# 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:

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

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

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

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

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

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

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

$x$ 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

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

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

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

$$\sum_m \quad \left\{\left[V_m(Q) - E + T_K\right] \chi_m(Q)\right\} \phi_m(x,Q) =$$

$$\sum_m \frac{\hbar^2}{M}\left(\frac{\partial \chi_m}{\partial Q}\right)\left(\frac{\partial \phi_m}{\partial Q}\right) - \sum_m \chi_m \left(T_K \phi_m\right)$$

$$\int \phi_n^* d^{3N}x : \quad \left(V_n + T_K - E\right)\chi_n =$$

$$= \sum_m \frac{\hbar^2}{M}\int \phi_n^* \frac{\partial \phi_m}{\partial Q}\frac{\partial \chi_m}{\partial Q} d^{3N}x$$

$$-\sum_m \chi_m \int \phi_n^* \left(T_K \phi_m\right) d^{3N}x$$

$$= \sum_m \Lambda_{nm}\chi_m \ .$$

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 $M_i \gg m_{el}$).

# Simple estimates for hierarchy of energy scales

$$E_{elec} \sim < T_e > \sim \frac{\hbar^2 \kappa_{elec}^2}{m} \sim \frac{\hbar^2}{md^2}$$

with $d \approx$ molecular dimension

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

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

$$E_{rot} \ \sim \ < T_{rot} > \ \sim \ \frac{\hbar^2}{I} \quad = \quad \frac{\hbar^2}{Md^2} = \frac{m}{M} E_{elec}$$

$$\boxed{\Longrightarrow \quad E_{rot} \quad \ll \quad E_{vib} \quad \ll \quad E_{elec}}$$

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

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

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

## ... and for nonadiabatic coupling elements

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

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

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

# 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

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

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

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

Remember symmetry:

$$H_n(-Q) = (-1)^n H_n(Q)$$

# The multidimensional harmonic oscillator

$$H = \sum_i H_i = \sum_i \frac{\hbar\omega_i}{2}\left(-\frac{\partial^2}{\partial Q_i^2} + Q_i^2\right)$$

From $[H_i, H_j] = 0$ (for all $i, j \leq M(= 3N - 6)) \Rightarrow$

Multidimensional eigenfunction $\Xi$ is product function:

$$\boxed{\Xi_{v_1,v_2,..}(Q_1, \ldots, Q_M) = \chi_{v_1}(Q_1)\,\chi_{v_2}(Q_2)\ldots\chi_{v_M}(Q_M)}$$

The individual eigenfunctions are well known and read as

$$\boxed{\chi_v(Q) = \{\sqrt{\pi}\ v!\ 2^v\}^{-1/2}\, e^{-Q^2/2}\ H_v(Q)}$$

The first Hermite polynomials $H_v$ are

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

Meaning of the coordinate $Q$: displacement as measured in units of the zero-point amplitude, i. e.,

$$\chi_0(1) = e^{-1/2}\chi_0(0).$$

## 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.

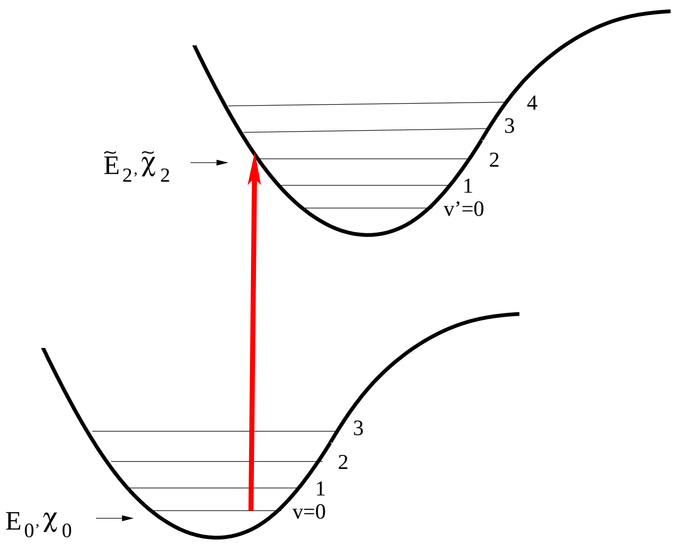
Interaction between the molecule and radiation field in the dipole approximation:

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

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:

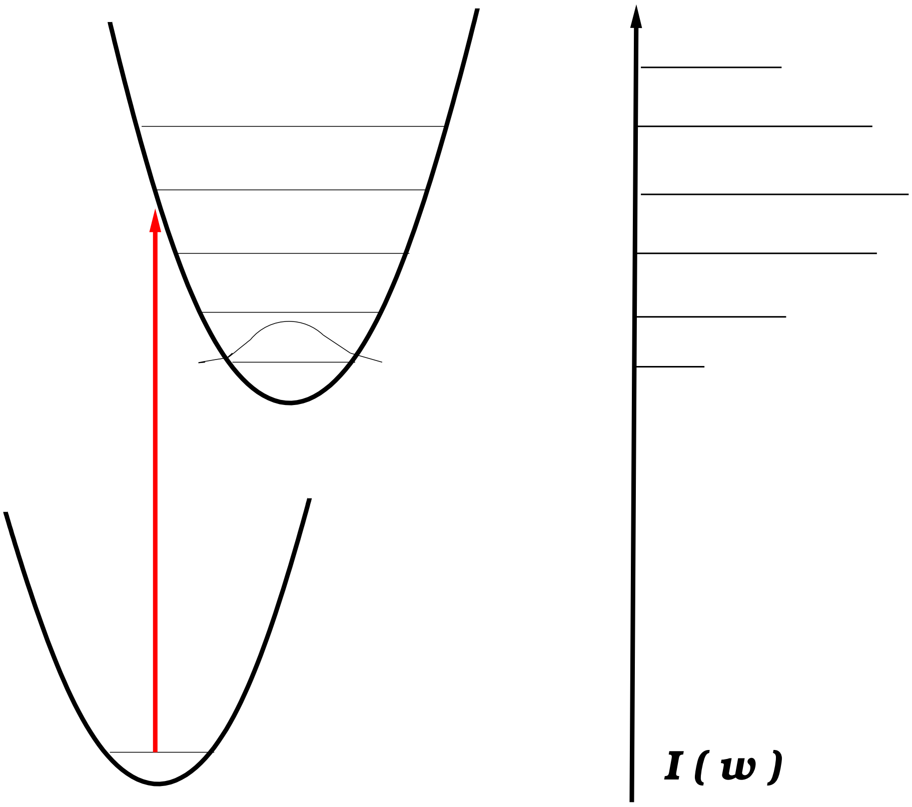
*Condon approximation* or *Franck-Condon principle*.

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

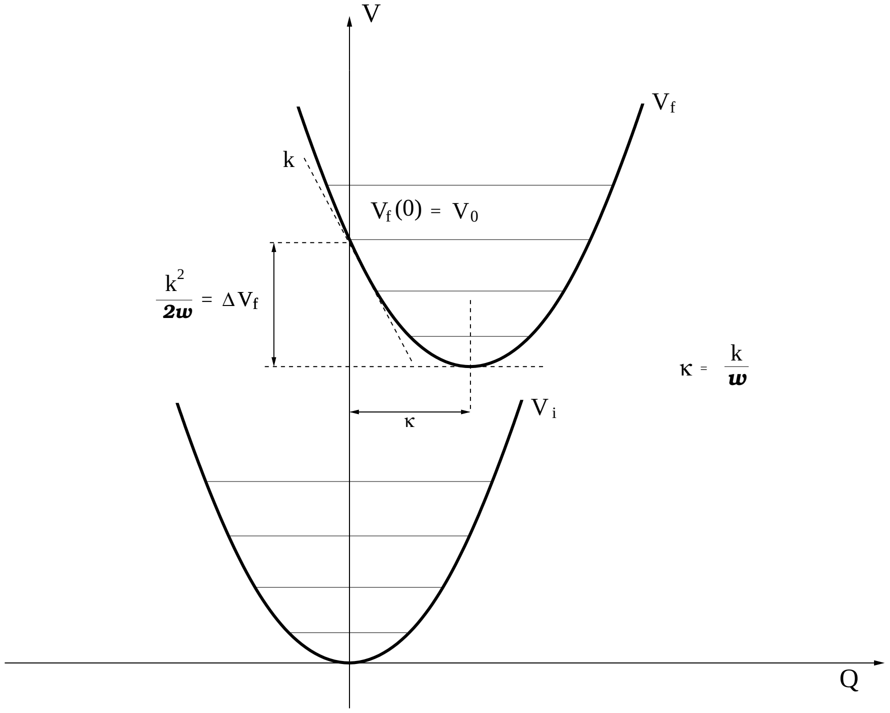
$$V_f(Q) = V_f(Q = 0) + \frac{\omega}{2}Q^2 + kQ$$

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);

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

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



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).

## Derivation of Poisson Distribution

Start from

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

and supplementary sheet on Hermite polynomials, item 2. Use $\lambda = \kappa/2, \quad z = Q' \to Q, \quad v' \to v$

$$\Rightarrow S_{v0} = N_v N_0 \int_{-\infty}^{\infty} dQ H_v \left(Q\right) e^{-Q^2} e^{-\kappa^2/4} \sum_{n=0}^{\infty} \frac{(\kappa/2)^n}{n!} H_n(Q)$$

$$\left[ N_v = \left\{ \sqrt{\pi} \; v! \; 2^v \right\}^{-\frac{1}{2}} \right]$$

$$= N_v N_0 e^{-\kappa^2/4} \sum_{n=0}^{\infty} \frac{(\kappa/2)^n}{n!} \;\; \frac{\delta_{v\,n}}{N_v N_n}$$

$$= e^{-\kappa^2/4} \;\; \frac{(\kappa/2)^v}{v!} \;\; \sqrt{2^v v!}$$

$$\Longrightarrow \boxed{\; |S_{v0}|^2 = \frac{(\kappa^2/2)^v}{v!} \;\; e^{-\kappa^2/2} \;}$$

## Poisson Intensity Distribution

# 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:*

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

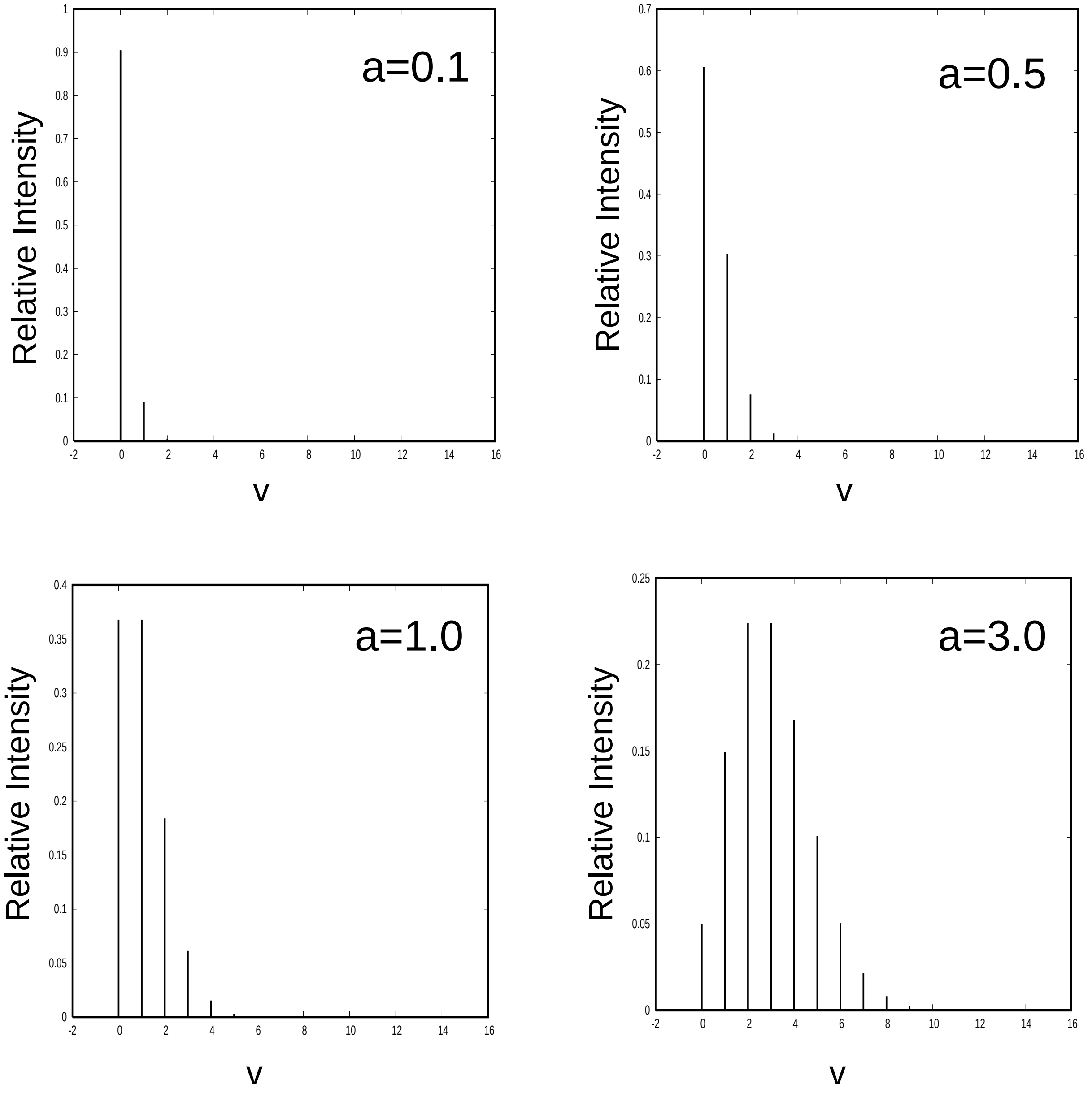
*Mean quantum number:*

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

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 $a \to 0$ 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):*

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

*Energetic width:*

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

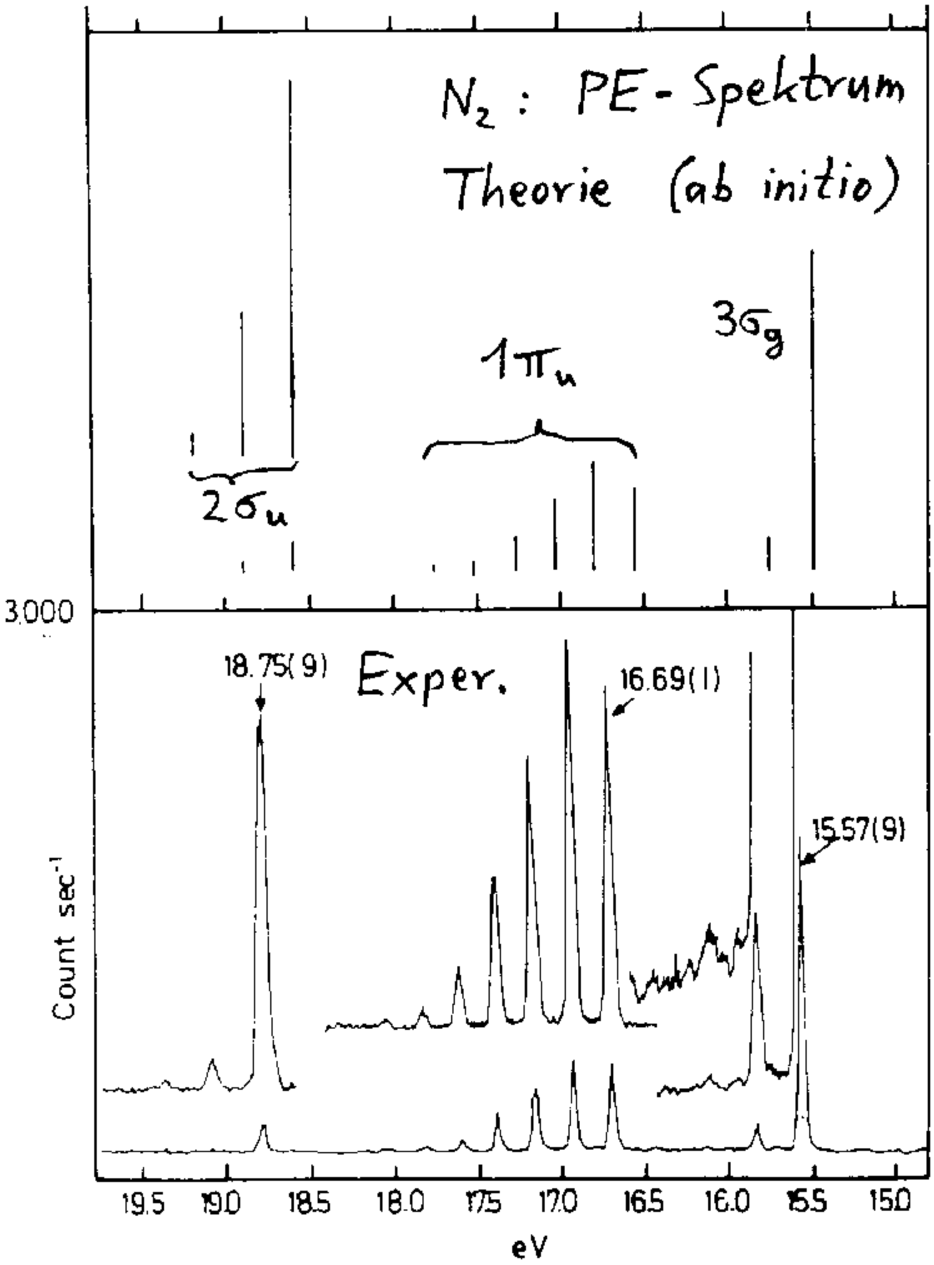
$$\Longrightarrow \boxed{\Delta E \sim \frac{k}{\sqrt{2}}}$$

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

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

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



$1\pi_u$ - Bande:

$a = 1.33$

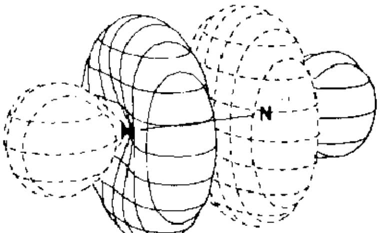
$$\frac{I_{v+1}}{I_v}(v+1) \approx$$

1.14, 1.38,
1.67, 1.60 ....

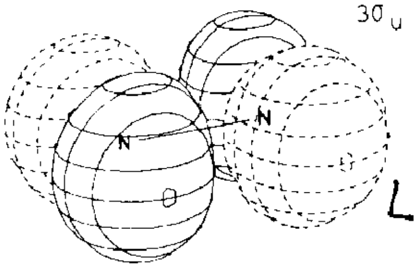
Cederbaum, Domcke, J. Chem. Phys. 60, 2878 ('74)

## 16. Nitrogen

Symmetry: $D_{\infty h}$

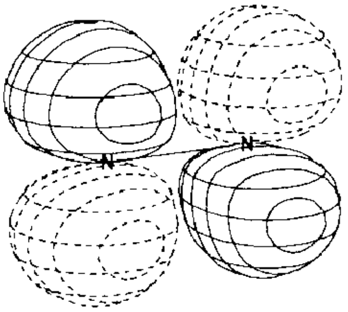


$3\sigma_u$ E= 1.2262



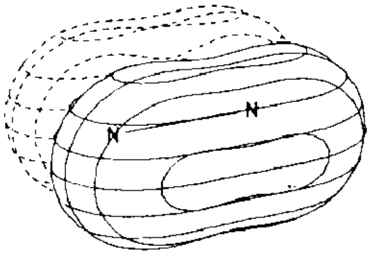
$1\pi_g$ E= 0.3002

LUMO

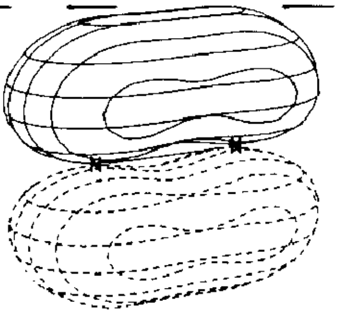


$1\pi_g$ E= 0.3002

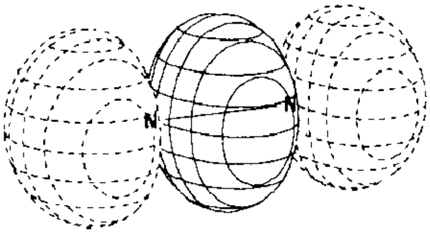
HOMO



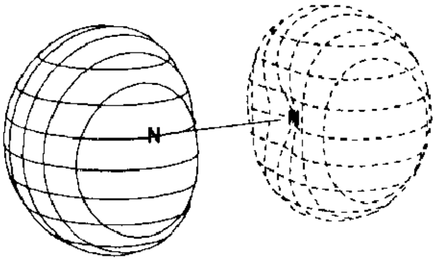
$1\pi_u$ E=-0.5454



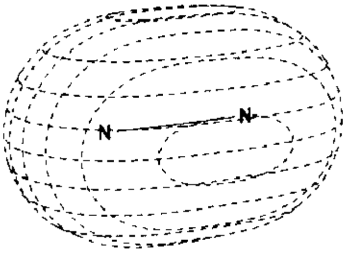
$1\pi_u$ E=-0.5454



$3\sigma_g$ E=-0.5555

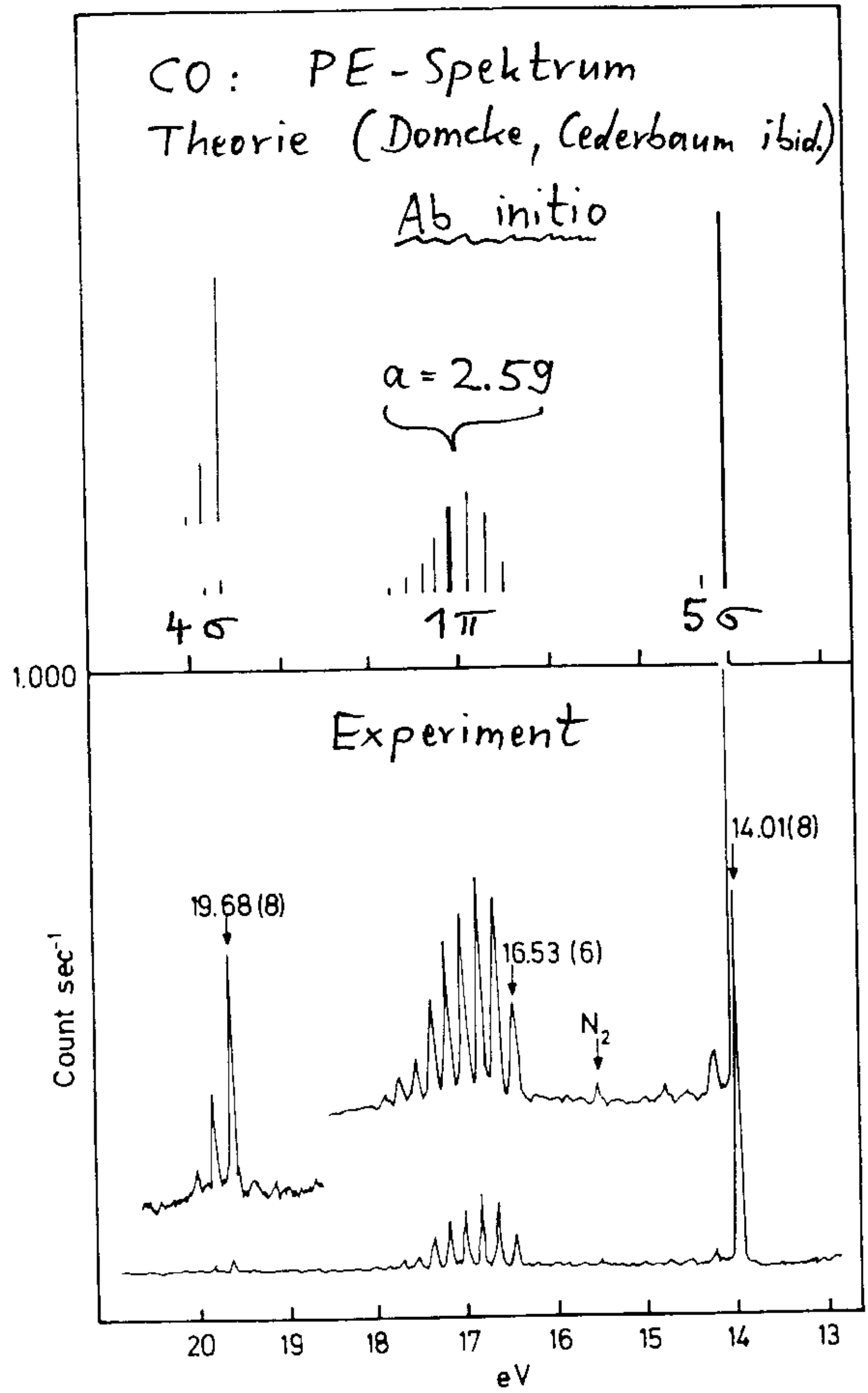


$2\sigma_u$ E=-0.7137



$2\sigma_g$ E=-1.4211

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



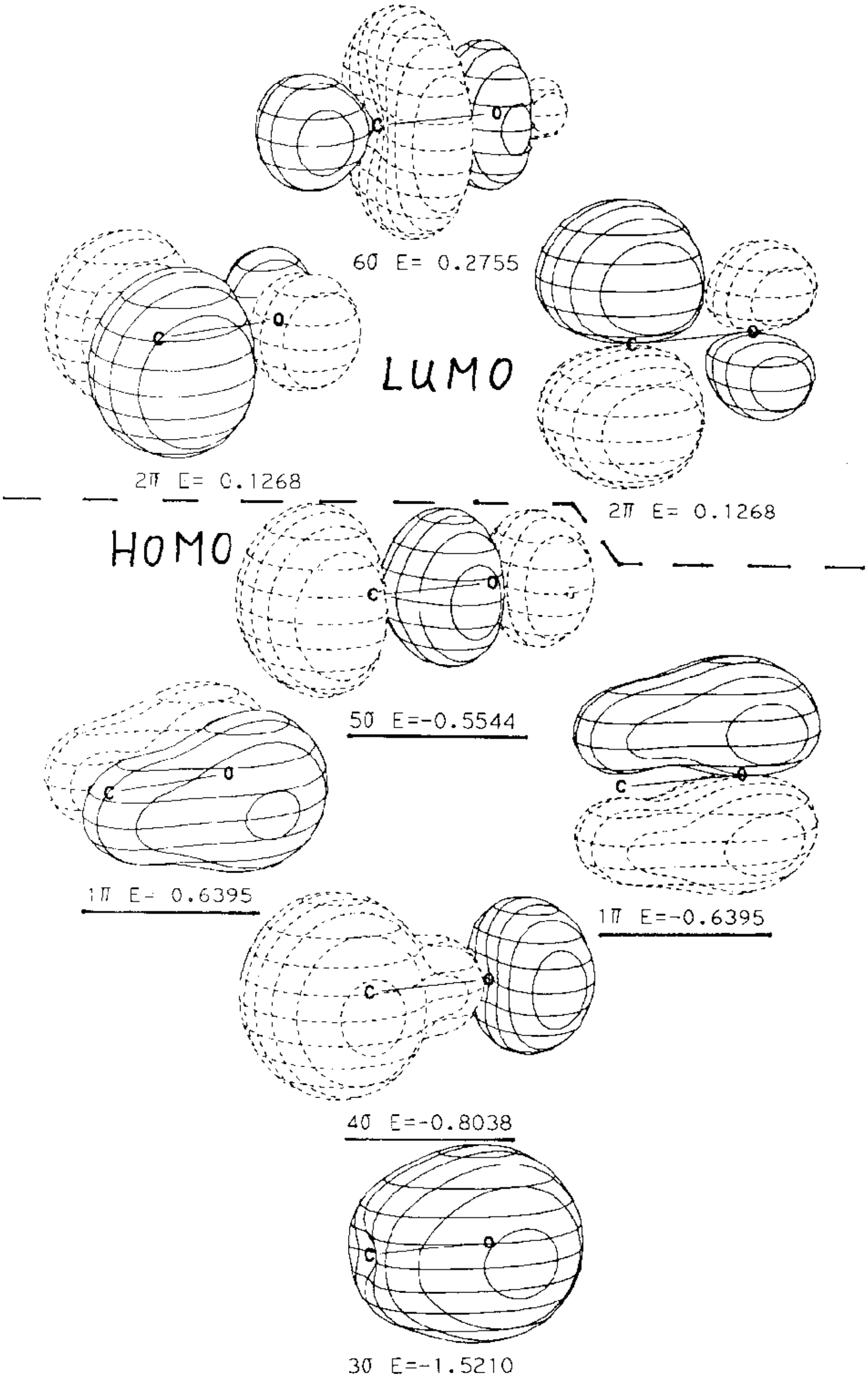
1π - Bande :

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

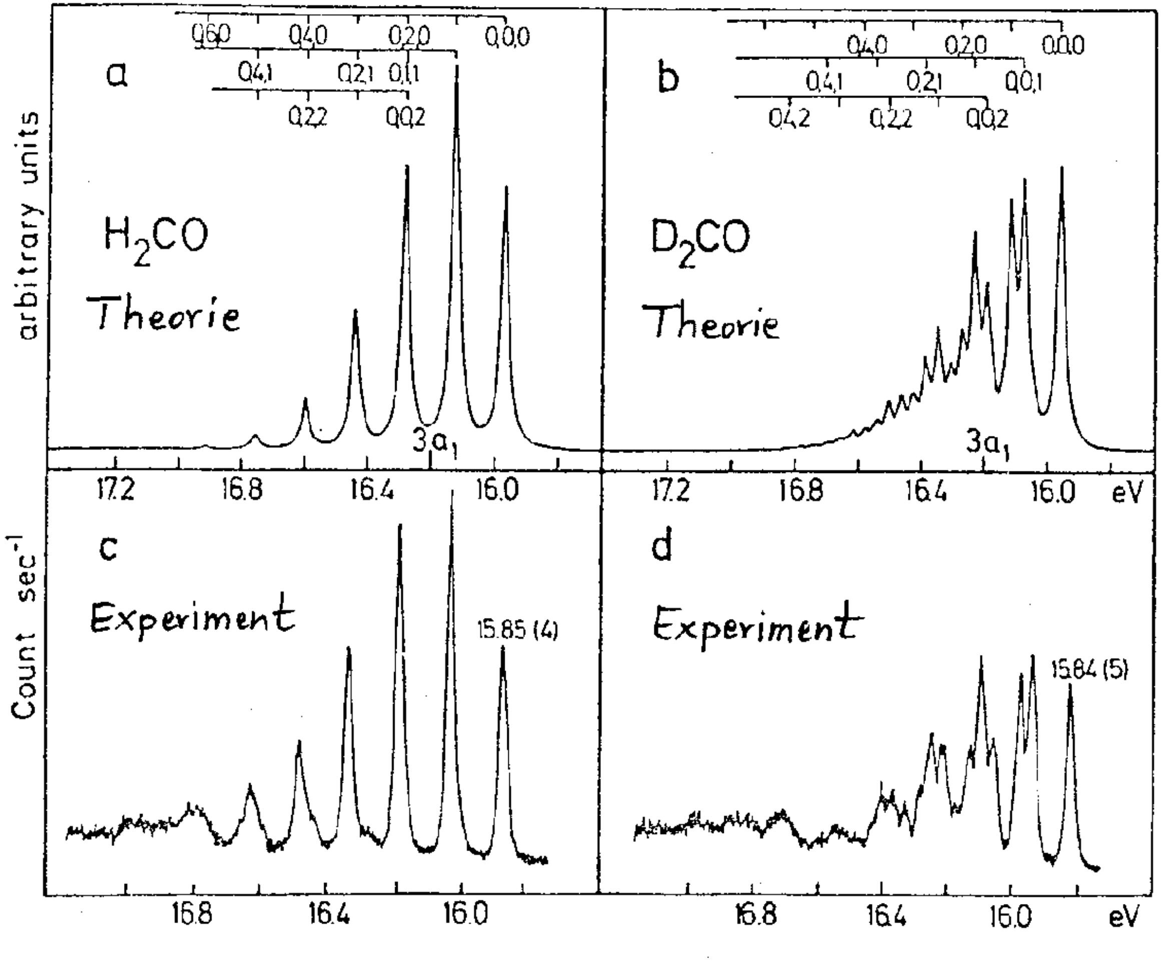
2.13, 2.19,
2.57, 3.47,
3.27, 2.82,
⋮

## 15. Carbon Monoxide

Symmetry: $C_{\infty v}$

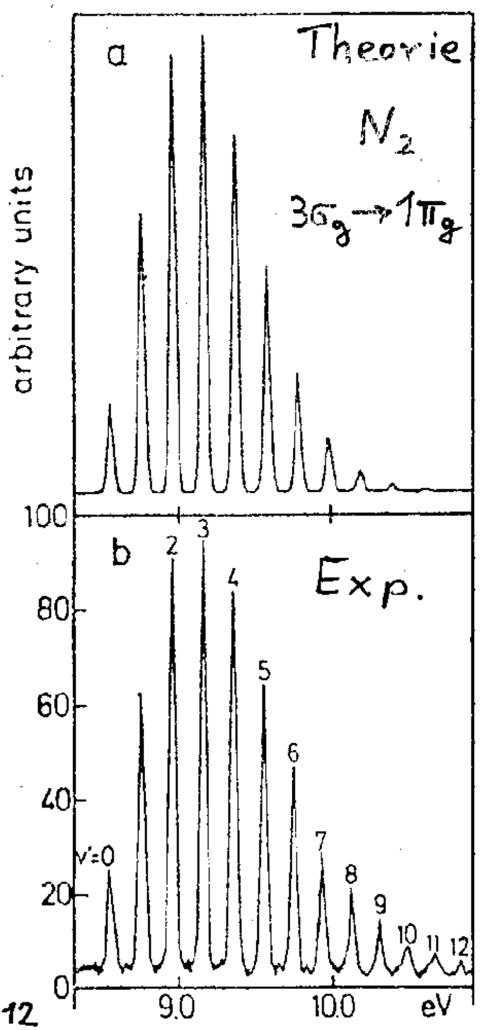


## Mehrmoden PE - Bande



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

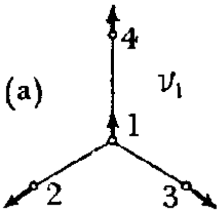
## Anregungsspektrum



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

(Freq. für $H_2CO$)

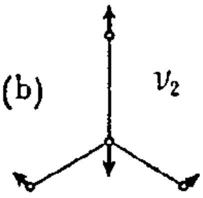
(a)



symm. C–H Streckmode

$\omega_1 = 2944\ cm^{-1}$

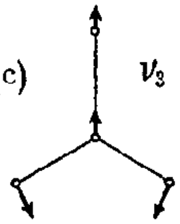
(b)



C–O Streckmode

$\omega_2 = 1764\ cm^{-1}$

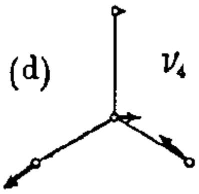
(c)



H-C-H Winkelschw.

$\omega_3 = 1563\ cm^{-1}$

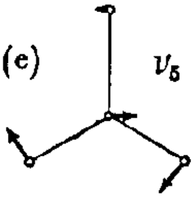
(d)



asymm. C–H Streckmode

$\omega_4 = 3009\ cm^{-1}$

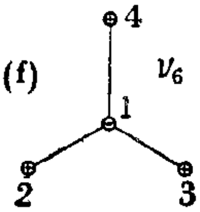
(e)



"C–O Winkelschw."

$\omega_5 = 1288\ cm^{-1}$

(f)



Nichtplanare Deformationsmode

$\omega_6 = 1191\ cm^{-1}$

# Two-dimensional shifted harmonic oscillator

$$V_i(Q_1, Q_2) = \sum_{j=1,2} \frac{\omega_j}{2} Q_j^2 \qquad (\hbar = 1)$$

$$V_f(Q_1, Q_2) = V_f(Q = 0) + \sum_{j=1,2} (\frac{\omega_j}{2} Q_j^2 + k_j Q_j)$$

$$\tilde{E}_{\upsilon_1,\upsilon_2} - E_{0,0} = V_0 - \frac{k_1^2}{2\omega_1} - \frac{k_2^2}{2\omega_2} + \omega_1 \upsilon_1 + \omega_2 \upsilon_2$$

$$\Psi_f = \phi_f \ \tilde{\chi}_{\upsilon_1}(Q_1) \ \tilde{\chi}_{\upsilon_2}(Q_2)$$

$$|S_{\upsilon_1 \upsilon_2,00}|^2 = |S_{\upsilon_1 0}|^2 |S_{\upsilon_2 0}|^2$$

$$P(E_{ph}) = \sum_{\upsilon_1,\upsilon_2} \frac{a_1^{\upsilon_1}}{\upsilon_1!} \frac{a_2^{\upsilon_2}}{\upsilon_2!} e^{-a_1 - a_2} \times$$

$$\times \quad \delta(E_{ph} - V_0 + a_1\omega_1 + a_2\omega_2 - \upsilon_1\omega_1 - \upsilon_2\omega_2)$$

where $a_j = \kappa_j^2/2 = k_j^2/(2\omega_j^2)$ $(j = 1, 2)$.

"Convolution" of two Poisson intensity distributions!

## 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:

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

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

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 !