# Molecular vibrations and molecular electronic spectra

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# A) VIBRATIONAL STRUCTURE IN ELECTRONIC SPECTRA

## A.1) The Born-Oppenheimer approximation [1]

Schrödinger equation for coupled electronic and nuclear motions:

$$H = H_{el} + T_K$$

$$H_{el} = T_{el} + U(x, Q)$$

$$H_{el}\phi_n(x, Q) = V_n(Q)\phi_n(x, Q) \qquad \text{(assume solved)}$$

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

$$\Psi(x, Q) = \sum_m \chi_m(Q)\phi_m(x, Q)$$

$$\boxed{[T_K + V_n(Q) - E]\chi_n(Q) = \textstyle\sum_m \Lambda_{nm}\chi_m(Q)}$$

$$\boxed{\Lambda_{nm} = \textstyle\sum \frac{\hbar^2}{M_i} \int d^{3N}x\phi_n^*(\frac{\partial\phi_m}{\partial Q_i})\frac{\partial}{\partial Q_i} - \int d^{3N}x\phi_n^*(T_K\phi_m)}$$

$x$ and $Q$ denote the sets of electronic and nuclear coordinates, respectively. Correspondingly $\phi$ and $\chi$ stands for the electronic and nuclear wave functions.

# Derivation of the coupled equations

For simplicity, put

$$T_K = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial Q^2}$$

$$\sum \left(T_{el} + U + T_K\right)\chi_m(Q)\phi_m(x,Q) = \sum E\chi_m(Q)\phi_m(x,Q)$$

$$\sum \left[V_m(Q) + T_K\right]\chi_m(Q)\phi_m(x,Q) = \sum E\chi_m(Q)\phi_m(x,Q)$$

$$\begin{aligned}\sum \quad & \left\{\left[V_m(Q) - E + T_K\right]\chi_m(Q)\right\}\phi_m(x,Q) = \\ & \sum_m \frac{\hbar^2}{M}\left(\frac{\partial\chi_m}{\partial Q}\right)\left(\frac{\partial\phi_m}{\partial Q}\right) - \sum_m \chi_m\left(T_K\phi_m\right)\end{aligned}$$

$$\begin{aligned}\int \phi_n^* d^{3N}x : \quad & \left(V_n + T_K - E\right)\chi_n = \\ & = \sum_m \frac{\hbar^2}{M}\int \phi_n^* \frac{\partial\phi_m}{\partial Q}\frac{\partial\chi_m}{\partial Q} d^{3N}x \\ & - \sum_m \chi_m \int \phi_n^*\left(T_K\phi_m\right)d^{3N}x \\ & = \sum_m \Lambda_{nm}\chi_m \ .\end{aligned}$$

So far still formally exact. Approximation: put

$$\boxed{\Lambda_{nm} = 0}$$

$$\Longrightarrow [T_K + V_n(Q) - E]\chi_n(Q) = 0 \ .$$

It follows:

- (Electronic) eigenvalues, $V_n(Q)$, of a given state correspond to the potential energy hypersurface for the nuclear motion.
- Total molecular wavefunction becomes a product of a nuclear and electronic wave function:

$$\Psi(x, Q) = \chi_n(Q)\phi_n(x, Q)$$

- Valid, e.g., when $\phi_n(x, Q) \approx \phi_n(x - Q)$.
- BO approximation!

Electrons follow the nuclear motion instantaneously (adiabatic), due to the large ratio between nuclear and electronic masses (i.e. the large effective mass of a nucleus compared to that of an electron $M \gg m_{el}$).

# Simple estimates for hierarchy of energy scales

$$E_{el} \sim < T_{el} > \sim \frac{\hbar^2 \kappa_{el}^2}{m} \sim \frac{\hbar^2}{md^2}$$

with $d \approx$ molecular dimension.

$$E_{vib} \;\sim\; \hbar\sqrt{\frac{f}{M}} \quad mit \quad f \sim \frac{\partial^2 E_{el}}{\partial R^2} \sim \frac{E_{el}}{d^2}$$

$$\Longrightarrow E_{vib} \sim \hbar^2\sqrt{\frac{1}{Mmd^4}} \;=\; \sqrt{\frac{m}{M}}\frac{\hbar^2}{md^2} = \sqrt{\frac{m}{M}}\,E_{el}$$

$$E_{rot} \;\sim\; < T_{rot} > \;\sim\; \frac{\hbar^2}{I} \;=\; \frac{\hbar^2}{Md^2} = \frac{m}{M}\,E_{el}$$

$$\boxed{\Longrightarrow \quad E_{rot} \;\ll\; E_{vib} \;\ll\; E_{el}}$$

Larger electronic energy scale, shorter time scale of the oscillations (for non-stationary states).

$$\Downarrow$$

Similar to classical picture; fast readjustment of electrons to nuclear changes.

## Analogous for relative nuclear displacements

$$< R^2 > \sim \frac{\hbar}{M\omega} < Q^2 > \sim \frac{\hbar^2}{M E_{vib}} \left( \frac{\hbar}{\sqrt{fM}} \right)$$

$$\kappa = \frac{\sqrt{< R^2 >}}{d} \sim \frac{\hbar}{d\sqrt{M}\hbar} \sqrt[4]{Mmd^4} = \sqrt[4]{m/M}$$

## ... and for nonadiabatic coupling elements

$$\begin{aligned}
< \Lambda_{nm} > \ &\sim \ \frac{\hbar^2}{M} < \frac{\partial^2}{\partial R^2} >_{el} + \frac{\hbar^2}{M} < \frac{\partial}{\partial R} >_{el} < \frac{\partial}{\partial R} >_{vib} \\
&\sim \ \frac{\hbar^2}{M} k_{el}^2 + \frac{\hbar^2}{M} k_{el} \sqrt{\frac{Mw}{\hbar}} < \frac{\partial}{\partial Q} >_{vib} \\
&\sim \ \frac{\hbar^2}{Md^2} + \frac{\hbar^2}{Md} \sqrt{\frac{\sqrt{fM}}{\hbar}} \\
&\sim \ \frac{m}{M} E_{el} + \frac{\hbar^2}{M^{\frac{3}{4}} d} \quad \sqrt[4]{\frac{\hbar^2}{md^2\hbar^2 d^2}} \\
&\sim \ \frac{m}{M} E_{el} + \frac{\hbar^2}{M^{\frac{3}{4}} d^2 m^{\frac{1}{4}}} \frac{m^{\frac{3}{4}}}{m^{\frac{3}{4}}} \\
&\sim \ \frac{m}{M} E_{el} + \left( \frac{m}{M} \right)^{\frac{3}{4}} E_{el}
\end{aligned}$$

$$\boxed{E_{rot} \approx Term(\partial^2/\partial R^2) \ll Term(\partial/\partial R) \ll E_{vib}}$$

$$\kappa^4 \qquad\qquad \kappa^4 \qquad\qquad \kappa^3 \qquad\qquad\qquad \kappa^2 \quad \times E_{el}$$

# Hellmann-Feynman relation

Re-writing the non-adiabatic (derivative) coupling terms:

$$\frac{\partial H_{el}}{\partial Q_i}\phi_n(x,Q) + H_{el}\frac{\partial \phi_n(x,Q)}{\partial Q_i} =$$
$$\frac{\partial V_n(Q)}{\partial Q_i}\phi_n(x,Q) + V_n(Q)\frac{\partial \phi_n(x,Q)}{\partial Q_i}$$

Multiplying from the left by $\phi_m^*$ and integrating over the electronic coordinates, $x$, leads to:

$$\langle\phi_m(Q)|\frac{\partial H_{el}}{\partial Q_i}|\phi_n(Q)\rangle_x + V_m(Q)\langle\phi_m(Q)|\frac{\partial \phi_n(Q)}{\partial Q_i}\rangle_x =$$
$$= \langle\phi_m(Q)|\frac{\partial V_n(Q)}{\partial Q_i}|\phi_n(Q)\rangle_x + V_n(Q)\langle\phi_m(Q)|\frac{\partial \phi_n(Q)}{\partial Q_i}\rangle_x$$

$n = m$ : $\qquad \langle\phi_n(Q)|\frac{\partial H_{el}}{\partial Q_i}|\phi_n(Q)\rangle_x = \frac{\partial V_n(Q)}{\partial Q_i}$

$n \neq m$:

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

In the vicinity of a degeneracy the derivative couplings can *diverge* and the adiabatic approximation is expected to break down!

# Harmonic oscillator and its eigenfunctions

The Hamiltonian of a quantum harmonic oscillator is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu}\,\frac{\partial^2}{\partial r^2} + \frac{1}{2}\,f\,r^2$$

Using the relationship between dimensioned ($r$) and dimensionless coordinates ($Q$),

$$\boxed{Q = \sqrt{\tfrac{\mu\ \omega}{\hbar}}\ r; \quad \omega = \sqrt{\tfrac{f}{\mu}}}$$

we get

$$\boxed{\hat{H} = \tfrac{\hbar\ \omega}{2}\left(-\tfrac{\partial^2}{\partial Q^2} + Q^2\right)}$$

The eigenfunctions of the harmonic oscillator involve the well-known Hermite polynomials and read as

$$\boxed{\Psi_n(Q) = \left\{\sqrt{\pi}\ n!\ 2^n\right\}^{-\frac{1}{2}}\ e^{-\frac{Q^2}{2}}\ H_n(Q)}$$

The first Hermite polynomials, $H_n(Q)$, are

$$H_0(Q) = 1, \qquad H_1(Q) = 2\,Q, \qquad H_2(Q) = 4\,Q^2 - 2.$$

One can identify the meaning of the Q coordinates: the displacement is measured in units of the so-called zero-point amplitude, i.e.,

$$\Psi_0(1) = e^{-\frac{1}{2}}\ \Psi_0(0)$$

## A.2) The Franck-Condon principle

Consider the transition between different electronic states, particularly, a transition from the electronic ground state , GS, to one of the excited states, ES (optical, UV-absorption).

The transition probability follows from first order time-dependent perturbation theory;

$$I(\omega_{ph}) \sim \sum_F |\langle \Psi_F | H_1 | \Psi_I \rangle^2 \delta(E_F - E_I - \hbar\omega_{ph})$$

where $\Psi_I$ and $\Psi_F$ are eigenfunctions of $H_0$ (isolated molecule) and correspond to the initial and final states during a transition.

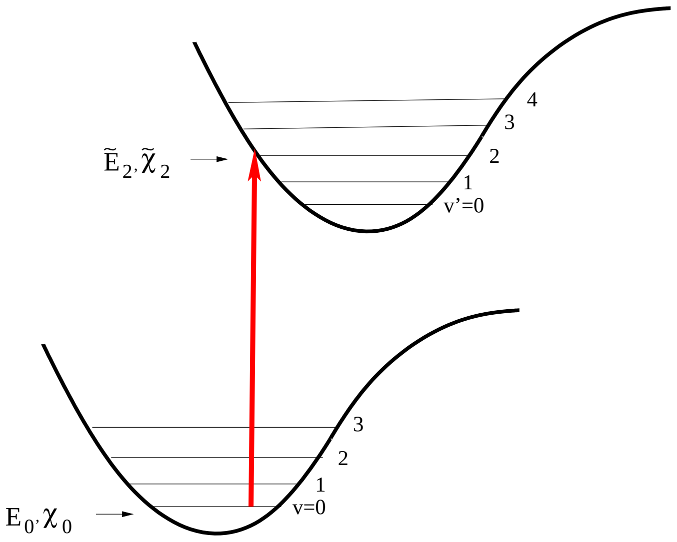
Interaction between the molecule and radiation field in the dipole approximation:

$$H_1(t) \sim -\sum_{j=1}^{N} e(\vec{\varepsilon}.\vec{r_j})E_0(t)$$

In contrast to the IR-spectrum the summation index, j, runs only over electronic coordinates (orthogonality of the electronic wave functions).

Within the Born-Oppenheimer approximation the wave functions are written in a product form;

$$\Psi_I = \phi_i \chi_v; \qquad \Psi_F = \phi_f \tilde{\chi}_{v'}$$



with

$$(T_k + V_i - E_v)\chi_v = 0$$
$$(T_k + V_f - \tilde{E}_{v'})\tilde{\chi}_{v'} = 0$$

Note that $\chi_v$ and $\tilde{\chi}_{v'}$ are vibrational functions of different potential energy curves.

Evaluate the matrix elements in the Born-Oppenheimer approximation;

$$\int \Psi_F^*(x,Q) H_1 \Psi_I(x,Q) d^{3N}x dQ =$$
$$= \int \tilde{\chi}_{v'}^*(Q) \underbrace{\int \phi_f^*(x,Q) H_1 \phi_i(x,Q) d^{3N}x}_{} \chi_v(Q) dQ$$

The integral $T_{fi}(Q) = \int \phi_f^*(x,Q) H_1 \phi_i(x,Q) dx$ is called the *electronic transition moment* or dipole-transition-(matrix) element. It replaces the dipole moments (=diagonal matrix elements) evaluated in IR-spectroscopy. Therefore, one can write the matrix elements as follows:

$$\int \Psi_F^* H_1 \Psi_I dx dQ = \int \tilde{\chi}_{v'}^*(Q) T_{fi}(Q) \chi_v(Q) dQ$$

The transition moment depends on $Q$ only through the electronic wave function. If the transition moment depends sufficiently weakly on $Q$, one can write;

$$T_{fi}(Q) \approx T_{fi}(Q=0)$$

with an appropriate reference geometry, $Q = 0$. It is natural to choose (mostly) the reference geometry to be the equilibrium geometry of the molecule in the initial state:

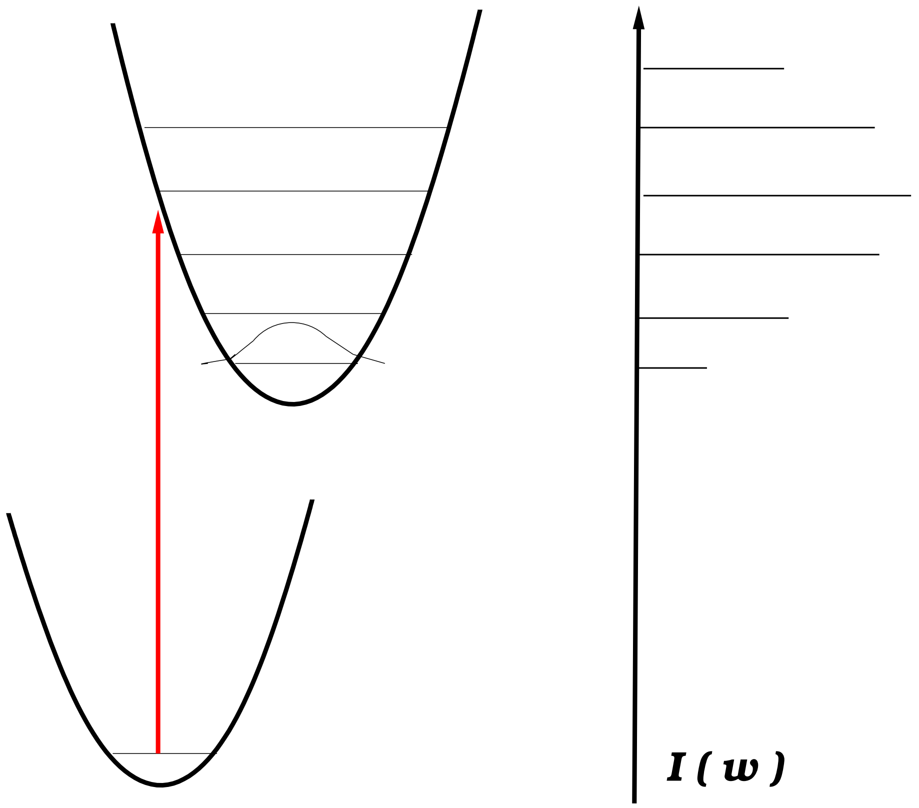
*Condon approximation* or *Franck-Condon principle*.

In the Condon approximation:

$$\int \Psi_F^* H_1 \Psi_I dx dQ = T_{fi}(Q=0) S_{v'v}$$

with $$S_{v'v} = \int \tilde{\chi}_{v'}^*(Q) \chi_v(Q) dQ.$$

$S_{v'v}$ and its square are *Franck-Condon overlap integral* and *Franck-Condon factor*, respectively (see also [2]).



The spectrum follows immediately:

$$\boxed{I(\omega_{ph}) \sim |T_{fi}(Q=0)|^2 \sum_{v'} |S_{v'v}|^2 \delta(\tilde{E}_{v'} - E_v - \hbar\omega_{ph})}$$

The relative intensities are determined only through vibrational wave functions, electronic wave functions play almost no role.

Principle of vertical transitions !

## A.3) Shifted harmonic oscillator

Important special case: harmonic potentials with the same curvature (force constant).

Define $Q$ as the dimensionless normal coordinate of initial state (mostly, electronic ground state).

$V_i(Q) = \frac{\omega}{2}Q^2 \qquad (\hbar = 1)$

With the same curvature (force constant) for $V_f(Q)$, we have

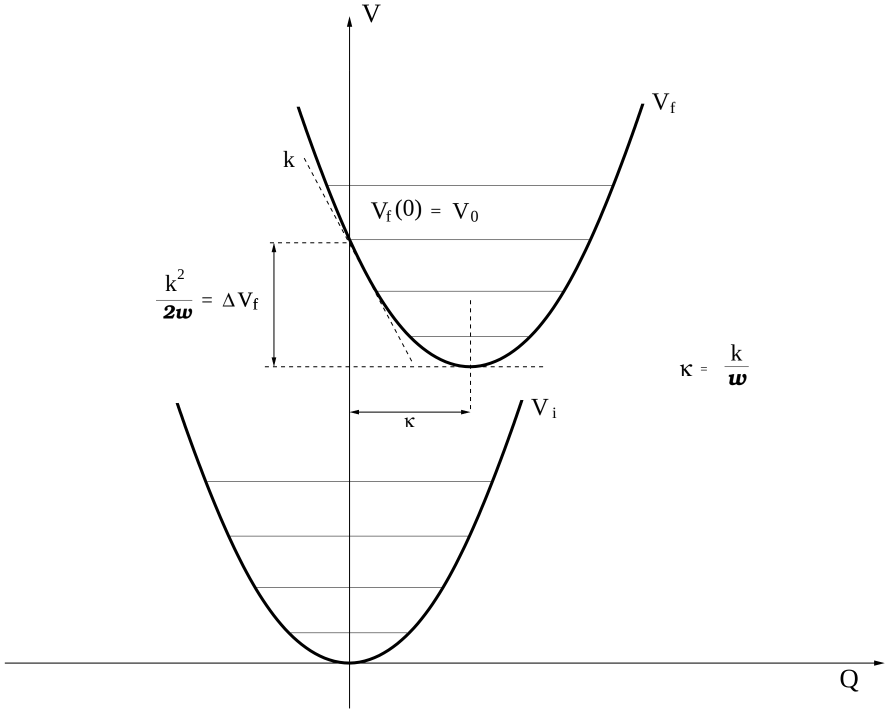
$$V_f(Q) = V_f(Q=0) + \frac{\omega}{2}Q^2 + kQ$$

with $k = \left(\frac{\partial V_f}{\partial Q}\right)_{Q=0}$ ; $V_f(Q=0) \equiv V_0$

The *linear coupling* leads to a shift in the equilibrium geometry and a stabilization energy along the distortion (see next Fig).
The oscillator can be easily solved by adding the quadratic terms (completing the square);

$$V_f(Q) = V_0 + \frac{\omega}{2}\left(Q + \frac{k}{\omega}\right)^2 - \frac{k^2}{2\omega}$$

$$= V_0 - \underset{\substack{\uparrow \\ \text{Stokes-shift}}}{\frac{k^2}{2\omega}} \; ; \; + \frac{\omega}{2}\underset{\substack{\uparrow \\ \text{New normal coordinate}}}{Q'^2}$$



Note: $\frac{\partial}{\partial Q} = \frac{\partial}{\partial Q'} \Longrightarrow$ same eigenfunctions $\Longrightarrow$

$$S_{v'v} = N_{v'}N_v \int_{-\infty}^{\infty} dQ H_{v'}\left(Q+\frac{k}{\omega}\right) H_v(Q) e^{-\frac{Q^2}{2}} e^{-\frac{1}{2}(Q+k/\omega)^2}$$

We restrict ourselves to the special case where $v = 0$. By substituting $Q' = Q + \kappa$ and $\kappa = k/\omega$, one can easily obtain:

$$S_{v'0} = N_{v'}N_0 \int_{-\infty}^{\infty} dQ' H_{v'}\left(Q'\right) e^{-Q'^2} e^{\kappa Q' - \frac{1}{2}\kappa^2}$$

There are several possibilities to evaluate these integrals, such as the method of generating functions (see exercises) or operator algebra (occupation number representation of harmonic oscillator).

# Summary of the shifted harmonic oscillator

$$P(E_{ph}) = \sum_{\upsilon} \frac{a^{\upsilon}}{\upsilon!} e^{-a} \delta(E_{ph} - V_0 + a\omega - \upsilon\omega)$$

where $a = \kappa^2/2 = k^2/(2\omega^2)$

*Sum rule:*

$$\sum_{\upsilon} |S_{\upsilon 0}|^2 = e^{-a} \sum_{\upsilon} \frac{a^{\upsilon}}{\upsilon!} = e^{-a} e^{+a} = 1$$

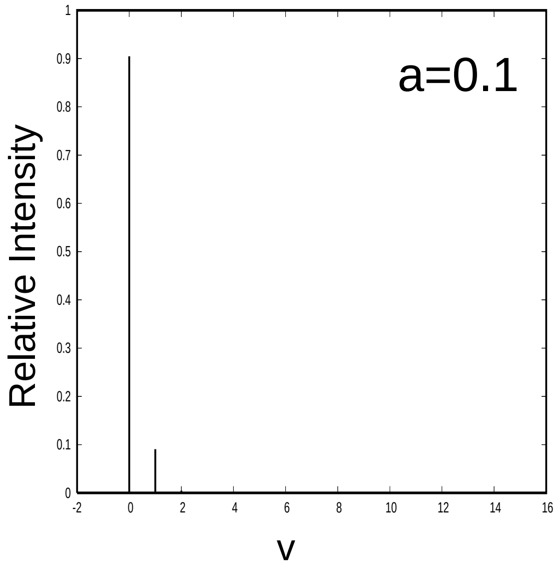
*Mean quantum number:*

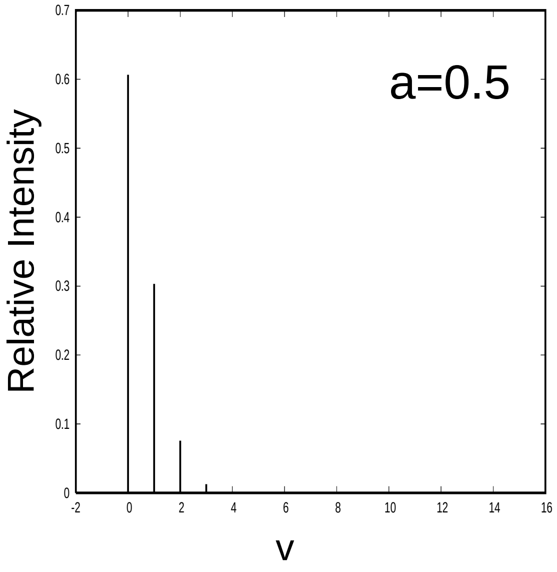
$$\bar{\upsilon} = \sum_{\upsilon} \frac{a^{\upsilon}\, \upsilon}{\upsilon!} e^{-a} = a \sum_{\upsilon>0} \frac{a^{\upsilon-1}}{(\upsilon-1)!} e^{-a} = a$$

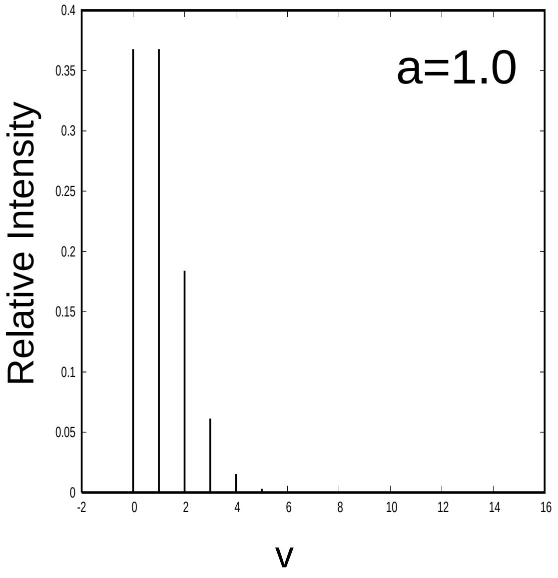
The parameter $a$ is a measure of the vibrational excitation in an electronic transition.
$a\omega$ is the mean vibrational energy during the transition ( = Stokes-shift $k^2/(2\omega)$)

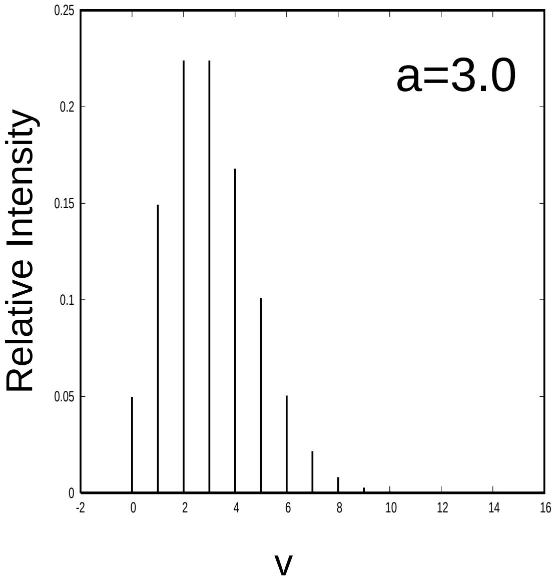
For $a \rightarrow 0$ we have $|S_{\upsilon 0}|^2 \longrightarrow \delta_{\upsilon 0}$, which means no excitation (potential curves $V_i$ and $V_f$ are identical).

# Poisson distributions for various values of the parameter $a$









*Intensity ratio:* $|S_{\upsilon+1,0}/S_{\upsilon,0}|^2 = \frac{a}{\upsilon+1}$

*Mean energy (center of gravity or centroid):*

$$\begin{aligned}
\bar{E} &= \int E P(E) dE \\
&= \sum (V_0 - a\omega + \upsilon\omega) \tfrac{a^\upsilon}{\upsilon!} e^{-a} \\
&= V_0 - a\omega + \omega \textstyle\sum_\upsilon \upsilon \tfrac{a^\upsilon}{\upsilon!} e^{-a} \\
&= V_0 - a\omega + \omega \textstyle\sum_\upsilon \tfrac{a^\upsilon}{(\upsilon-1)!} e^{-a} = V_0
\end{aligned}$$

*Energetic width:*

$$\begin{aligned}
(\Delta E)^2 &= \overline{(E-\bar{E})^2} = \overline{E^2} - \overline{\bar{E}^2} \\
&= \textstyle\sum_\upsilon (\upsilon - a)^2 \omega^2 \tfrac{a^\upsilon}{\upsilon!} e^{-a} \\
&= \textstyle\sum \{\upsilon(\upsilon-1) + \upsilon - 2a\upsilon + a^2\} \omega^2 \tfrac{a^\upsilon}{\upsilon!} e^{-a} \\
&= \textstyle\sum \omega^2 \tfrac{a^\upsilon}{(\upsilon-2)!} e^{-a} + (a - 2a^2 + a^2)\omega^2 \\
&= (a^2 + a - a^2)\omega^2 = a\omega^2 = \tfrac{k^2}{2}
\end{aligned}$$

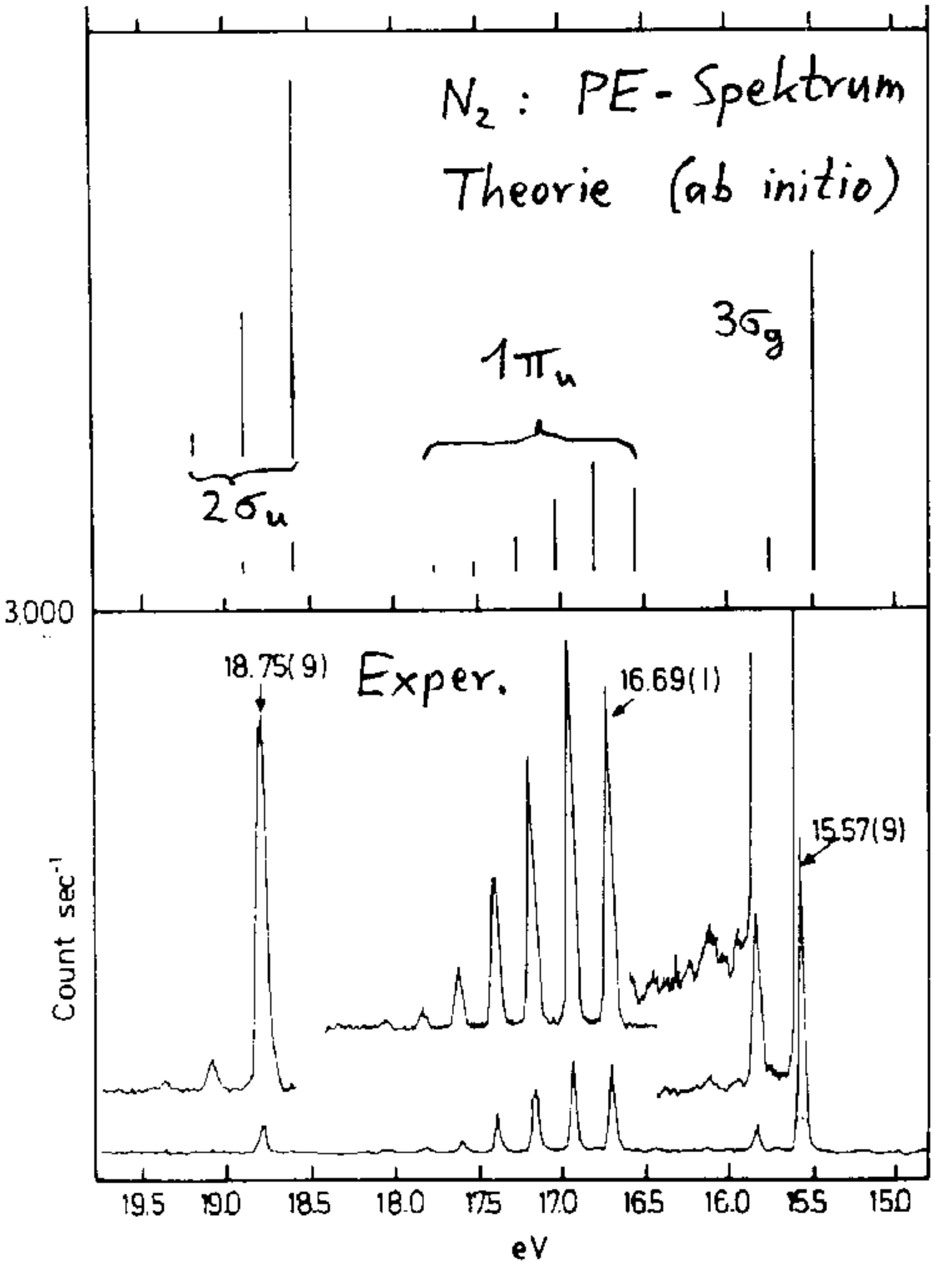
$$\Longrightarrow \boxed{\Delta E \sim \frac{k}{\sqrt{2}}}$$

Width is defined through the gradient of the final state, $V_f(Q)$, at $Q = 0$ (because of the finite extension of $\chi_0(Q)$).

# TESTS FÜR POISSON-VERTEILUNG

$$I_v = \frac{a^v}{v!} e^{-a} , \quad a = \frac{1}{2} \frac{k^2}{\omega^2}$$

$$\rightarrow \quad I_{v+1}/I_v = \frac{a}{v+1}$$



1π_u - Bande:

$a = 1.33$

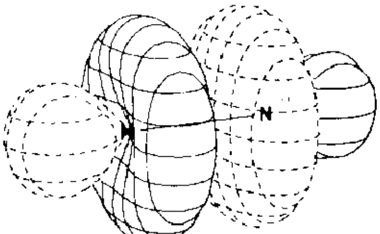
$$\frac{I_{v+1}}{I_v} (v+1) \approx$$

1.14, 1.38, 1.67, 1.60 ....

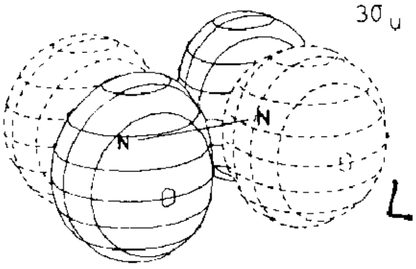
Cederbaum, Domcke, J. Chem. Phys. 60, 2878 ('74)

## 16. Nitrogen

Symmetry: $D_{\infty h}$

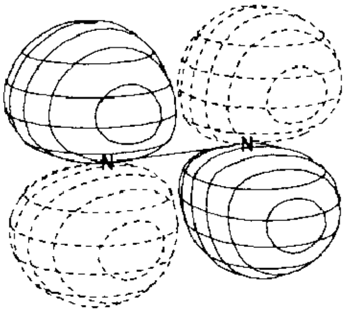


$3\sigma_u$ E= 1.2262



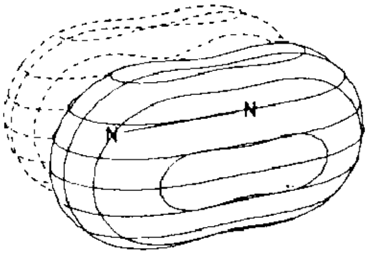
$1\pi_g$ E= 0.3002

LUMO

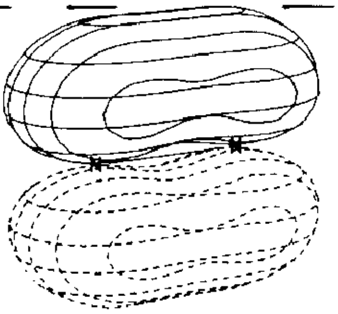


$1\pi_g$ E= 0.3002

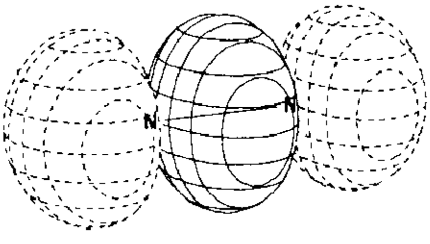
HOMO



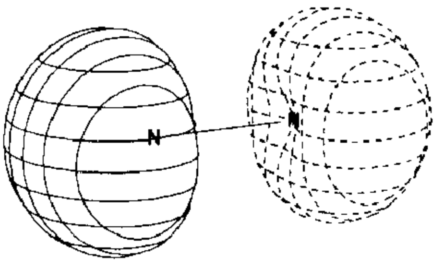
$1\pi_u$ E=-0.5454



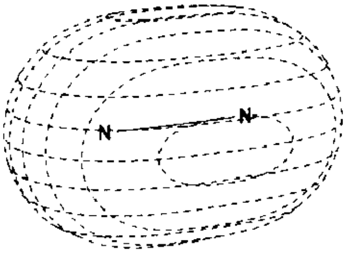
$1\pi_u$ E=-0.5454



$3\sigma_g$ E=-0.5555

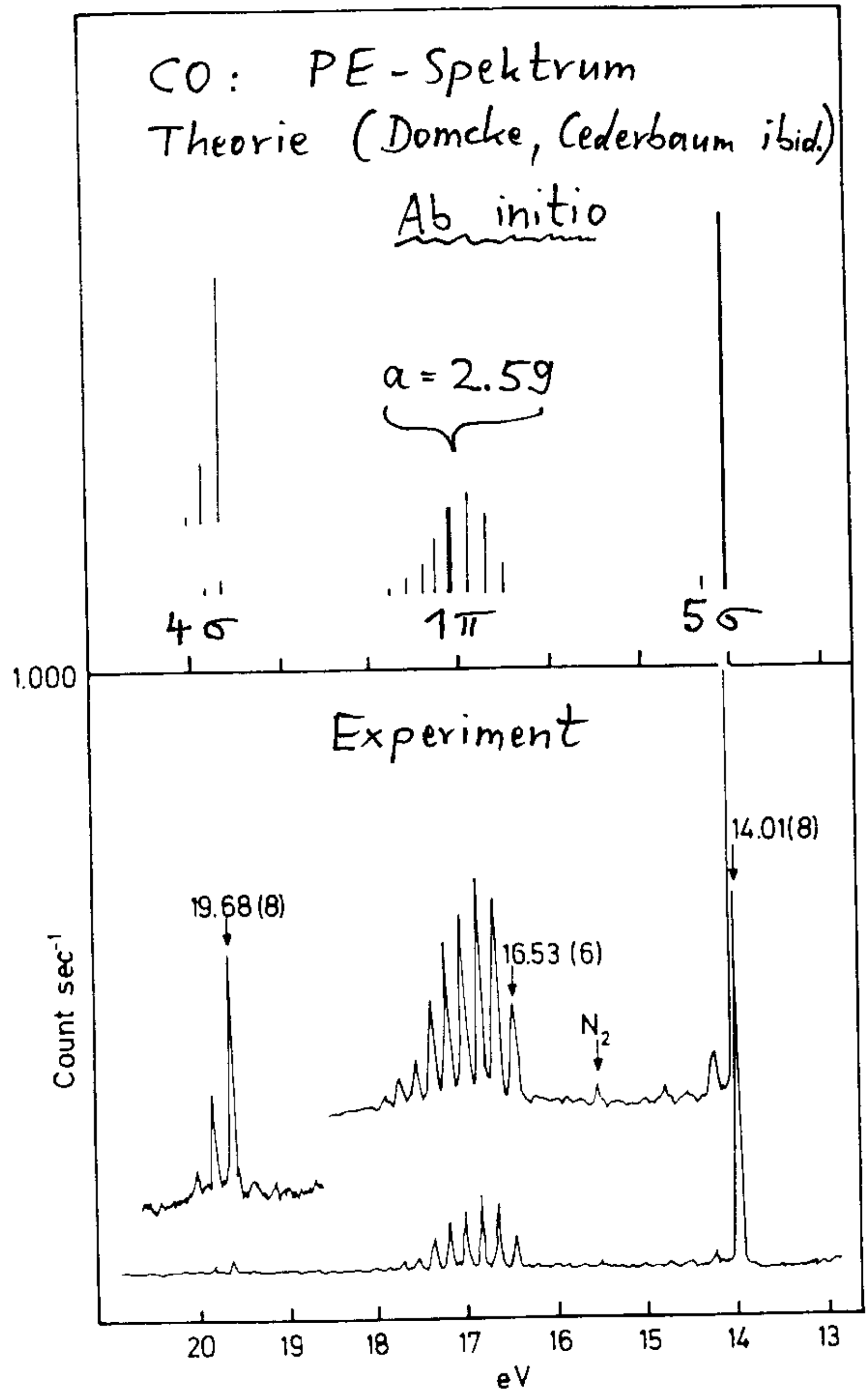


$2\sigma_u$ E=-0.7137



$2\sigma_g$ E=-1.4211

POISSON : $\underline{\dfrac{I_{v+1}}{I_v} = \dfrac{a}{v+1}}$



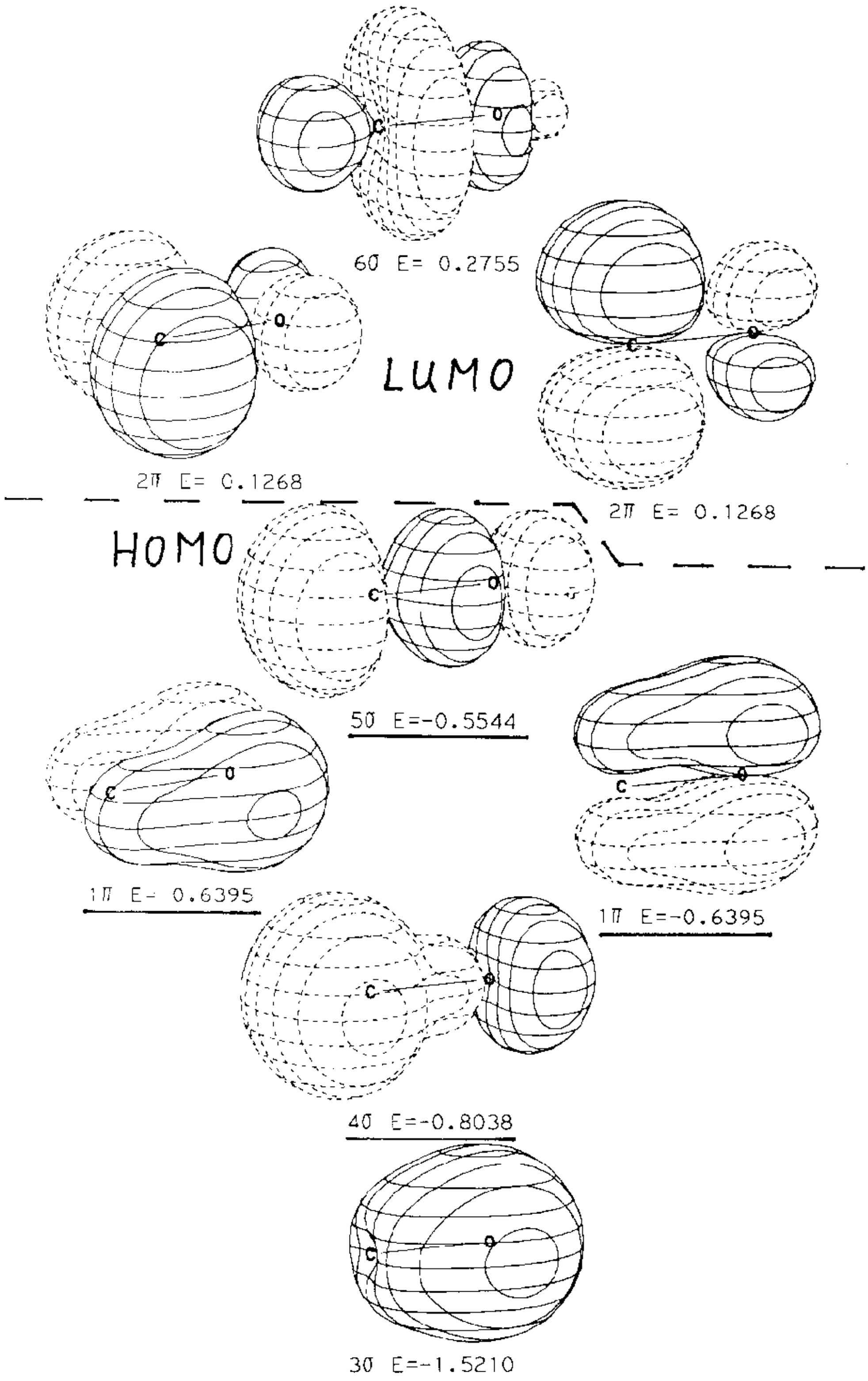
1π - Bande:

$\dfrac{I_{v+1}}{I_v}(v+1) \approx$

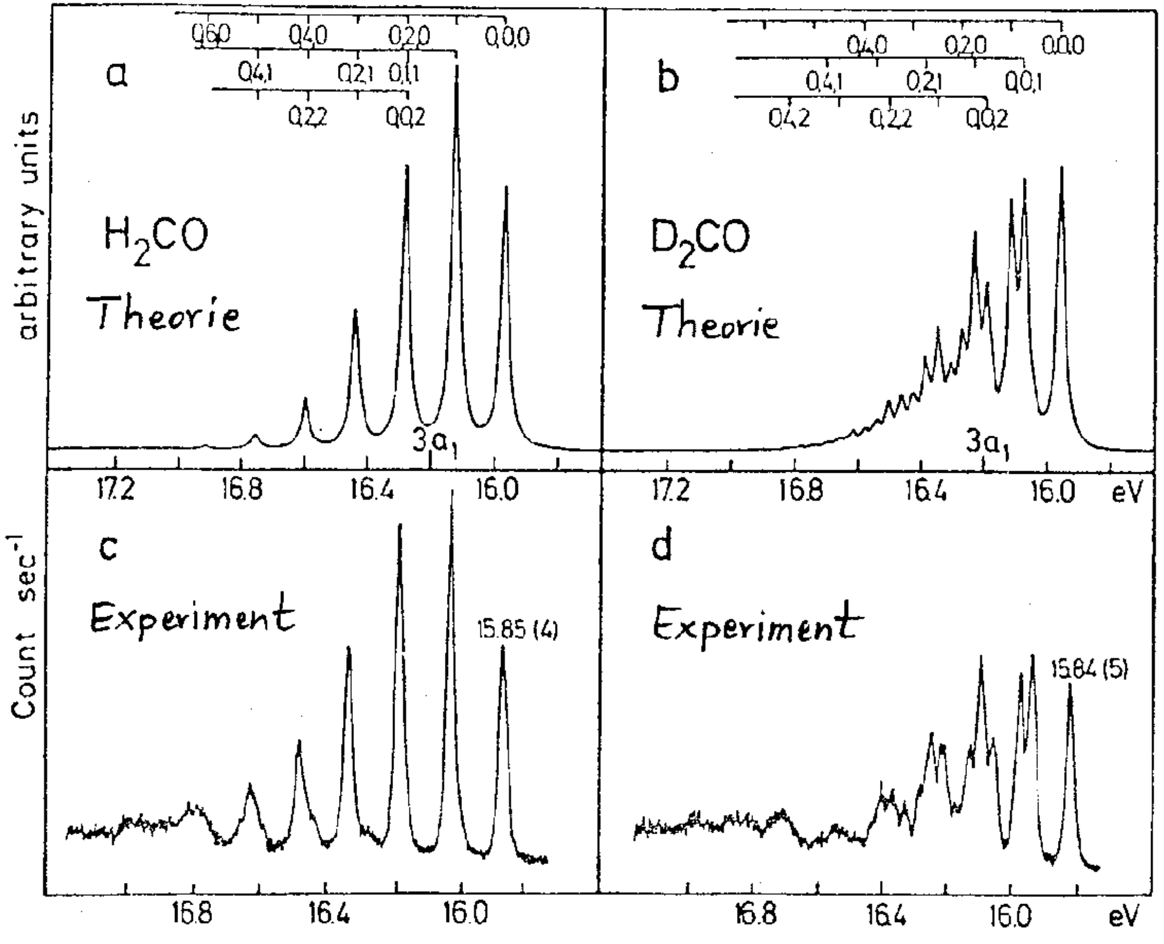
2.13, 2.19,
2.57, 3.47,
3.27, 2.82,
⋮

## 15. Carbon Monoxide

Symmetry: $C_{\infty v}$

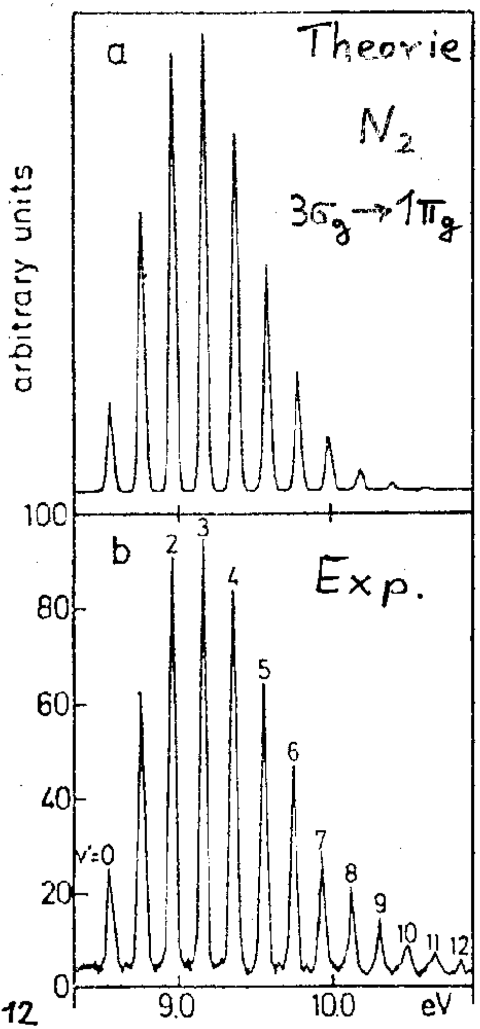


# Mehrmoden PE - Bande



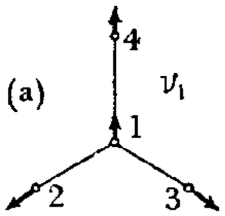
**Domcke, Cederbaum:** J. Chem. Phys., Vol. 64, No. 2, 15 January 1976, **612**

# Anregungsspektrum

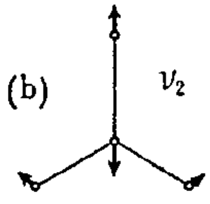


# Normalmoden eines (symm. plan.) $XYZ_2$-Moleküls

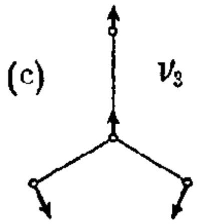
(Freq. für $H_2CO$)



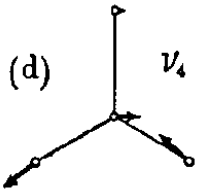
symm. C–H Streckmode
$\omega_1 = 2944\ \mathrm{cm}^{-1}$



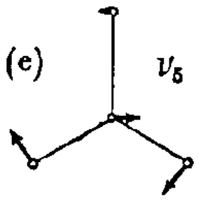
C–O Streckmode
$\omega_2 = 1764\ \mathrm{cm}^{-1}$



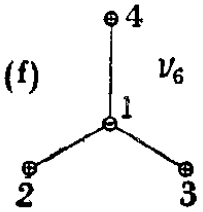
H-C-H Winkelschw.
$\omega_3 = 1563\ \mathrm{cm}^{-1}$



asymm. C–H Streckmode
$\omega_4 = 3009\ \mathrm{cm}^{-1}$



"C-O Winkelschw."
$\omega_5 = 1288\ \mathrm{cm}^{-1}$



Nichtplanare Deformationsmode
$\omega_6 = 1191\ \mathrm{cm}^{-1}$

## A.4) The frequency-modified harmonic oscillator

Non-totally symmetric modes : $\frac{\partial V_f(Q)}{\partial Q} = 0$

Next order in expansion: $V_f(Q) = V_f(0) + \frac{\gamma}{2}Q^2 + \frac{\omega}{2}Q^2$

New frequency : $\omega_f \equiv \hat{\omega} = \sqrt{\omega(\omega+\gamma)}$
New dimensionless normal coordinate:

$$\hat{Q} = \sqrt{\frac{\hat{\omega}}{\omega}}Q = \sqrt[4]{\frac{\omega+\gamma}{\omega}}Q$$

$$\Longrightarrow H_f = -\frac{\omega}{2}\frac{\partial^2}{\partial Q^2} + \frac{\omega+\gamma}{2}Q^2 \equiv -\frac{\hat{\omega}}{2}\frac{\partial^2}{\partial \hat{Q}^2} + \frac{\hat{\omega}}{2}\hat{Q}^2$$

One can find the Franck-Condon factors as follows:

$$\boxed{\begin{array}{l} |S_{0,2v+1}|^2 = 0 \\ |S_{0,2v}|^2 = \frac{2\sqrt{\omega\hat{\omega}}}{\omega+\hat{\omega}} \ \left(\frac{\hat{\omega}-\omega}{\hat{\omega}+\omega}\right)^{2v} \frac{(2v-1)!!}{2^v v!} \end{array}}$$

Example:

$\hat{\omega} = 2\omega \Longrightarrow$

$|S_{0,0}|^2 = \frac{\sqrt{8}}{3} \approx 0.94$, $|S_{0,2}|^2 \approx 0.05$, $|S_{0,2}|^2 \approx 0.004$

Only weak vibrational excitation !

# B) THE JAHN-TELLER EFFECT AND VIBRONIC INTERACTIONS

## B.1) The theorem of Jahn and Teller

**Theorem** (1937):
*'Any molecule in a spatially degenerate electronic state is unstable unless the degeneracy is accidental or the molecule is linear.'*

Or alternatively:
*'Any non-linear molecule undergoes distortion when its electronic state is degenerate by symmetry.'*

Remarks:
-Spin degeneracy is not considered.
-When the degeneracy comes from an orbital that contributes weakly to the bond, the distortion will be small.

In other words:
*'At the equilibrium geometry of a non-linear molecule the electronic state cannot be degenerate by symmetry.'*

Formal:
The instability comes from linear terms of the potential energy matrix, which are missing in the case of linear molecules.

Proof:

We will point out here just the basic ideas.

Principle: (Group theory)

Let $E_o$ be the energy of the equilibrium geometry in a degenerate electronic state, i.e., the geometry is optimized with respect to the totally symmetric modes:

$$\mathcal{H}_o \phi_l^o = E_o \phi_l^o \qquad \text{(e.g. } 1 \le l \le 3)$$

where $\mathcal{H}_o$ and $\phi_l^o$ are the Hamiltonian and the wavefunction of the system, respectively, in the high-symmetry situation.

Let us consider a small displacement, $\delta Q_r$, along the non-totally symmetric modes:

$$\mathcal{H}(\delta Q_r) = \mathcal{H}_o + \mathcal{H}_r \cdot \delta Q_r + \mathcal{O}(\delta Q_r^2)$$

$$E(\delta Q_r) = E_o + E_r \cdot \delta Q_r + \mathcal{O}(\delta Q_r^2)$$

with

$$\det \; |\langle \phi_l^o | \mathcal{H}_r | \phi_m^o \rangle - E_r \delta_{lm}| = 0$$

that is, $E_r$ are the eigenvalues of this secular equation.

The energy correction is negative for $\delta Q_r \longrightarrow -\delta Q_r$. The first-order contribution yields unstability. It vanishes when all the matrix elements are zero. Using the symmetry selection rules, the matrix elements are, therefore, non zero when:

$$\boxed{(\Gamma(\phi^o) \times \Gamma(\phi^o))_{sym} \times \Gamma(Q_r) \supset \Gamma_{A_1}}$$

where *sym* refers to the symmetrized direct product.

Group theory shows that the symmetrized direct product, $(\Gamma(\phi^o)\times\Gamma(\phi^o))_{sym}$, also contains non-totally symmetric representations.

## Jahn and Teller (1937):

In all molecular point groups, except for $C_{\infty v}$ and $D_{\infty h}$, there are non-totally symmetric modes that are contained in the symmetrized direct product of any degenerate irreducible representation.

Proof: Enumerative!
One considers the minimum number of equivalent points for all topologically distinct realisations of a point group and its irreducible representations.

**Examples:**

1. Linear Molecules, $C_{\infty v}$ and $D_{\infty h}$:

   For all the degenerate irreducible representations, $E_1(=\Pi), E_2(=\Delta), \cdots, E_k$,

   $$\boxed{(E_k)^2 = A_1 + E_{2k}}$$

   Let us consider the irreducible representation corresponding to the bending mode:

   $$\boxed{\Gamma(Q_2) = E_1(=\Pi)}$$

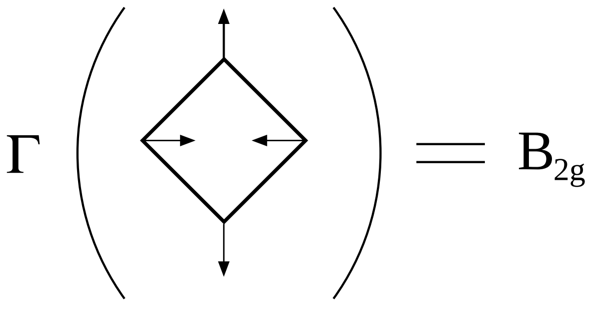
   so that $(E_k)^2 \times \Gamma(Q_2) \not\supset \Gamma_{A_1} \quad \Longrightarrow$
   no linear coupling terms are possible.

2. Planar X$_4$-systems, $D_{4h}$:

   Two doubly-degenerate irreducible representations,

   $$\boxed{(E_g)^2 = (E_u)^2 = A_{1g} + B_{1g} + B_{2g}}$$

   The following vibrational mode transforms like $B_{2g}$.

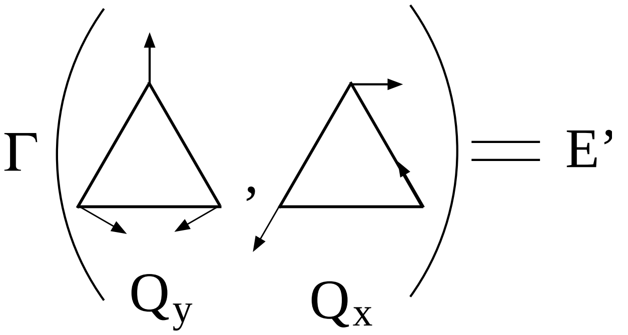


## 3. Planar X$_3$-systems, $D_{3h}$:

Two doubly-degenerate irreducible representations

$$\boxed{(E')^2_{sym} = (E'')^2 = A' + E'}$$

The following normal mode transforms like $E'$.

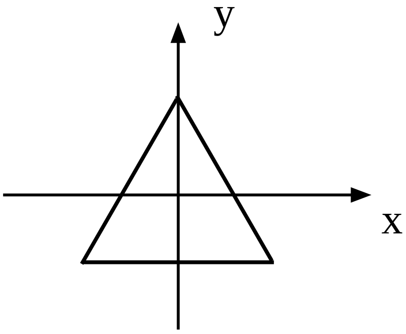


Comments:

Most of the Jahn-Teller active modes are degenerate, cf., $D_{3h}$. The tetragonal point groups are, however, exceptions: $C_4$, $C_{4v}$, $C_{4h}$, $D_4$, $D_{4h}$, $S_4$, $D_{2d}$. For them, there are non-degenerate modes that are Jahn-Teller active. The latter is due to the symmetry selection rules and not to the lack of degenerate normal modes.

## B.2) The $E \otimes e$ Jahn-Teller effect

a) *The $E \otimes e$ Hamiltonian:*
As a starting point, the common case will be considered, i.e., a three-fold axis in a $C_{3v}$ or a $D_{3h}$ point group. The simplest system to think of would be a triatomic molecule in an E electronic state, whose atoms are located at the corners of an equilateral triangle. For example, the $H_3$, $Li_3$ or $Na_3$ molecule.



In such a molecule, as also in $NH_3$ or $BF_3$, there is a degenerate vibrational normal mode of E symmetry. The components transform like $(x, y)$ and they will be hereafter denoted as $(Q_x, Q_y)$.

In this situation it is convenient to use polar coordinates in the x,y plane.

$$Q_x = \rho\ \cos\chi, \qquad Q_y = \rho\ \sin\chi$$

Next, we are going to define the complex coordinates, $Q_+$ and $Q_-$,

$$\underline{Q_+ = Q_x + iQ_y} = \rho\,(\cos\chi + i\sin\chi) = \underline{\rho\ e^{i\chi}}$$

$$\underline{Q_- = Q_x - iQ_y} = \rho\,(\cos\chi - i\sin\chi) = \underline{\rho\ e^{-i\chi}}$$

Let us now consider the effect of the $C_3$ operation on the coordinates, that is, a $\frac{2\pi}{3}$ rotation.

$$\underline{C_3\ Q_x = \cos(\frac{2\pi}{3})\ Q_x - \sin(\frac{2\pi}{3})\ Q_y}$$

$$\underline{C_3\ Q_y = \sin(\frac{2\pi}{3})\ Q_x + \cos(\frac{2\pi}{3})\ Q_y}$$

so that

$$\begin{aligned} C_3\ Q_+ &= \cos(\frac{2\pi}{3})\ Q_x - \sin(\frac{2\pi}{3})\ Q_y \\ &= i\ \sin(\frac{2\pi}{3})\ Q_x + i\ \cos(\frac{2\pi}{3})\ Q_y \\ &= e^{(\frac{+2\pi i}{3})}\ Q_x + i\ e^{(\frac{+2\pi i}{3})}\ Q_y \\ &= \underline{e^{(\frac{+2\pi i}{3})}\ Q_+} \end{aligned}$$

and also,

$$C_3\ Q_- = \underline{e^{(\frac{-2\pi i}{3})}\ Q_-}$$

A $(2\pi/3)$ rotation yields the multiplication of the complex coordinates with a complex phase factor $e^{(\frac{\pm 2\pi i}{3})}$. We can express the transformation in a matrix form as

$$C_3 \begin{pmatrix} Q_+ \\ Q_- \end{pmatrix} = \begin{pmatrix} e^{\frac{+2\pi i}{3}} & 0 \\ 0 & e^{\frac{-2\pi i}{3}} \end{pmatrix} \begin{pmatrix} Q_+ \\ Q_- \end{pmatrix}$$

The components of the electronic states transform also like (x,y) and will be denoted here as $\Phi_x$, $\Phi_y$. As done for the nuclear coordinates, we define also a set of complex functions:

$$\underline{\Phi_+ = \frac{1}{\sqrt{2}}\,(\Phi_x + i\Phi_y),} \qquad \underline{\Phi_- = \frac{1}{\sqrt{2}}\,(\Phi_x - i\Phi_y)}$$

(The factor $1/\sqrt{2}$ comes from the fact that both sets, $\Phi_x$, $\Phi_y$ and $\Phi_+$, $\Phi_-$, must be normalized.)

A rotation by $2\pi/3$ yields,

$$\boxed{C_3\Phi_\pm = e^{\pm 2\pi/3}\,\Phi_\pm}$$

$Q_\pm$ and $\Phi_\pm$ are the most suitable coordinates and functions to use, since they are adapted to the symmetry of the problem.

Let us consider now the matrix elements of the electronic Hamiltonian in the $\Phi_\pm$ basis set up to second order in the coordinates $Q_\pm$. We have:

$$\begin{aligned}\int dx\ \Phi_+^{*o}\ H_{el}\ \Phi_+^o\ &=\ W^{(0)} + W_+^{(1)} Q_+ + W_-^{(1)} Q_- \\ +\frac{1}{2} W_{++}^{(2)} Q_+ Q_+\ &+\ \frac{1}{2} W_{--}^{(2)} Q_- Q_- + W_{+-}^{(2)} Q_+ Q_-\end{aligned}$$

By applying $C_3$ to this equation, the left side is multiplied by

$$\left(e^{+2\pi i/3}\right)^*\ e^{+2\pi i/3} = 1$$

since $\mathcal{H}_{el}$ is invariant. Thus the left side is also invariant. On the right side, all the $W's$, for which the combination of the $Q's$ is not invariant, have to vanish, i.e.,

$$W_+^{(1)} = W_-^{(1)} = W_{++}^{(2)} = W_{--}^{(2)} = 0$$

So that:

$$\int dx\ \Phi_+^{*o}\ H_{el}\ \Phi_+^o = W^{(0)} + W_{+-}^{(2)} Q_+ Q_-$$

and also

$$\int dx\ \Phi_-^{*o}\ H_{el}\ \Phi_-^o = W^{(0)} + W_{+-}^{(2)} Q_+ Q_-$$

with the same coefficients.

The off-diagonal matrix elements are:

$$\begin{aligned}\int dx\ \Phi_+^{*o}\ H_{el}\ \Phi_-^o &= V^{(0)} + V_+^{(1)}Q_+ + V_-^{(1)}Q_- + \frac{1}{2}V_{++}^{(2)}Q_+Q_+ \\ &+ \frac{1}{2}V_{--}^{(2)}Q_-Q_- + V_{+-}^{(2)}Q_+Q_-\end{aligned}$$

Applying $C_3$ to the l.h.s. yields a factor

$$\underline{e^{-2\pi i/3}e^{-2\pi i/3}} = e^{-4\pi i/3} = \underline{e^{+2\pi i/3}},$$

so that we finally get:

$$\underline{V^{(0)} = V_-^{(1)} = V_{++}^{(2)} = V_{+-}^{(2)} = 0}$$

i.e.,

$$\underline{\int dx\ \Phi_+^{*o}\ H_{el}\ \Phi_-^o = V_+^{(1)} + \frac{1}{2}V_{--}^{(2)}Q_-Q_-}$$

We have thus determined the nonvanishing coefficients. Abbreviations:

$$\begin{aligned} W^{(0)} &= 0 \ \text{(zero of energy)} \\ W_{+-}^{(2)} &= \tfrac{\omega}{2} \\ V_+^{(1)} &= k \\ V_{--}^{(2)} &= g \end{aligned}$$

Finally, the electronic Hamiltonian in the $\Phi_\pm$ basis set is:

$$\boxed{\mathcal{H}_{el} = \tfrac{\omega}{2}\ Q_+Q_-\ \mathbf{1} + \begin{pmatrix} 0 & kQ_+ + \frac{1}{2}gQ_-^2 \\ kQ_- + \frac{1}{2}gQ_+^2 & 0 \end{pmatrix}}$$

or with $\qquad Q_+ = \rho\ e^{i\chi}, \qquad Q_- = \rho\ e^{-i\chi}$

$$\boxed{\mathcal{H}_{el} = \tfrac{\omega}{2}\rho^2 \; \mathbf{1} + \begin{pmatrix} 0 & k\rho e^{i\chi} + \frac{1}{2} g\rho^2 e^{-2i\chi} \\ k\rho e^{-i\chi} + \frac{1}{2} g\rho^2 e^{2i\chi} & 0 \end{pmatrix}}$$

This is a Diabatic Representation, where the electronic Hamiltonian matrix, $\mathcal{H}_{el}$ is not diagonal.

The total $E \otimes e$-JT Hamiltonian is formed by adding the kinetic operator for the nuclear motion:

$$\underline{T_k = -\frac{\omega}{2}\left(\frac{\partial^2}{\partial Q_x^2} + \frac{\partial^2}{\partial Q_y^2}\right)}$$

In polar coordinates $(\rho, \chi)$ $T_k$ reads as:

$$\boxed{T_k = -\tfrac{\omega}{2\rho^2}\left(\rho\tfrac{\partial}{\partial\rho}\rho\tfrac{\partial}{\partial\rho} + \tfrac{\partial^2}{\partial\chi^2}\right)}$$

$$\boxed{\mathcal{H} = \left(T_k + \tfrac{\omega}{2}\rho^2\right) 1 + \begin{pmatrix} 0 & k\rho e^{i\chi} + \frac{1}{2} g\rho^2 e^{-2i\chi} \\ k\rho e^{-i\chi} + \frac{1}{2} g\rho^2 e^{2i\chi} & 0 \end{pmatrix}}$$

The term $k\rho e^{i\chi}$ is called linear JT-coupling.
The term $\frac{1}{2} g\rho^2 e^{-2i\chi}$ is called quadratic JT-coupling.

### b) *The adiabatic potential energy surfaces and wavefunctions:*

The JT-Hamiltonian in the form specified above is the easiest one from symmetry considerations and most suitable for the calculation of spectra, but is not, however, too descriptive. Therefore, for a better understanding of the problems, we will consider also the adiabatic representation.

The adiabatic potential energy surfaces are obtained as follows

$$\det \begin{pmatrix} -\lambda & x \\ x^* & -\lambda \end{pmatrix} = 0, \qquad x = k\rho e^{i\chi} + \frac{1}{2} g\rho^2 e^{-2i\chi}$$

and:

$$\lambda^2 - |x|^2 = 0 \longrightarrow \lambda_{1,2} = \pm |x|$$

Then,

$$V_{1,2} = \frac{\omega}{2}\rho^2 \pm \lambda_{1,2} = \frac{\omega}{2}\rho^2 \pm |k\rho e^{i\chi} + \frac{1}{2} g\rho^2 e^{-2i\chi}|$$

$$\boxed{V_{1,2} = \tfrac{\omega}{2}\rho^2 \pm \left| k\rho + \tfrac{1}{2} g\rho^2 e^{-3i\chi} \right|}$$

In most of the situations the quadratic coupling terms are smaller than the linear ones. If we set $g = 0$, we obtain the potential energy surfaces of the linear JT-effect:

$$\boxed{V_{1,2} = \tfrac{\omega}{2}\rho^2 \pm k\rho}$$

Within this approach the potential energy surface shows a rotational symmetry, i.e, it is $\chi$-independent. This surface is the prototype of a so-called conical intersection of potential energy surfaces.

Including the quadratic coupling term we have:

$$\boxed{V_{1,2} = \tfrac{\omega}{2}\rho^2 \pm \sqrt{k^2\rho^2 + \tfrac{1}{4}g^2\rho^4 + gk\rho^3 cos(3\chi)}}$$

For small displacements, the $\rho^4$ term can be dropped out:

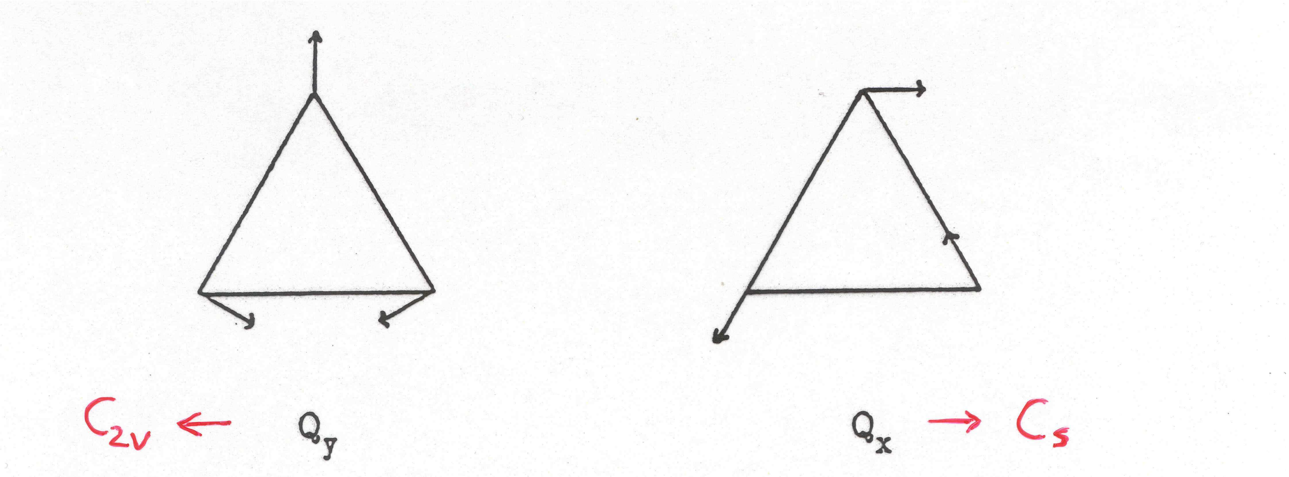
$$\boxed{V_{1,2} = \tfrac{\omega}{2}\ \rho^2 \pm k\ \rho\sqrt{1 + \tfrac{g}{k}\rho\ \cos(3\chi)}}$$

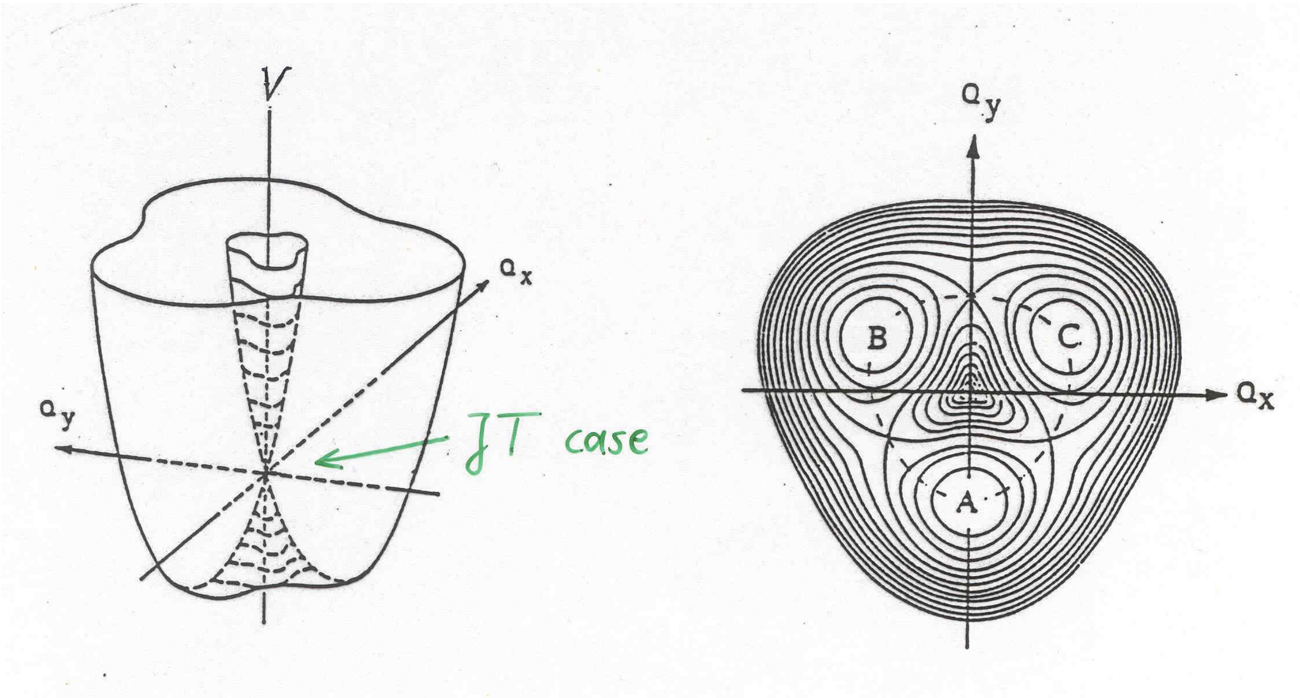
By expansion of the square root:

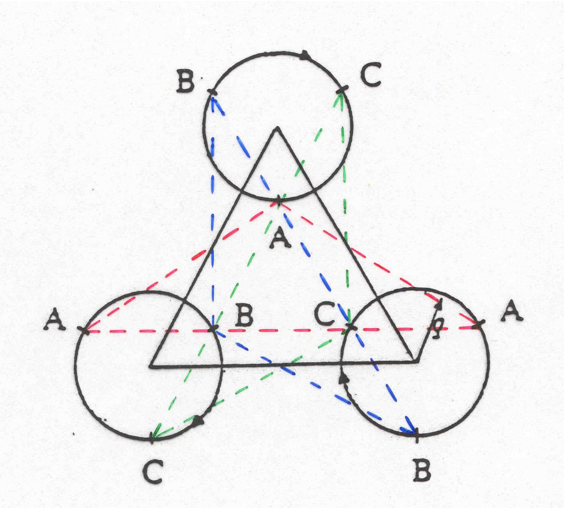
$$\boxed{V_{1,2} = \tfrac{\omega}{2}\ \rho^2 \pm k\ \rho + \tfrac{1}{2}\ g\ \rho^2\ cos(3\chi)}$$

In the linear + quadratic JT-effect, the potential energy surfaces have a threefold symmetry. The lower surface has three minima and three saddle points.

# Coordinates and JT surfaces for $X_3$ molecules







For the calculation of the adiabatic wavefunctions and the non-adiabatic coupling terms, we are going to consider just the linear JT-effect. We have

$$S^{+}\begin{pmatrix} 0 & k\rho e^{i\chi} \\ k\rho e^{-i\chi} & 0 \end{pmatrix} S = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

with $\quad \lambda_1 = k\rho \quad$ and $\quad \lambda_2 = -k\rho.$

Obtaining the eigenvectors:

(a) $\lambda_1$:

$$\begin{pmatrix} -k\rho & k\rho e^{i\chi} \\ k\rho e^{-i\chi} & -k\rho \end{pmatrix}\begin{pmatrix} s_{11} \\ s_{21} \end{pmatrix} = 0$$

$$-s_{11} + e^{i\chi}s_{21} = 0$$
$$s_{21} = e^{-i\chi}s_{11}$$

With $\quad \underline{s_{11} = \frac{1}{\sqrt{2}}\, e^{i\chi/2}} \longrightarrow \underline{s_{21} = \frac{1}{\sqrt{2}}\, e^{-i\chi/2}}.$

(b) $\lambda_2$:

$$\begin{pmatrix} +k\rho & k\rho e^{i\chi} \\ k\rho e^{-i\chi} & +k\rho \end{pmatrix}\begin{pmatrix} s_{12} \\ s_{22} \end{pmatrix} = 0$$

$$e^{-i\chi}s_{12} + s_{22} = 0$$

and $\quad \underline{s_{22} = \frac{1}{\sqrt{2}}\, e^{-i\chi/2}}; \qquad \underline{s_{12} = -\frac{1}{\sqrt{2}}\, e^{+i\chi/2}}$

we get,

$$\boxed{S = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{i\chi/2} & -e^{i\chi/2} \\ e^{-i\chi/2} & e^{-i\chi/2} \end{pmatrix}}$$

The adiabatic wavefunctions, $\Phi_{1,2}^{ad}$, are obtained from the diabatic ones, $\Phi_\pm$, as,

$$\begin{pmatrix} \Phi_1^{ad} \\ \Phi_2^{ad} \end{pmatrix} = S^+ \begin{pmatrix} \Phi_+ \\ \Phi_- \end{pmatrix}$$

$$S^+ = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\chi/2} & e^{i\chi/2} \\ -e^{-i\chi/2} & e^{i\chi/2} \end{pmatrix}$$

i.e.,

$$\begin{aligned} \Phi_1^{ad} &= \frac{1}{\sqrt{2}} \left( e^{-i\chi/2}\Phi_+ + e^{i\chi/2}\Phi_- \right) \\ \Phi_2^{ad} &= \frac{1}{\sqrt{2}} \left( -e^{-i\chi/2}\Phi_+ + e^{i\chi/2}\Phi_- \right) \end{aligned}$$

Using $\Phi_+ = \frac{1}{\sqrt{2}}(\Phi_x + i\ \Phi_y)$, $\Phi_- = \frac{1}{\sqrt{2}}(\Phi_x - i\ \Phi_y)$, we get:

$$\begin{aligned} \Phi_1^{ad} &= \cos(\frac{\chi}{2})\Phi_x + \sin(\frac{\chi}{2})\Phi_y \\ i\ \Phi_2^{ad} &= -\sin(\frac{\chi}{2})\Phi_x + \cos(\frac{\chi}{2})\Phi_y \end{aligned}$$

It is also interesting to analyze the dependence of the adiabatic wavefunctions on $\chi/2$. When following a $\underline{2\pi\text{-loop}}$ around $\rho = 0$, the adiabatic wavefunctions do not transform into themselves, but:

$$\begin{aligned} \Phi_1^{ad}(2\pi) &= -\Phi_1^{ad}(0) \\ \Phi_2^{ad}(2\pi) &= -\Phi_2^{ad}(0) \end{aligned}$$

They transform again into themselves after a $\underline{4\pi\text{-loop}}$. This is the $\underline{\text{general behaviour for two-dimensional conical intersections.}}$

Finally, we are going to calculate the non-adiabatic coupling operator $\mathbf{\Lambda}$. Since $S$ depends only on the $\chi$ angle, we have to consider just the term $-\frac{\omega}{2\rho^2}\partial^2/\partial\chi^2$:

$$T_k \begin{pmatrix} \Phi_1^{ad} \\ \Phi_2^{ad} \end{pmatrix} = -\frac{\omega}{2\rho^2} \begin{pmatrix} -\frac{1}{4} & i\frac{\delta}{\delta\chi} \\ i\frac{\delta}{\delta\chi} & -\frac{1}{4} \end{pmatrix} \begin{pmatrix} \Phi_1^{ad} \\ \Phi_2^{ad} \end{pmatrix} + \begin{pmatrix} \Phi_1^{ad} \\ \Phi_2^{ad} \end{pmatrix} T_k$$

The non-adiabatic coupling operator $\mathbf{\Lambda}$ reads:

$$\boxed{\mathbf{\Lambda} = +\frac{\omega}{2\rho^2} \begin{pmatrix} -\frac{1}{4} & i\frac{\delta}{\delta\chi} \\ i\frac{\delta}{\delta\chi} & -\frac{1}{4} \end{pmatrix}}$$

Note that $\mathbf{\Lambda}$ diverges at $\rho = 0$.

The BO-approximation breaks down in the JT case. Therefore, the diabatic representation is more suitable. The nuclear motion on the adiabatic surfaces $V_1$ and $V_2$ is strongly coupled. As a consequence, the vibrational energy levels on the adiabatic energy surfaces have no longer physical meaning.

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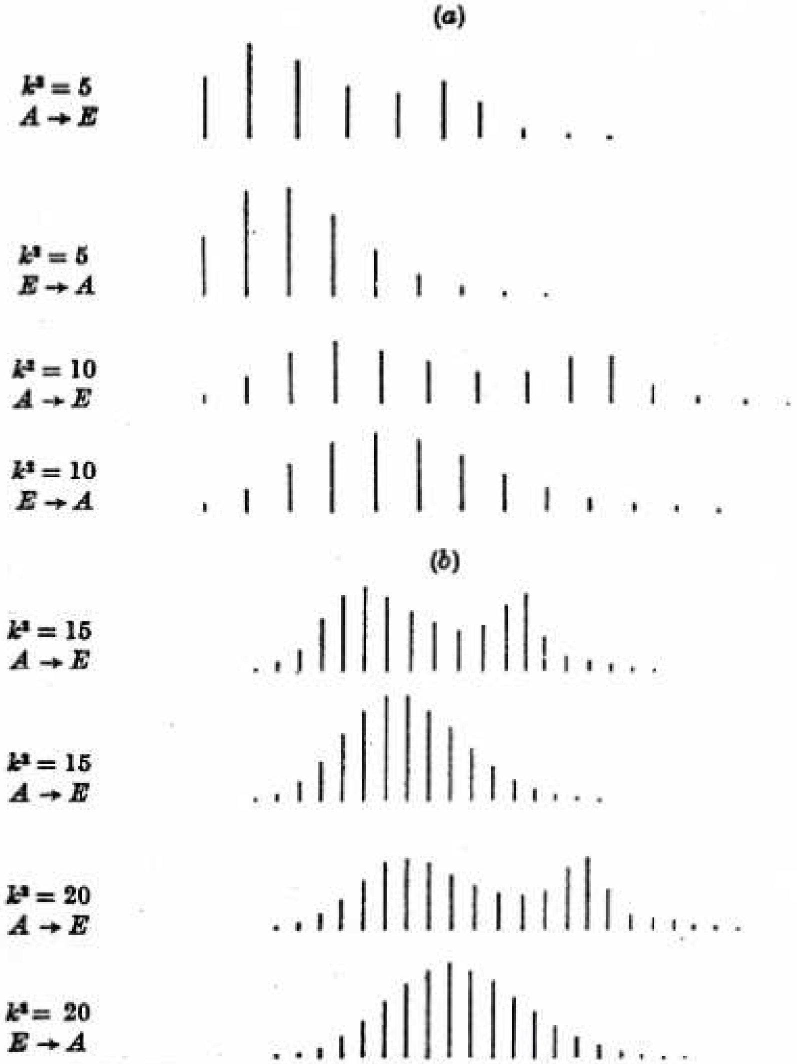


FIGURES 4a and 4b. Vibrational structure of (allowed) electronic transitions $A_{10} \rightarrow E_{p\frac{1}{2}}$ and $E_{1\frac{1}{2}} \rightarrow A_{n0}, A_{n1}$. The 0–0 line is that on the left in each diagram.

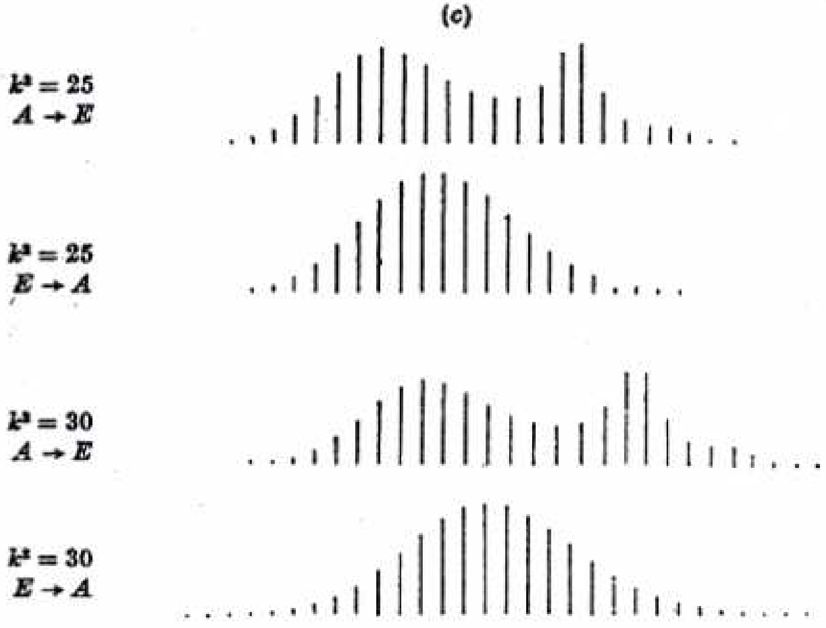
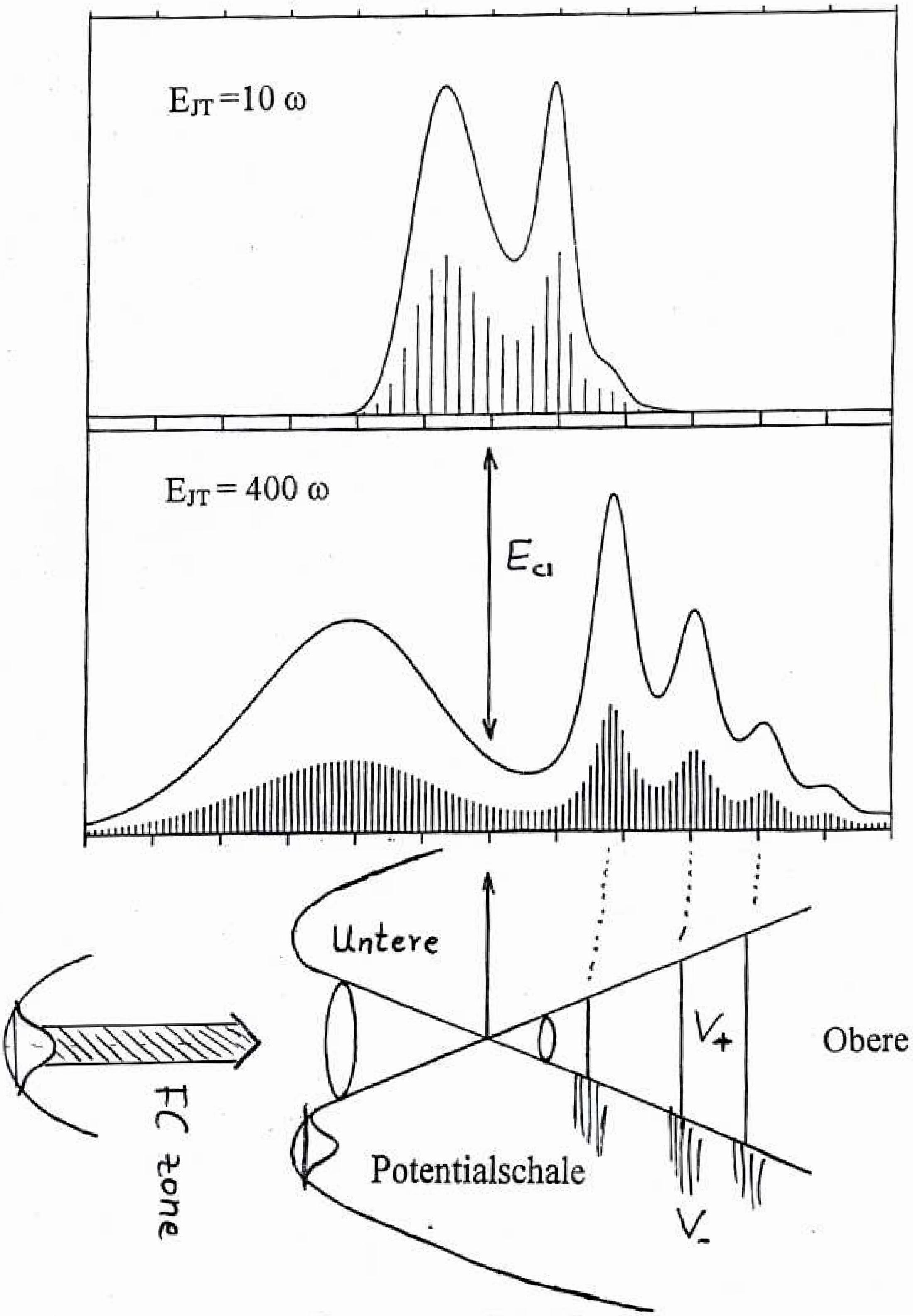


FIGURE 4c. Vibrational structure of (allowed) electronic transitions $A_{10} \rightarrow E_{p\frac{1}{2}}$ and $E_{1\frac{1}{2}} \rightarrow A_{n0}, A_{n1}$. For large distortions the 0–0 line is no longer visible.

# Vibronic Line Spectrum for an $A \longrightarrow E$ transition with strong coupling.



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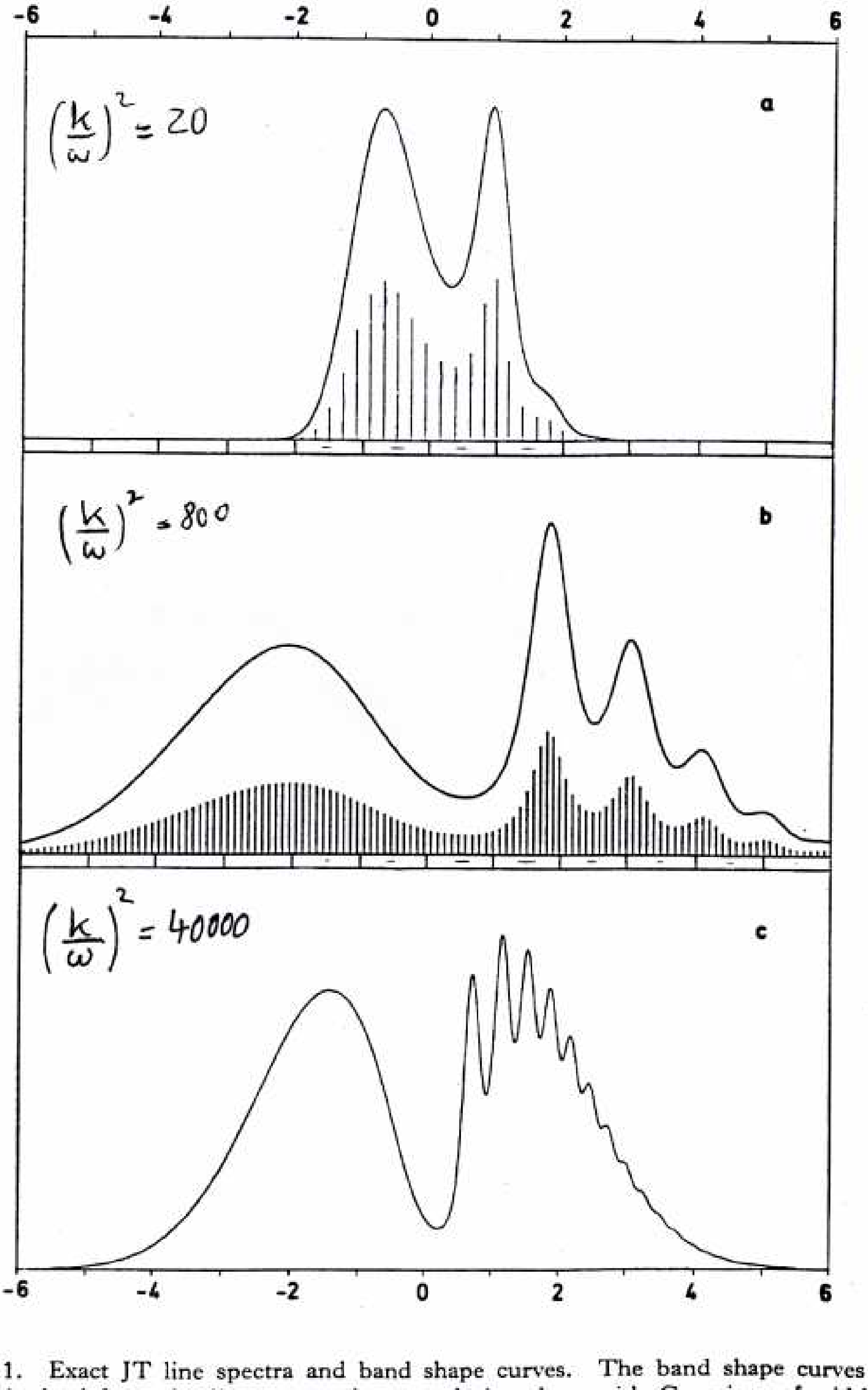


Figure 1. Exact JT line spectra and band shape curves. The band shape curves are obtained from the line spectra by convoluting them with Gaussians of width $\gamma$. (*a*) $\omega=0{\cdot}1$, $\kappa=\sqrt{0{\cdot}2}$, $\gamma=0{\cdot}1$ ; (*b*) $\omega=0{\cdot}1$, $\kappa=2\sqrt{2}$, $\gamma=0{\cdot}2$ ; (*c*) $\omega=0{\cdot}01$, $\kappa=2$, $\gamma=0{\cdot}1$.

## B.3) A simple model of vibronic coupling

Use a diabatic electronic basis and expand coupling terms:

$$\mathcal{H} = T_N \mathbf{1} + \mathbf{W}$$

$$\boxed{\begin{aligned} W_{nn}(Q) &= V_0(Q) + E_n + \textstyle\sum_i k_i^{(n)} Q_i + \sum_{i,j} \gamma_{ij}^{(n)} Q_i Q_j + \cdots \\ W_{nn'}(Q) &= \textstyle\sum_i \lambda_i^{(nn')} Q_i + \cdots \qquad (n \neq n') \end{aligned}}$$

with $Q_i$: normal coordinates of $V_0(Q)$,
and, for instance, $k_i^{(n)} = (\partial V_n / \partial Q_i)_{Q=0}$.

$k_i^{(n)}$ is the gradient of the excited potential energy surface at the Franck-Condon zone centre.

Analogously for the other coupling constants.

The coupling constants can therefore be determined from *ab initio* calculations (few points are needed).

*Selection rule for* $\lambda_i^{(nn')}$

$$\boxed{\Gamma_n \times \Gamma_Q \times \Gamma_{n'} \supset \Gamma_A}$$

a) *Hamiltonian for a two-state case:*

$$\mathcal{H} = \left(-\frac{1}{2}\sum \omega_i \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\sum \omega_i Q_i^2\right)\mathbf{1} + \left(\begin{array}{cc} E_g + \sum k_j^{(g)} Q_j & \sum \lambda_l Q_l \\ \sum \lambda_l Q_l & E_u + \sum k_j^{(u)} Q_j \end{array}\right)$$

Electronic states with different symmetries → Modes $l$ and $j$ are different.

For a first insight into the phenomena, the g mode will be dropped and only one term will be considered in the off-diagonal element:

$$\mathcal{H} = (-\frac{\omega_u}{2}\frac{\partial^2}{\partial Q_u^2} + \frac{\omega_u}{2} Q_u^2)\mathbf{1} + \left(\begin{array}{cc} E_g & \lambda Q_u \\ \lambda Q_u & E_u \end{array}\right)$$

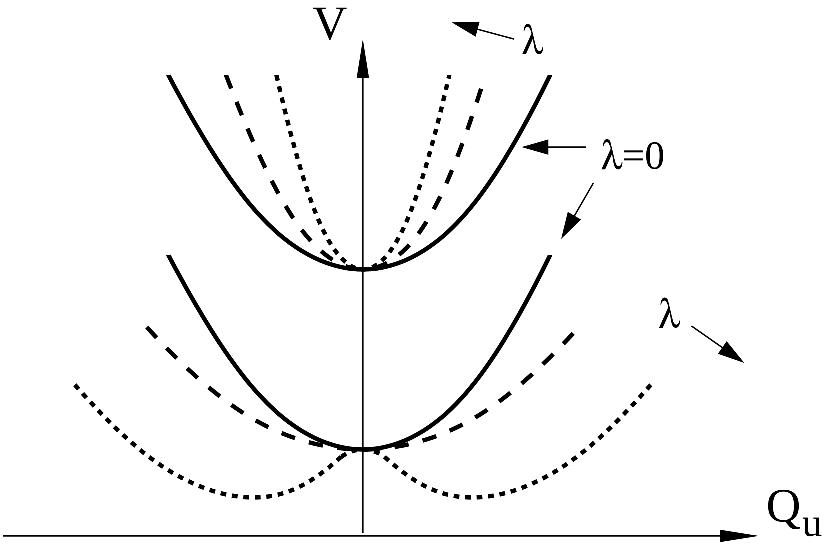
This is almost the simplest case that one can think of, but it still shows many of the representative effects of vibronic interactions.
In the diabatic representation $\mathcal{H}$ is not too descriptive. Let us have a look then at the adiabatic potential energy curves:

$$E = \frac{E_g + E_u}{2} \quad ; \quad \Delta E = \frac{E_g - E_u}{2}$$

$$\Longrightarrow V_{\pm} = \frac{\omega_u}{2} Q_u^2 + E \pm \sqrt{\Delta E^2 + \lambda^2 Q_u^2}$$

$$\text{If } Q_u = 0 \quad \text{then} \quad V_\pm = E \pm \Delta E = \begin{cases} E_g \\ E_u \end{cases},$$

i.e., the diabatic and the adiabatic potential energy curves are identical (how it should be). $Q_u \neq 0$ yields repulsion between the potential energy curves. A qualitative picture is displayed next,



The upper potential energy curves, $V_+$, are always steeper due to the interaction.

For $V_-$ a double minimun can be obtained for strong couplings: Symmetry breaking.

Repulsion of potential energy curves and symmetry lowering (linear → non-linear; planar → non-planar) are important signs of vibronic interaction with other electronic states.

Calculation of the curvature using Taylor expansion:

$$\begin{aligned}V_\pm &= E + \frac{\omega_u}{2}Q_u^2 \pm \Delta E\left(1 + \frac{1}{2}\frac{\lambda^2 Q_u^2}{\triangle E^2} + ...\right)\\ &= E + \frac{\omega_u}{2}Q_u^2 \pm \Delta E \pm \frac{\lambda^2 Q_u^2}{2\Delta E^2}\\ &= E \pm \Delta E + \frac{1}{2}\left(\omega_u \pm \frac{\lambda^2}{\Delta E}\right)Q_u^2\end{aligned}$$

$$\boxed{\Longrightarrow \omega_u^\pm = \omega_u \pm \tfrac{\lambda^2}{\Delta E}}$$

The change in the curvature is symmetric, as the repulsion of the potential energy curves. The expression for $\omega_u^-$ holds only for positive frequences. This yields a critical coupling strength, $\lambda_c$, for obtaining a double minimum:

$$\boxed{\lambda_c^2 = \Delta E \cdot \omega_u}$$

If $\lambda > \lambda_c$, $Q_u = 0$ represents a local maximum. The minima are the non-trivial solutions of the equation:

$$0 = \frac{\partial V_-}{\partial Q_u} = \omega_u\ Q_u - \frac{\lambda^2 Q_u}{\sqrt{\Delta E^2 + \lambda^2 Q_u^2}}$$

$$\Longrightarrow Q_u^o = \pm\sqrt{\frac{\lambda^2}{\omega_u^2} - \frac{\Delta E^2}{\lambda^2}}$$

The solutions are real and $\neq 0$ if $\lambda > \lambda_c$. The stabilization energy, $E_s$, represents the lowering of the minimum of the lower potential energy curve relative to the minimum in the absence of vibronic coupling ($\lambda = 0$) due to an asymmetric distortion:

$$E_s = V_-(0) - V_-(Q_u^o) = \frac{\omega_u}{2}\left(\frac{\lambda}{\omega_u} - \frac{\Delta E}{\lambda}\right)^2$$

This expression is formally always defined, but holds only for $\lambda > \lambda_c$.

Beside the potential energy curves, we are interested also in the non-adiabatic couplings, given by the derivative of the rotation angle, $\alpha'$:

$$\alpha(Q_u) = \frac{1}{2}\arctan\frac{2\,W_{12}}{W_{11} - W_{22}}$$

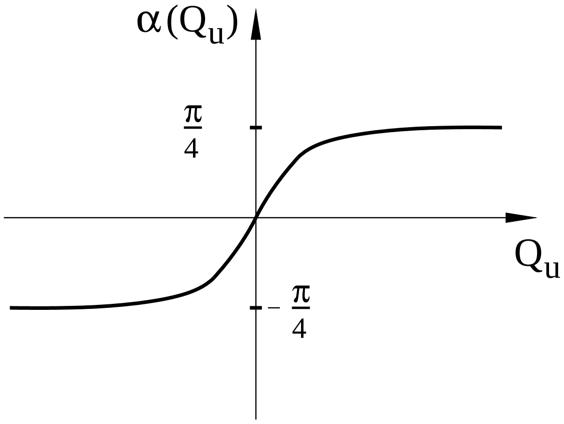
Substituting and differentiating:

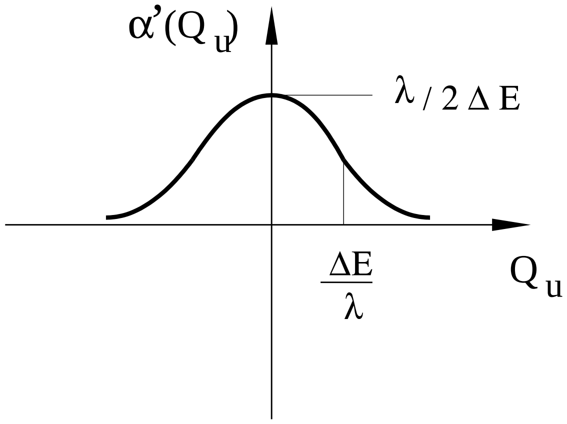
$$\alpha(Q_u) = \frac{1}{2}\arctan\frac{\lambda Q_u}{\Delta E}$$

$$\Longrightarrow \alpha' = \frac{1}{2}\cdot\frac{1}{1+\frac{\lambda^2 Q_u^2}{\Delta E^2}}\cdot\frac{\lambda}{\Delta E} = \frac{\lambda \Delta E/2}{\Delta E^2 + \lambda^2 Q_u^2}$$

One obtains a Lorentzian curve with a width and a height given by $hwhm = \frac{\Delta E}{\lambda}$ and $\alpha'(0) = \frac{\lambda}{2\Delta E}$, respectively.

The area under the $\alpha'(Q_u)$ curve has to be $\frac{\pi}{2}$ and, therefore, the limits for $\alpha(\pm\infty)$ are $\pm\frac{\pi}{4}$.





One can see from this expression that for fixed values of $\lambda$ and $\omega_u$, the non-adiabatic effects increase with decreasing $\Delta E$.

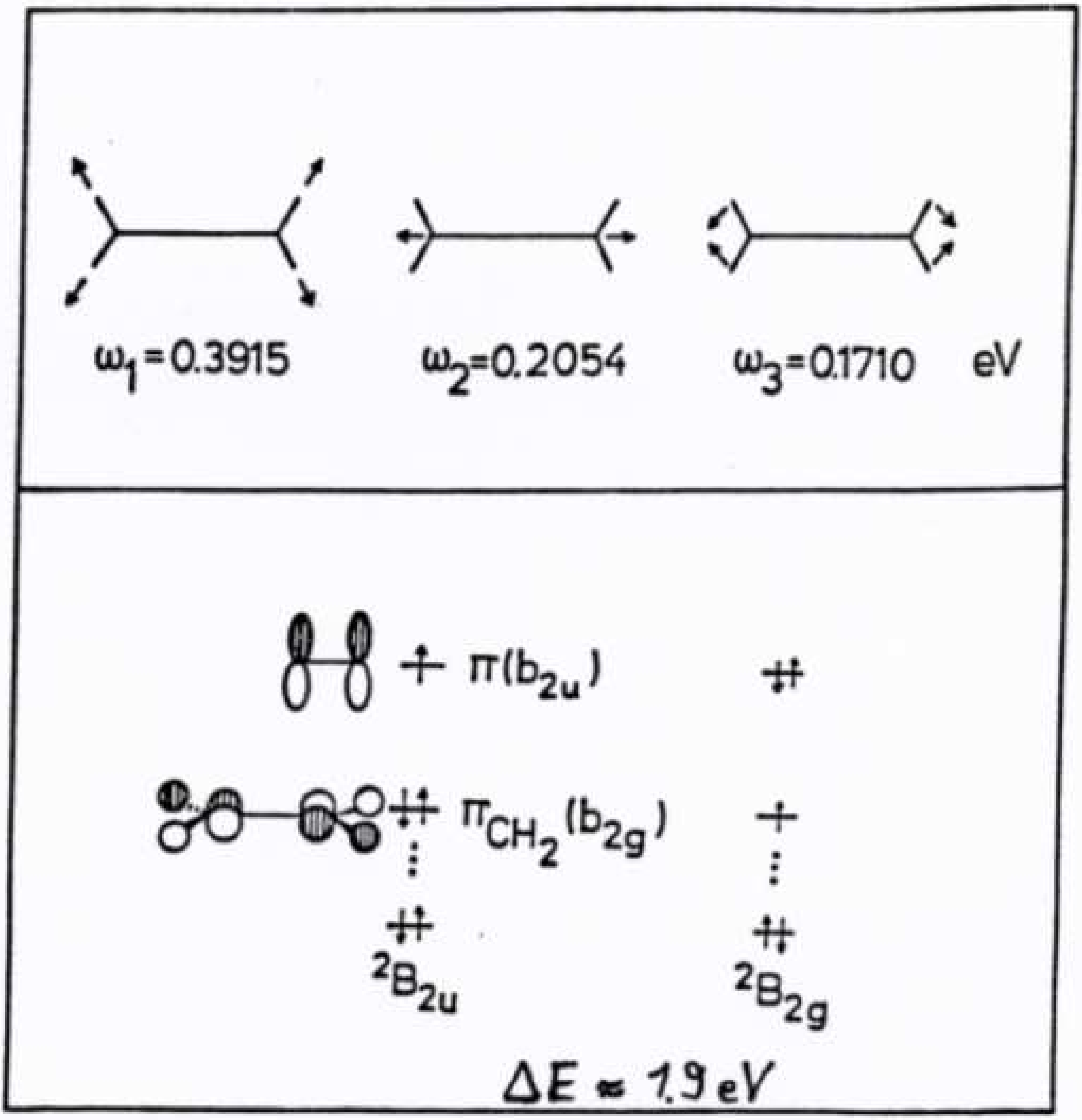
Comparison of criteria:
Double minimum: $\lambda^2 > \omega_u \cdot \Delta E$
Non-adiabatic effects: $\lambda > \Delta E,\ \omega_u \geq \Delta E$
For $\omega_u < \Delta E$, the criterium for the double minimum is easier to fulfill than for non-adiabatic effects.
$\longrightarrow$ different validity of the diagonal approximation in the adiabatic and the diabatic basis!

$$\omega_u\, \Delta E < \lambda^2 < \Delta E^2$$

Double minimum / adiabatic app. valid

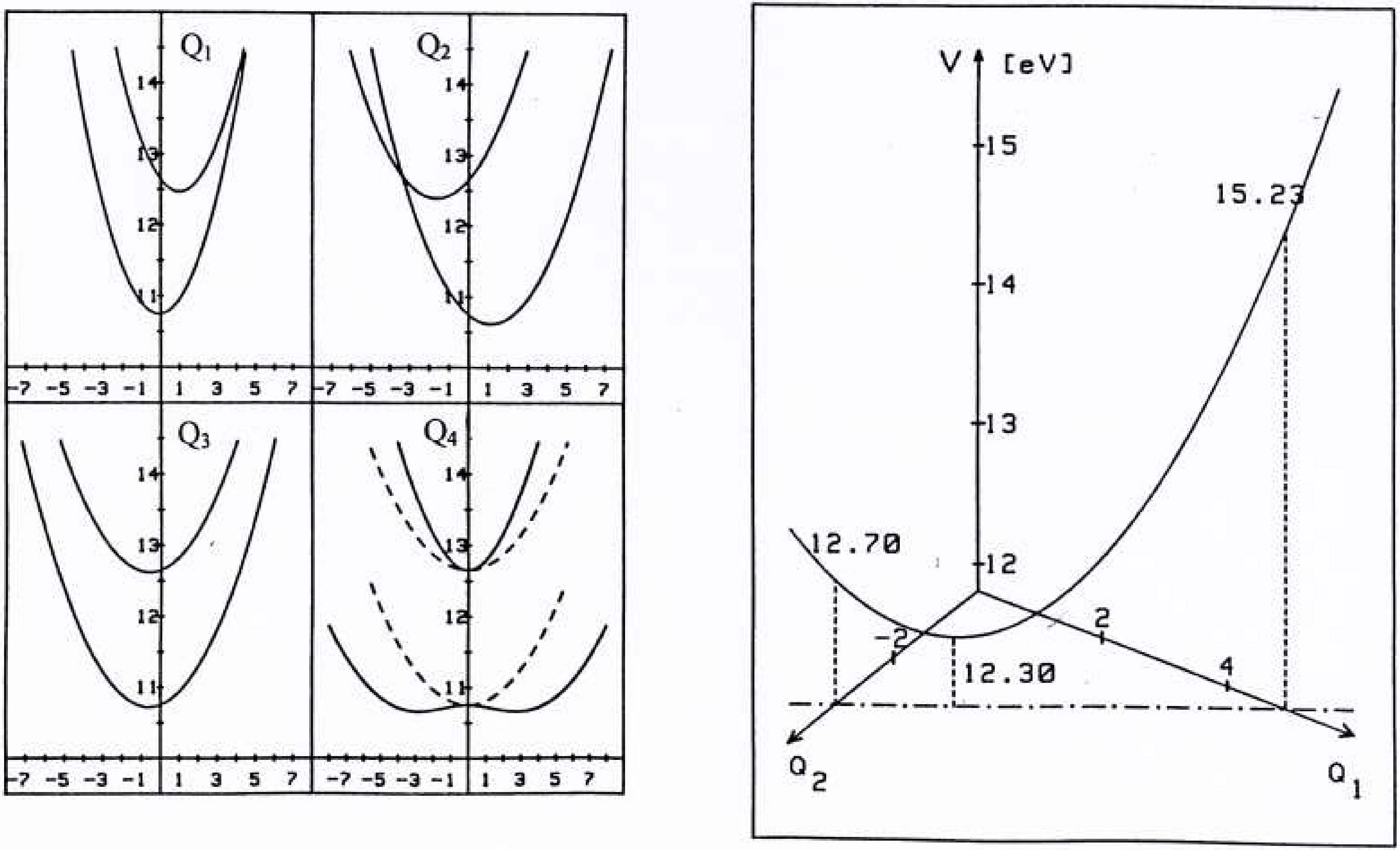
# B.4) Conical intersection and vibronic dynamics in the ethene radical cation, $C_2H_4^+$

Schematic representation of the relevant vibrational normal modes and molecular orbitals of $C_2H_4^+$
(Mode 1-3: totally symmetric modes, Mode 4: Torsion)

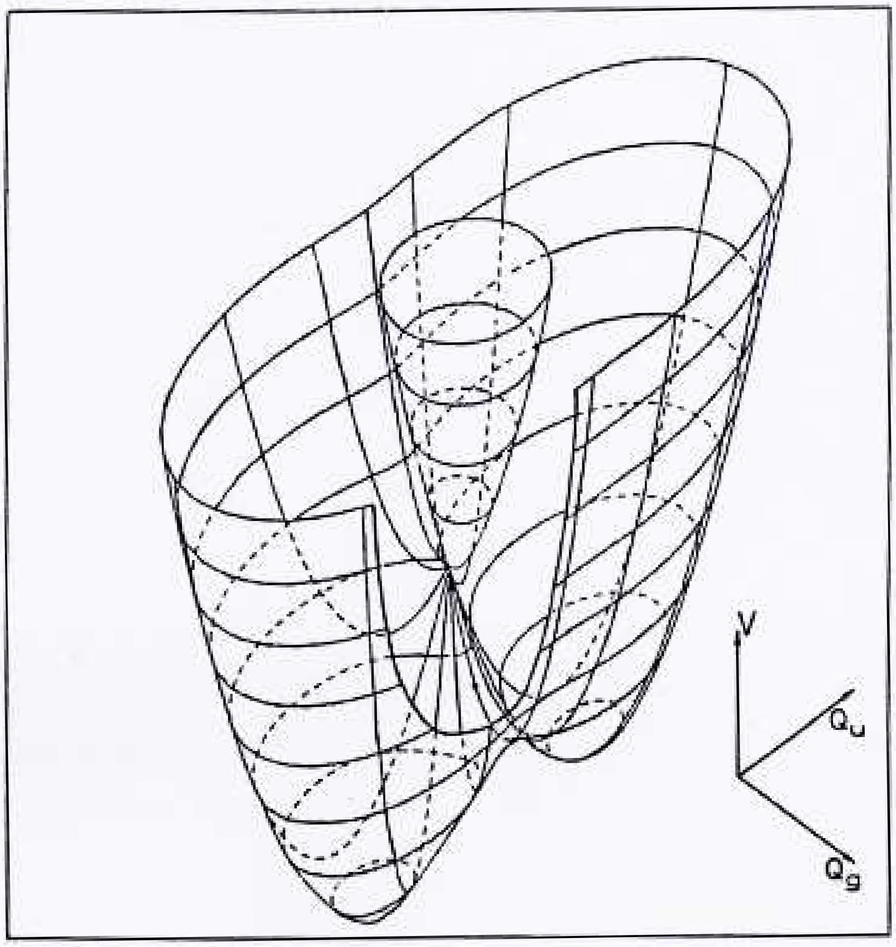


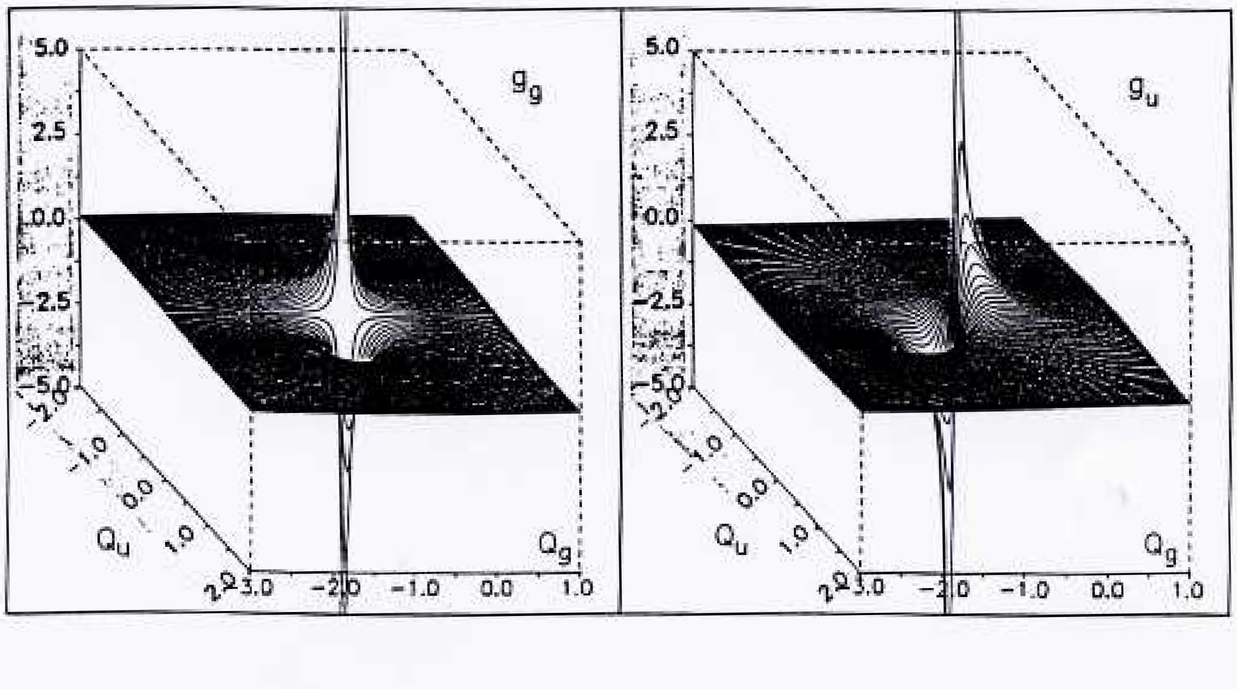
$\underline{B_{2u} \times B_{2g} = A_u}$ (Torsion)

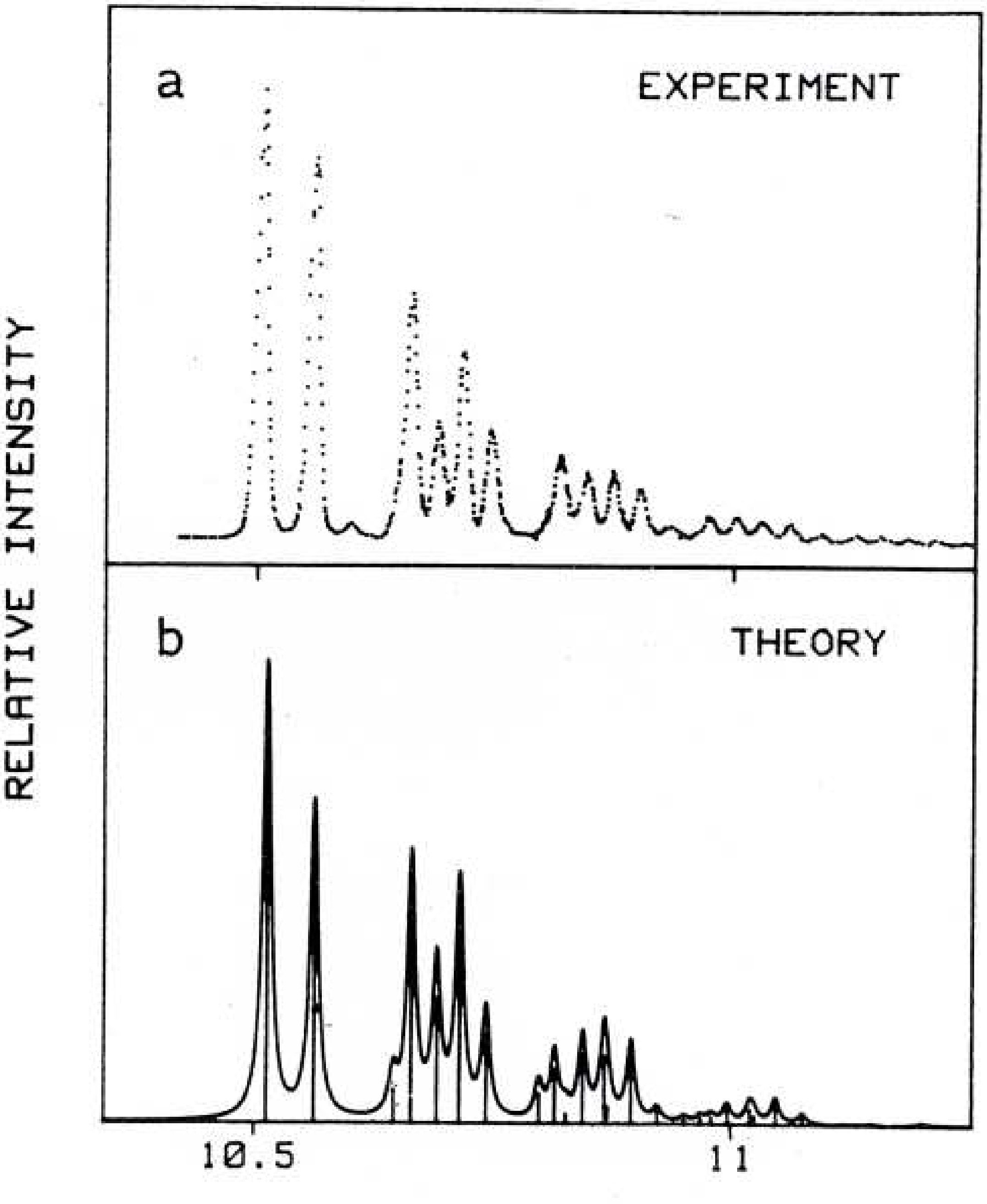
# Potentialkurven (links) und Durchschneidungssaum (rechts) von $C_2H_4^+$ $(\tilde{X}, \tilde{A})$



# *Perspektiv. Darstellung der konischen Durchschneidung und nichtadiabatischen Kopplungselemente des Prototyp g-u - Problems :* $C_2H_4^+$ $(\tilde{X}, \tilde{A})$

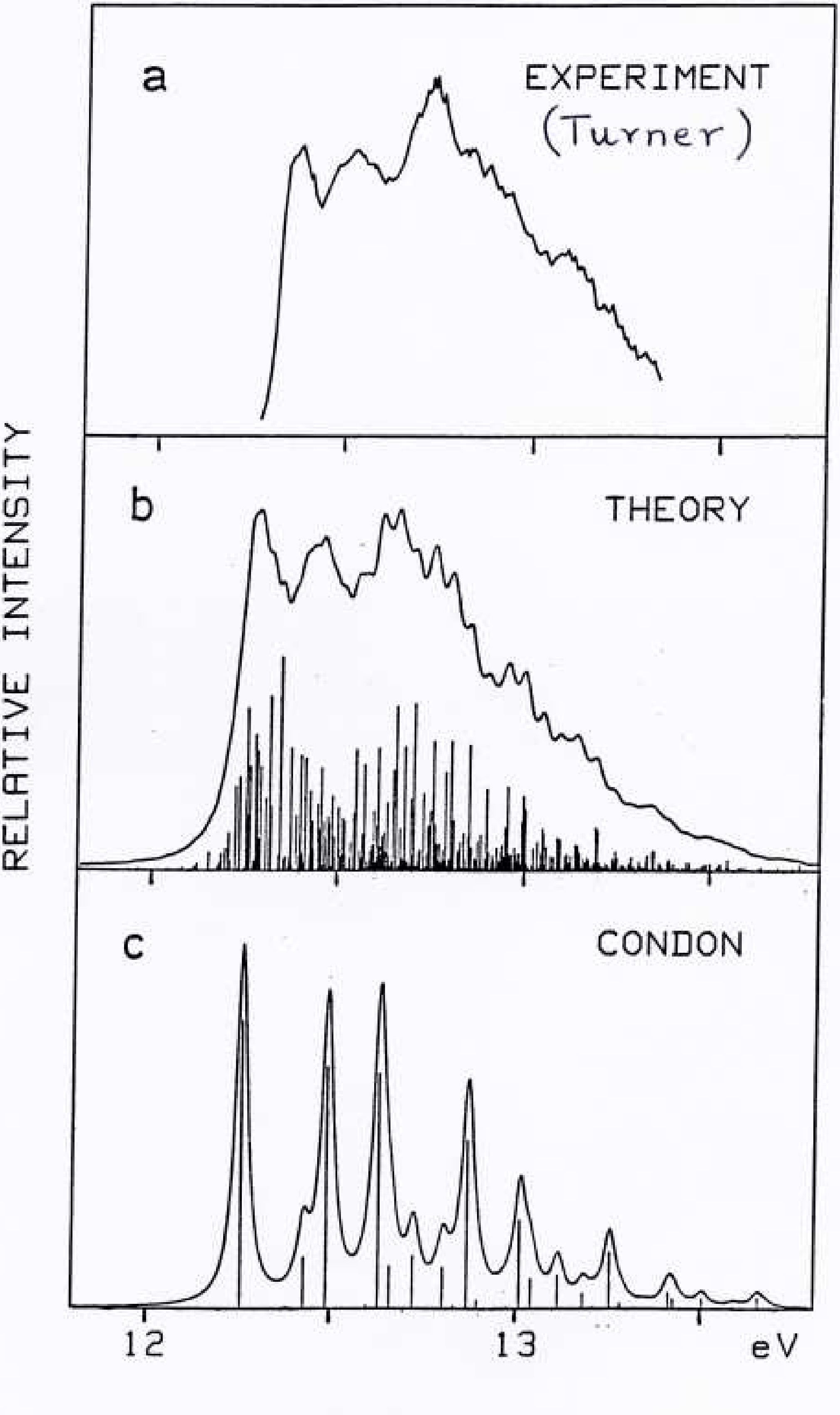




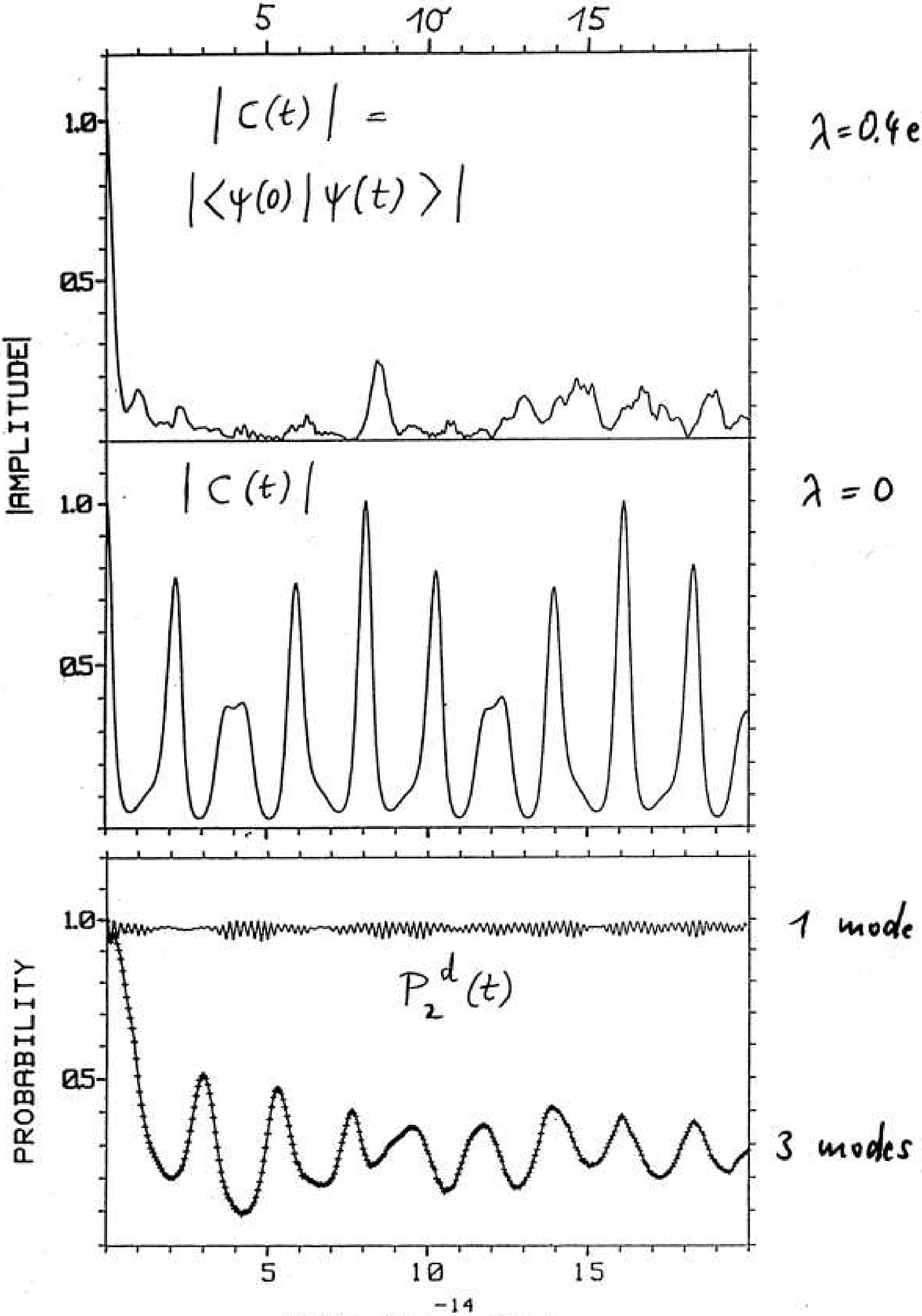


g. 26. The first band in the photoelectron spectrum of ethylene. (*a*) The experime
ing according to Pollard et al.[209] (*b*) The result of the vibronic coupling calculation
fwhm = 0.01 eV). For the values of the parameters see Table V.

# *Zweite Photoelektronenbande von Ethen: Vergleich Theorie - Experiment*

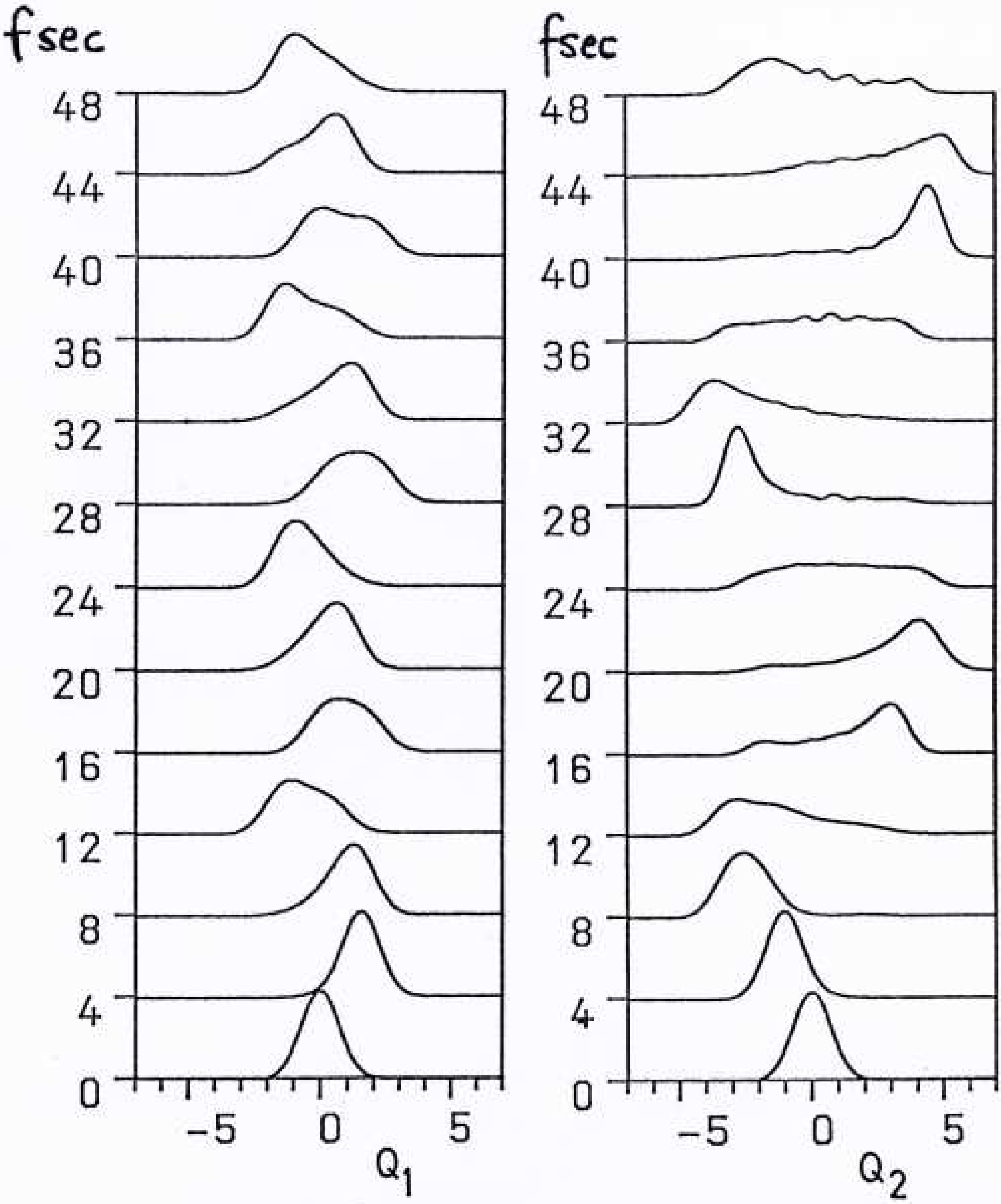


## Wavepackets dynamics for $C_2H_4^+$ $(\tilde{X},\tilde{A})$



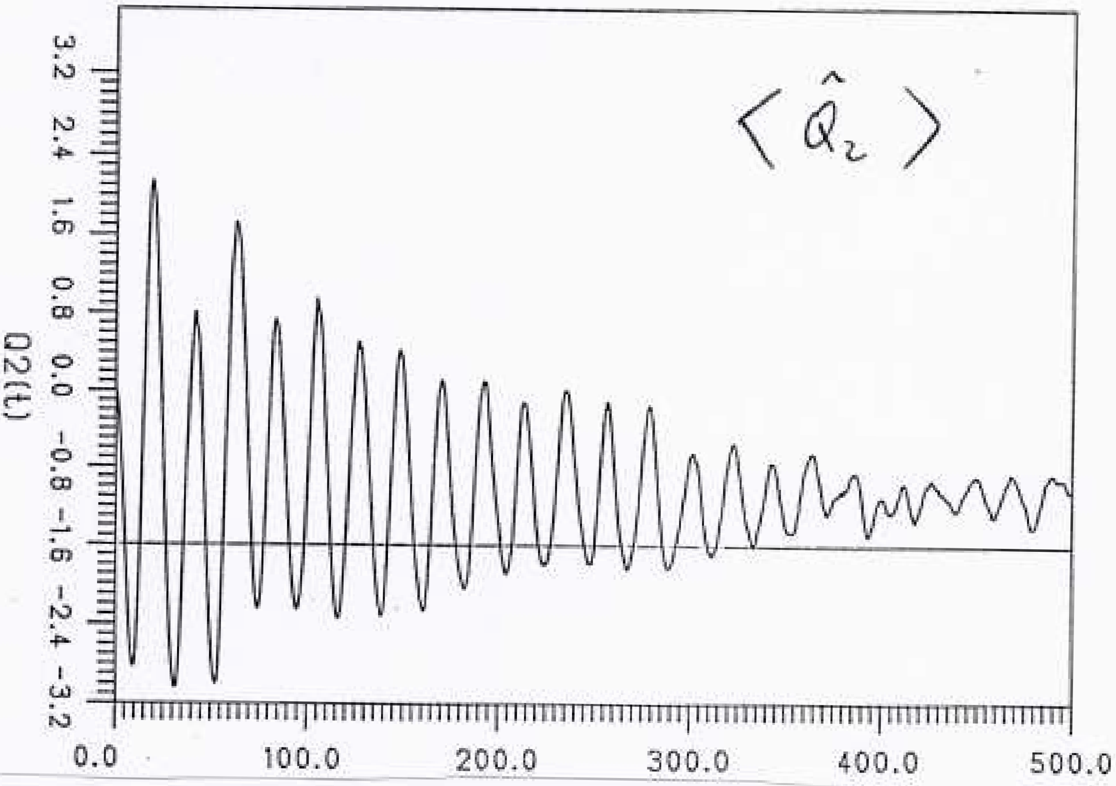
## **Short-time dynamics for** $C_2H_4^+$ $(\tilde{X},\tilde{A})$

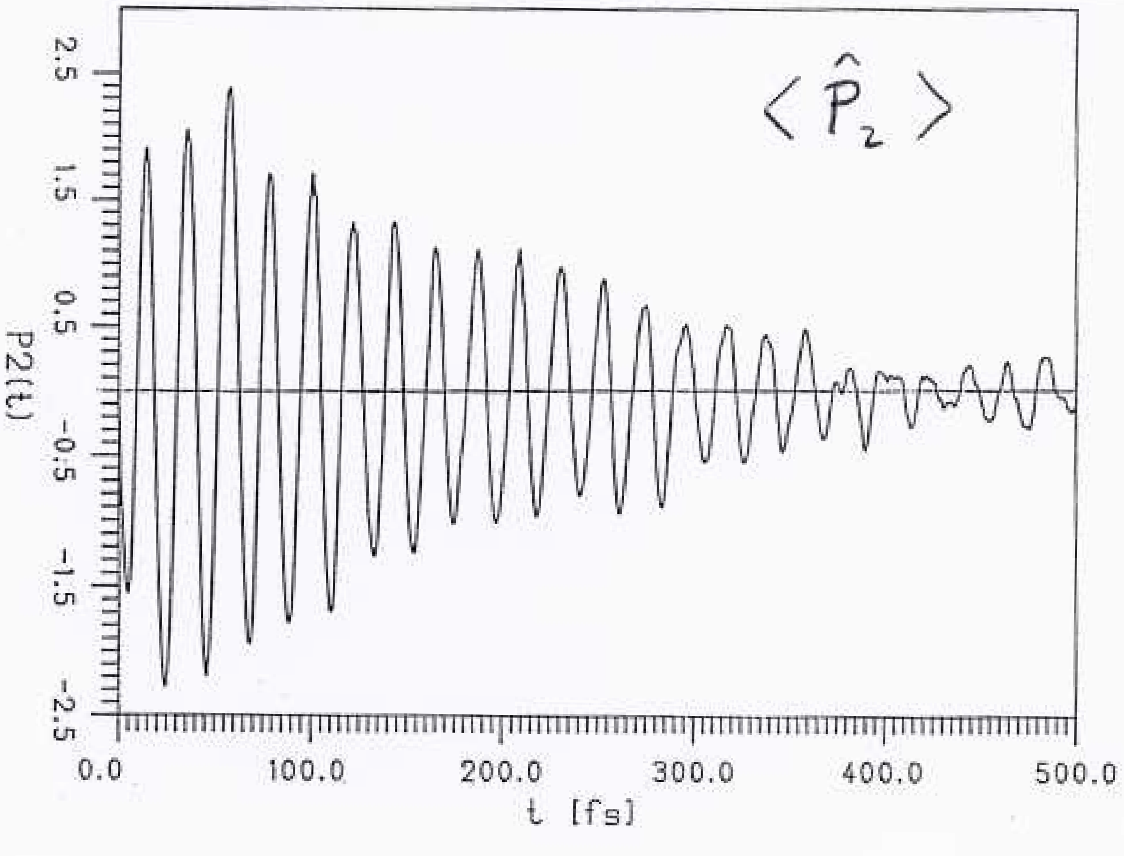
Coherent motion for $Q_1$ and $Q_2$



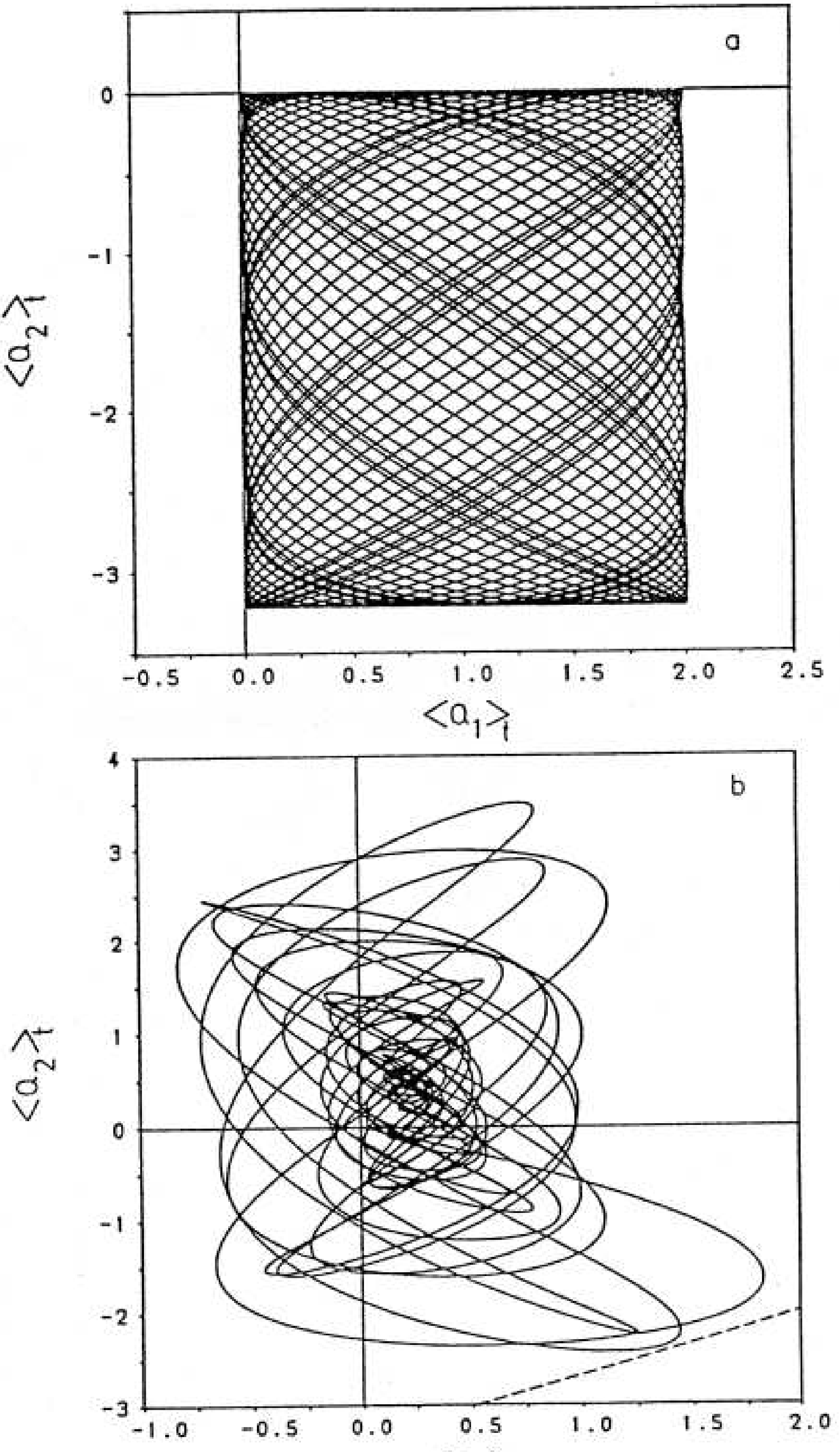
## **Long-time dynamics for $C_2H_4^+$ ($\tilde{X}$,$\tilde{A}$)**

Damping of the coherent motion in $Q_2$

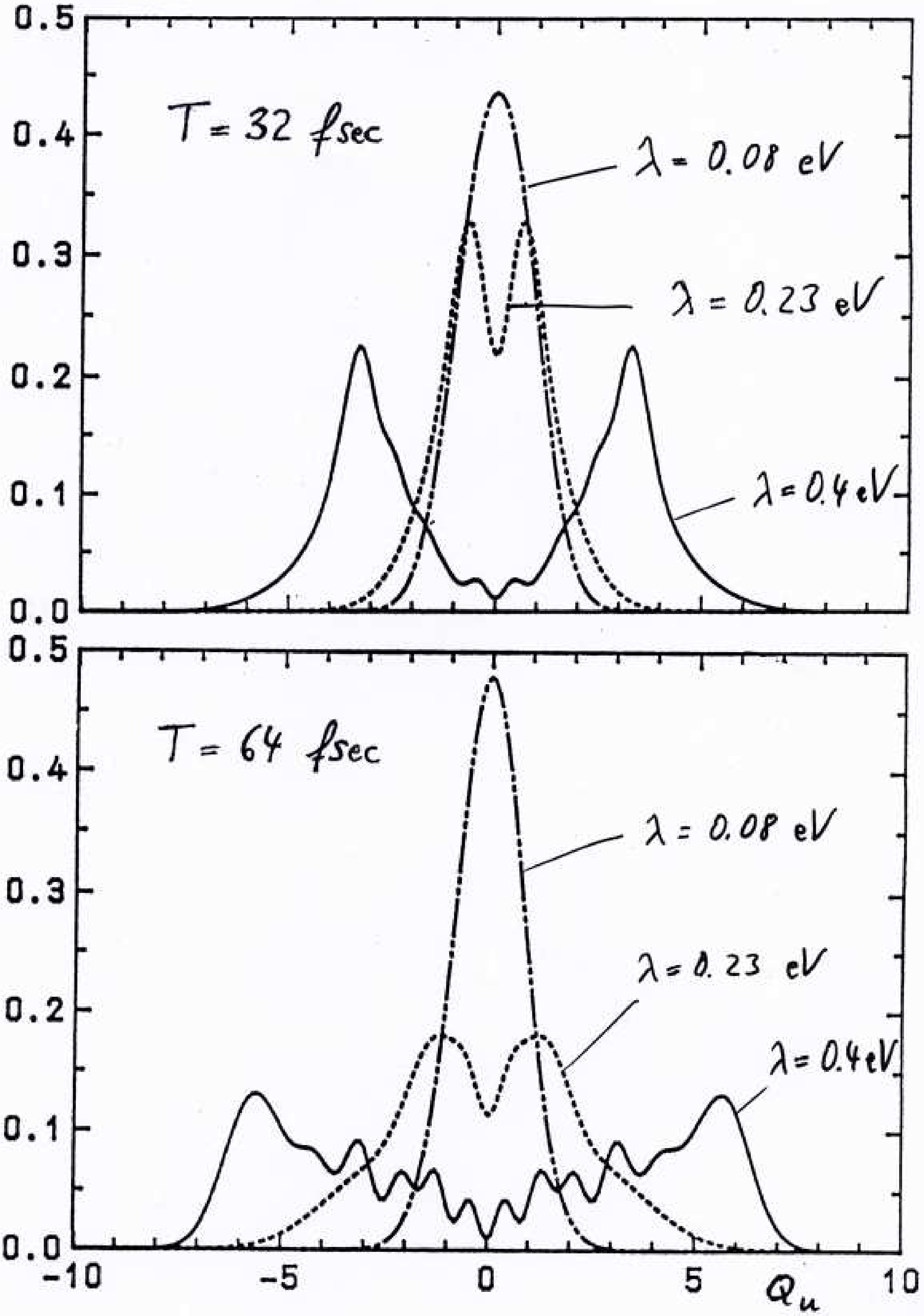




# Trajektorien im Raum $Q_1$ - $Q_2$ für $C_2H_4^+(\tilde{X}, \tilde{A})$ [22]



## $C_2H_4^+(\tilde{X}, \tilde{A})$: *Wahrscheinlichkeitsdichte entlang der Koordinate $Q_4$ der koppelnden Mode [23]*



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