The multi-mode vibronic-coupling approach

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Motivation

- Application of *Vibronic-Coupling*.
    - Molecular Spectroscopy and Molecular Dynamics.
        - Absorption, emisson spectroscopy
        - Raman Scattering
        - Circular Dichroism
        - Radiationless transitions
        - Multi-photon absorptions
        - Electron paramagnetic resonances
    - Solid state
        - Crystal impurities
        - Phonon scattering
        - Paraelectric resonances

…………… & many more !!!

- *Multimode* Vibronic-Coupling (Diatomics Vs. Polyatomics).

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  - Molecular Spectroscopy and Molecular Dynamics.
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nore !!!

- *Multimode* Vibron g (Diatomics Vs. Polyatomics).

....is Jahn Teller effect beyond comprehension and merely introduced when we are at a loss for an explanation of certain peculiarities in the analysis of electronic spectra?????

Gad Fischer

Formulation of Vibronic-Coupling Hamiltonians

$$
\begin{aligned}
H &= T_N + H_e \\
&= T_N + T_e + U(\mathbf{r},\mathbf{R})
\end{aligned}
$$

The Coupled equations in the ***diabatic representation*****;**

$$(T_N + W_{nn}(\mathbf{R}) - E)\chi_n(\mathbf{R}) = \sum_{m\neq n} W_{nm}(\mathbf{R})\chi_m(\mathbf{R})$$

$$W_{nm}(\mathbf{R}) = \left\langle \phi_n \middle| H_e(\mathbf{r},\mathbf{R}) \middle| \phi_m \right\rangle$$

Molecular Hamiltonian in ***diabatic basis;***

$$
\boldsymbol{H} = \begin{matrix} T_N + W_{nn}(\mathbf{R}) & W_{nm}(\mathbf{R}) \\ W_{mn}(\mathbf{R}) & T_N + W_{mm}(\mathbf{R}) \end{matrix}
\quad
\begin{matrix} \langle\phi_n| \\ \langle\phi_m| \end{matrix}
$$

Choice of Nuclear Coordinates:

- Simplifying the electronic PE and KE operators. ⟶ Cartesian/Mass-weighted Cartesian coordinates.
- Drop translational and rotational motion. ⟶ Internal coordinates
- Only small amplitude motions are involved.
- Introduce normal coordinates.

$$\mathbf{q} = L^{-1}\delta\mathbf{R}$$

$$\mathbf{Q_i} = (\omega_i / \hbar)^{1/2}\mathbf{q_i}$$

Q_i : dimensionless NC.
ω_i : harmonic freq. of i^{th} mode.

KE and PE operators of the electronic ground state:

$$T_N = -\sum_i \frac{\hbar\omega_i}{2}\frac{\partial^2}{\partial Q_i^2}$$

$$V_0 = \sum_i \frac{\hbar\omega_i}{2} Q_i^2$$

Taylor Series Expansion of W_{nm}

(W_{nm} are the slow varying functions of Q)

$$W_{nn}(Q) = W_0^{(n)}(Q) + \sum_i \frac{\partial W_{nn}(0)}{\partial Q_i} Q_i + \frac{1}{2}\sum_{ij} \frac{\partial W_{nn}(0)}{\partial Q_i \partial Q_j} Q_i Q_j + \cdots$$

$$= W_0^{(n)}(Q) + \sum_i \kappa_i^{(n)} Q_i + \sum_{ij} \gamma_{ij}^{(n)} Q_i Q_j + \cdots$$

$$W_{nm}(Q) = W_{nm}^{(0)}(Q) + \sum_i \frac{\partial W_{nm}(0)}{\partial Q_i} Q_i + \frac{1}{2}\sum_{ij} \frac{\partial W_{nm}(0)}{\partial Q_i \partial Q_j} Q_i Q_j + \cdots$$

$$= W_{nm}^{(0)}(Q) + \sum_i \lambda_i^{(nm)} Q_i + \sum_{ij} \eta_{ij}^{(nm)} Q_i Q_j + \cdots$$

$\kappa^{(n)}$: 1st order *intra-state* electronic-vibrational coupling constant.
$\lambda^{(nm)}$: 1st order *inter-state* electronic-vibrational coupling constant.
$\gamma^{(n)}$: 2nd order *intra-state* electronic-vibrational coupling constant.
$\eta^{(nm)}$: 2nd order *inter-state* electronic-vibrational coupling constant.

Problems:

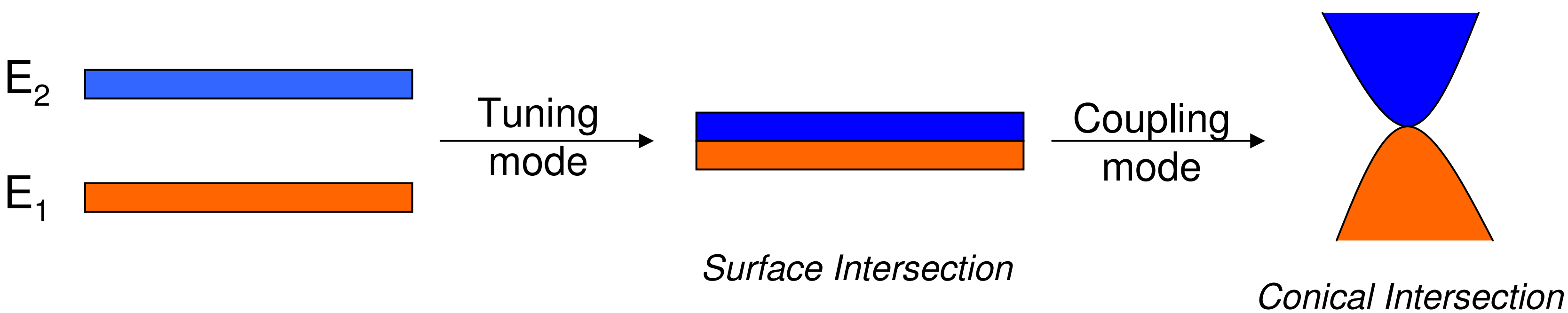
- Number of electronic states (n,m,....) in the Hilbert space.
- Number of vibrational modes (i,j.....) to be considered.

Symmetry selection of coupling parameters:

$W_0^{(n)} \rightarrow \langle n \vert n \rangle$	$\Rightarrow$ Any Irrep.
$\kappa_i^{(n)} \rightarrow \langle n \vert Q_i \vert n \rangle$	$\Rightarrow \Gamma(Q_i) \equiv \Gamma(A)$
$\gamma_{ij}^{(n)} \rightarrow \langle n \vert Q_i Q_j \vert n \rangle$	$\Rightarrow \Gamma(Q_i) \times \Gamma(Q_j) \supset \Gamma(A)$
$W_{nm}^{(0)} \rightarrow \langle n \vert m \rangle$	$\Rightarrow \Gamma(n) \equiv \Gamma(m)$
$\lambda_i^{(nm)} \rightarrow \langle n \vert Q_i \vert m \rangle$	$\Rightarrow \Gamma(n) \times \Gamma(Q_i) \times \Gamma(m) \supset \Gamma(A)$
$\eta_{ij}^{(nm)} \rightarrow \langle n \vert Q_i Q_j \vert m \rangle$	$\Rightarrow \Gamma(n) \times \Gamma(Q_i) \times \Gamma(Q_j) \times \Gamma(m) \supset \Gamma(A)$

A two state model:

$$H = \mathbf{h_0 1} + \begin{pmatrix} E_1 + \sum_{i=1}^{N_t} \kappa_i^{(1)} Q_i & \sum_{j=1}^{Nc} \lambda_j^{(12)} Q_j \\ \sum_{j=1}^{Nc} \lambda_j^{(21)} Q_j & E_2 + \sum_{i=1}^{N_t} \kappa_i^{(2)} Q_i \end{pmatrix} \quad \text{where } \mathbf{h_0} = \frac{\hbar}{2} \sum_{i=1}^{N_t} \left(-\omega_i \frac{\partial^2}{\partial Q_i^2} + \omega_i Q_i^2 \right) + \frac{\hbar}{2} \sum_{j=1}^{Nc} \left(-\omega_j \frac{\partial^2}{\partial Q_j^2} + \omega_j Q_j^2 \right)$$



Specific Models

1. *Jahn-Teller Effect:*

Two components of a *degenerate electronic state* coupled by an appropriate *vibrational mode*.

Symmetry requirements for a JT active mode:

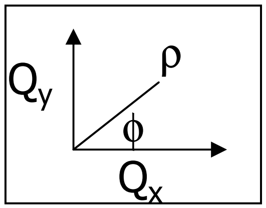
$$\Gamma_{el} \times \Gamma_{el} \supset \Gamma_{vib}$$

E×e
E×b
T×t

a. *E×e Jahn-Teller Effect:*

$$|\Phi_{\pm}\rangle = \frac{1}{\sqrt{2}}(|\Phi_x\rangle \pm i|\Phi_y\rangle)$$

$$Q_{\pm} = (Q_x \pm iQ_y) = \rho e^{\pm i\phi}$$



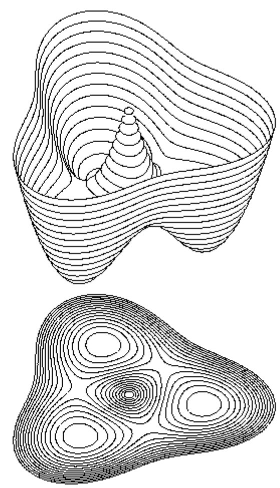
$$C_3 Q_{\pm} = e^{\pm 2\pi i/3} Q_{\pm}$$

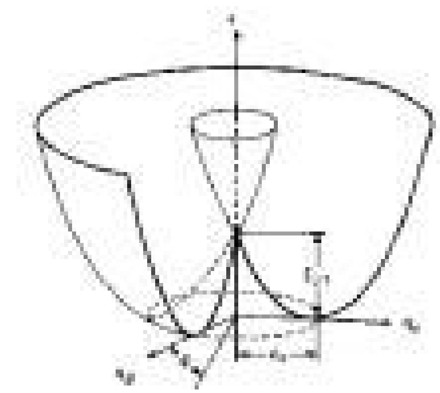
$$C_3 \Phi_{\pm} = e^{\pm 2\pi i/3} \Phi_{\pm}$$

$$H_{el} = \begin{pmatrix} H_{++} & H_{+-} \\ H_{-+} & H_{--} \end{pmatrix}$$

$$\boldsymbol{H} = -\frac{\hbar\omega}{2\rho^2}\left(\rho\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho} + \rho\frac{\partial^2}{\partial\phi^2}\right)\mathbf{1} + \begin{pmatrix} \frac{1}{2}\hbar\omega\rho^2 & \lambda\rho e^{i\phi} + \eta\rho^2 e^{-2i\phi} \\ \lambda\rho e^{-i\phi} + \eta\rho^2 e^{2i\phi} & \frac{1}{2}\hbar\omega\rho^2 \end{pmatrix}$$

$$V_{\pm} = \frac{1}{2}\hbar\omega\rho^2 \pm \sqrt{\lambda^2\rho^2 + \eta^4\rho^4 + 2\lambda\eta\rho^3\cos(3\phi)}$$





Effect of additional vibrational modes:

$$H = \sum_j H_j$$
$$[H_i, H_j] \neq 0$$

Effective single mode approach

Example: System with C_3 symmetry and N_t tuning and N_c coupling modes.

$$C_3 Q_\pm = e^{\pm 2\pi i/3} Q_\pm \qquad C_3 Q_A = Q_A$$
$$C_3 \Phi_\pm = e^{\pm 2\pi i/3} \Phi_\pm$$

$$C_3 |\Phi_+\rangle\langle\Phi_+| = e^{+2\pi i/3} e^{-2\pi i/3} |\Phi_+\rangle\langle\Phi_+| = |\Phi_+\rangle\langle\Phi_+|$$
$$C_3 |\Phi_+\rangle\langle\Phi_-| = e^{+2\pi i/3} e^{+2\pi i/3} |\Phi_+\rangle\langle\Phi_-| = e^{-2\pi i/3} |\Phi_+\rangle\langle\Phi_-|$$

$$H_{el} = \begin{pmatrix} H_{++} & H_{+-} \\ H_{-+} & H_{--} \end{pmatrix}$$

$$W^{(0)} + \sum_{i=1}^{N_t} W_i^{(1)} Q_i + \sum_{i=1}^{N_c} W_{+i}^{(1)} Q_{+i} + \sum_{i=1}^{N_c} W_{-i}^{(1)} Q_{-i} +$$
$$\sum_{i,j=1}^{N_t} W_i^{(2)} Q_i Q_j + \sum_{i,j=1}^{N_c} W_{+i}^{(2)} Q_{+i} Q_{+j} + \sum_{i,j=1}^{N_c} W_{-i}^{(2)} Q_{-i} Q_{-j} +$$
$$\sum_{i=1}^{N_t} \sum_{j=1}^{N_c} W_{i,+j}^{(2)} Q_i Q_{+j} + \sum_{i=1}^{N_t} \sum_{j=1}^{N_c} W_{i,-j}^{(2)} Q_i Q_{-j} + \sum_{i,j=1}^{N_c} W_{+i,-j}^{(2)} Q_{+i} Q_{-j}$$

$$H_{++} = E_1 + \sum_{i=1}^{N_t} \kappa_i Q_i + \sum_{i,j=1}^{N_t} \gamma_{ij} Q_i Q_j + \sum_{i,j=1}^{N_c} \gamma_{ij} Q_{+i} Q_{-j}$$

$$H_{+-} = \sum_{i=1}^{N_c} \lambda_i Q_{-i} + \sum_{i,j=1}^{N_t} \eta_{ij} Q_{+i} Q_{+j} + \sum_{i=1}^{N_t} \sum_{j=1}^{N_c} b_{ij} Q_i Q_{-j}$$

b. (E+A)×e Pseudo-JT Effect:

$$E \times E \supset E$$
$$E \times A \equiv E$$

$$H = \mathbf{h}_0 \mathbf{1} + \begin{pmatrix} E_E + \sum_i \kappa_i^{(E)} Q_i & \lambda' \rho e^{i\phi} & \lambda \rho e^{i\phi} \\ \lambda' \rho e^{-i\phi} & E_A + \sum_i \kappa_i^{(A)} Q_i & \lambda' \rho e^{i\phi} \\ \lambda \rho e^{-i\phi} & \lambda' \rho e^{-i\phi} & E_E + \sum_i \kappa_i^{(E)} Q_i \end{pmatrix}$$

2. Renner-Teller Effect:

$$C_\varphi Q_\pm = e^{\pm i\varphi} Q_\pm$$
$$C_\varphi \Phi_\pm = e^{\pm i\Lambda\varphi} \Phi_\pm$$

a. Π×π RT Effect:

$$H = \mathbf{h}_0 \mathbf{1} + \begin{pmatrix} E_\Pi + \sum_i \kappa_i^{(\pi)} & c\rho^2 e^{2i\phi} \\ c\rho^2 e^{-2i\phi} & E_\Pi + \sum_i \kappa_i^{(\pi)} \end{pmatrix}$$

$$[H_c, H_t] = 0$$

b. (Π+Σ)×π RT Effect:

$$H = \mathbf{h}_0 \mathbf{1} + \begin{pmatrix} E_\Pi + \sum_i \kappa_i^{(\pi)} & \lambda \rho e^{i\phi} & c\rho^2 e^{2i\phi} \\ \lambda \rho e^{-i\phi} & E_\Sigma + \sum_i \kappa_i^{(\sigma)} & \lambda \rho e^{i\phi} \\ c\rho^2 e^{-2i\phi} & \lambda \rho e^{-i\phi} & E_\Pi + \sum_i \kappa_i^{(\pi)} \end{pmatrix}$$

$$[H_c, H_t] \neq 0$$

Determination of electron-vibrational coupling parameters

•Systems with closed-shell electronic ground state.
•Equlibrium geometry of the ground state is *reference geometry.*

Geometry optimization and force field calculations can be done readily with methods like: RHF, MP2, CCSDT.....with appropriate/affordable basis sets.

Intra-state coupling constats:

$\kappa_i^{(n)}$, $\gamma_{ij}^{(n)}$ ⟶

1st and 2nd derivatives of the excitation energy of the nth excited state with respect to ground state normal coordinates.

Inter-state coupling constats:

$$\lambda_{ij}^{(1,2)} = \left[\frac{1}{8} \frac{\partial^2}{\partial Q_j^2} | V_1(Q) - V_2(Q) |^2 \right]_0^{1/2}$$

A robust alternative : Optimize the coupling parameters by a non-linear fitting of the diabatic Hamiltonian with *ab initio* computed adiabatic energy*.*

Methods: CASSCF→PT / MRCI
EOM-CC (Linear response)
MBGF

Calculation of the Spectrum

$$P(E) = \frac{2\pi}{\hbar} \sum_n \left| \langle \Psi_i | \hat{\mathbf{T}} | \Psi_n \rangle \right|^2 \delta(E - E_i - E_n)$$

Fermi's Golden Rule

State Vector is given by,

$$|\Psi_n\rangle = \sum_{i, n_1, n_2, \ldots, n_k} a_{i, n_1, n_2, \ldots, n_k} |\Phi_i\rangle |n_1\rangle |n_2\rangle \ldots\ldots |n_k\rangle$$

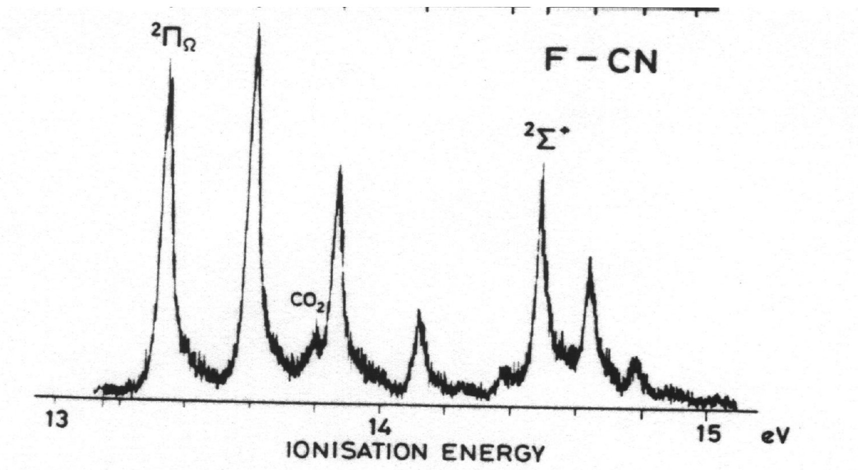
$\{|n_i\rangle\}$ ⟶ Unperurbed harmonic oscillator basis functions

Example:

20 HO basis functions for each mode and 6 modes → Dimension of vibronic secular matrix :

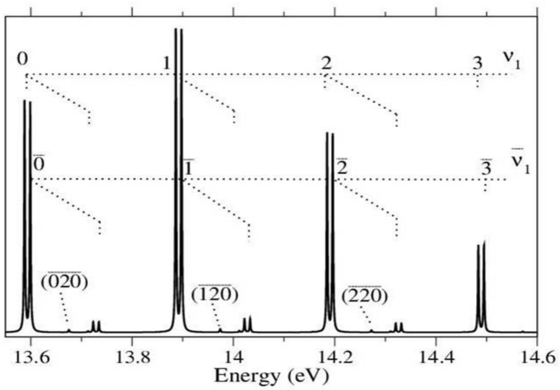
20× 20× 20× 20× 20× 20= **6.4×10^7**

Example1: FCN^{+} * Vs. HCN^{+}



$$
\mathbf{h}_0\mathbf{1} + \begin{pmatrix} E_\Pi + \sum_i \kappa_i^{(\pi)} & \lambda\rho e^{i\phi} & c\rho^2 e^{2i\phi} \\ \lambda\rho e^{-i\phi} & E_\Sigma + \sum_i \kappa_i^{(\sigma)} & \lambda\rho e^{i\phi} \\ c\rho^2 e^{-2i\phi} & \lambda\rho e^{-i\phi} & E_\Pi + \sum_i \kappa_i^{(\pi)} \end{pmatrix}
$$

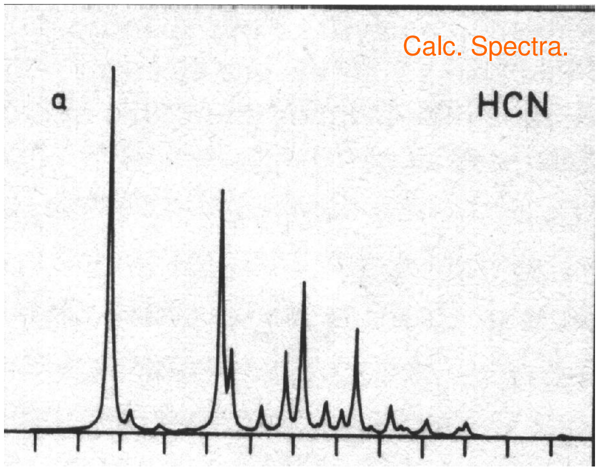
$\Delta_{(\Sigma-\Pi)} > 1$ eV.

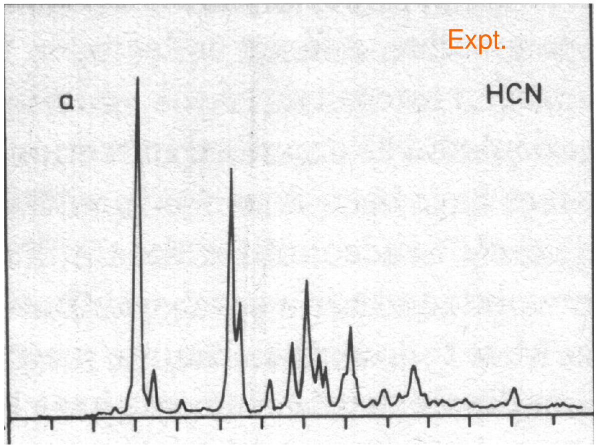


Weak FC stretching mode.
Weak RT coupling.

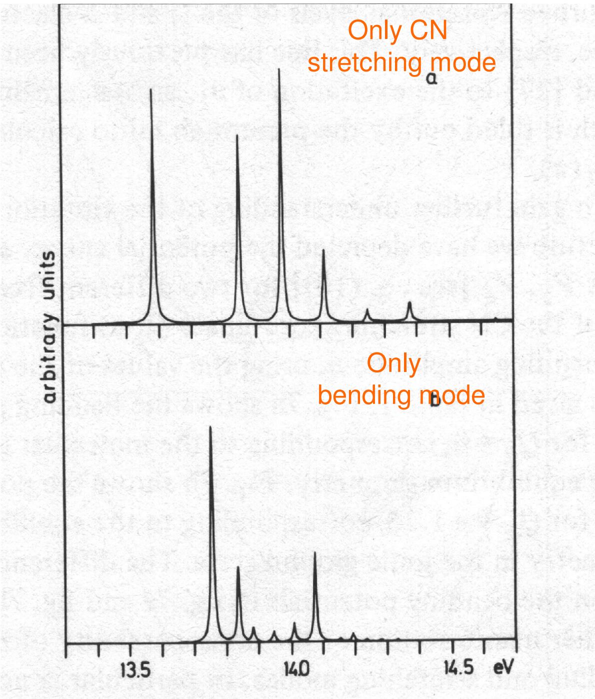
* Mishra, Vallet, Poluyanov, Domcke, to be submitted

Example1: FCN^+ Vs. HCN^+ *





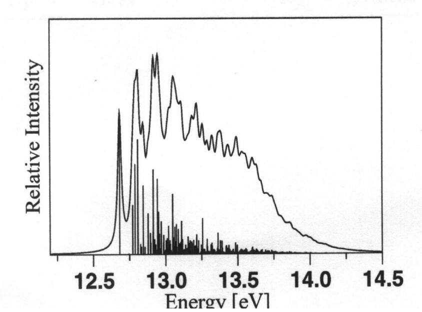
$$\Delta_{(\Sigma-\Pi)} = 0.2 \text{ eV.}$$



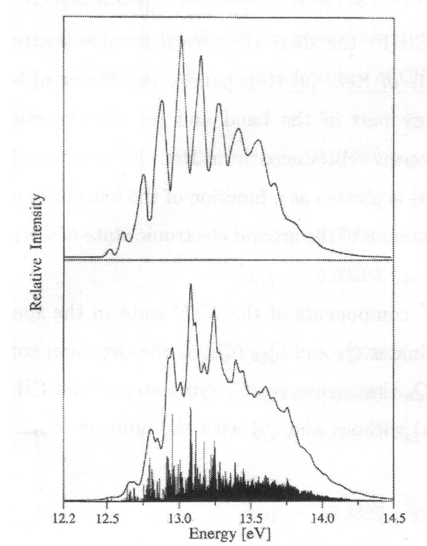
* Koeppel, Domcke, Cederbaum, Von Niessen, Chem Phys, 1979 **37** 310

Example2: CH_3F^+ *

§ 3 tuning modes (a_1) and 3 coupling (degenerate) modes (e)



Calculated without bilinear coupling.



Experiment.

Calculated with bilinear coupling.

$$H_{+-} = \sum_{i=1}^{N_c} \lambda_i Q_{-i} + \sum_{i,j=1}^{N_t} \eta_{ij} Q_{+i} Q_{+j} + \sum_{i=1}^{N_t} \sum_{j=1}^{N_c} b_{ij} Q_i Q_{-j}$$

* Mahapatra, Vallet, Woywod, Koeppel, Domcke, JCP, to be published