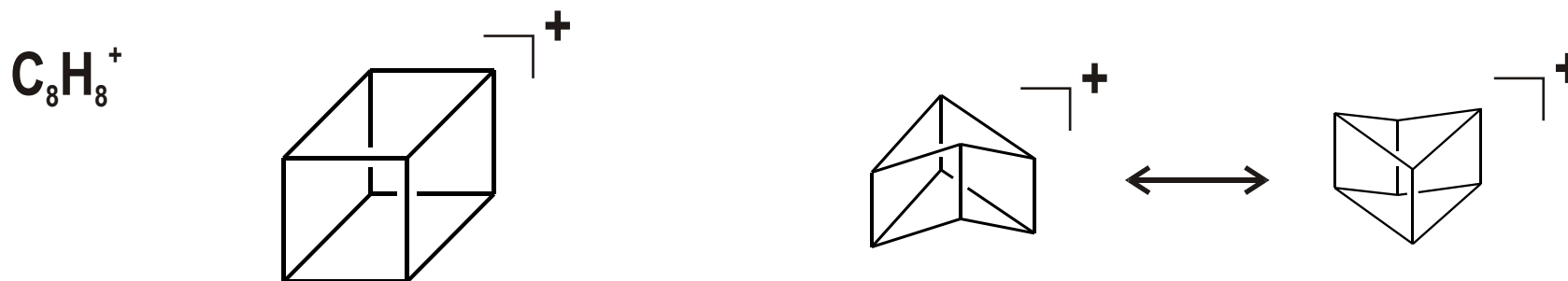
Outlook : understanding the higher vibronic states



Other molecular ions exhibiting the T e t) Jahn-Teller effect

H_4^+ in T_d configuration

SiH_4^+ : C_s symmetrical minimum predicted (JT + PJT effect) : Frey and Davidson, JCP, 89,4227(1988)



Further applications of the theoretical model

Charged fullerenes have T,G,H electronic states interacting with g and h modes.

Some of the problems (e.g. T h in C_{60}^-) are very similar to T e+t ;

C_{60}^{3-} is believed to be responsible for the superconducting properties of K_3C_{60} and Rb_3C_{60} .

C_{60}^+ is probably a G (g+h) problem and is experimentally almost unexplored...

Columbus, 21.06.2006

The methane cation