

## B.5) 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:

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

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 instability. It vanishes when all the matrix elements are zero. Using the symmetry selection rules, the matrix elements are, therefore, non zero when:

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

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,  
 $E_1(= \Pi), E_2(= \Delta), \dots, E_k,$

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

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

$$\Gamma(Q_2) = E_1(= \Pi)$$

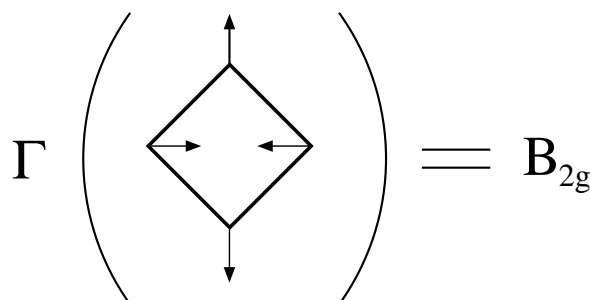
so that  $(E_k)^2 \times \Gamma(Q_2) \not\supseteq \Gamma_{A_1} \implies$   
no linear coupling terms are possible.

### 2. Planar $X_4$ -systems, $D_{4h}$ :

Two doubly-degenerate irreducible representations,

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

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

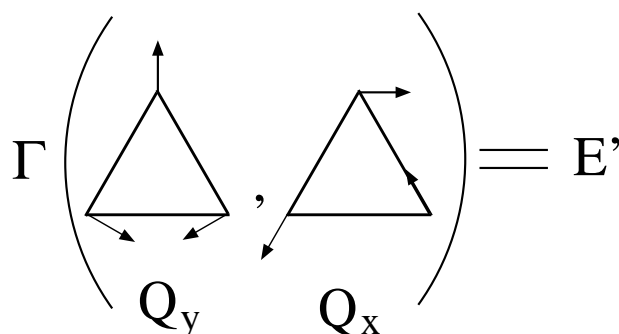


### 3. Planar $X_3$ -systems, $D_{3h}$ :

Two doubly-degenerate irreducible representations

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

The following normal mode transforms like  $E'$ .



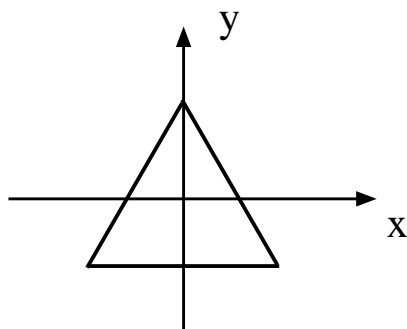
#### Comments:

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.6) 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.

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

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

$$\begin{aligned} \underline{Q_+} &= \underline{Q_x + iQ_y} = \rho (\cos \chi + i \sin \chi) = \underline{\rho e^{i\chi}} \\ \underline{Q_-} &= \underline{Q_x - iQ_y} = \rho (\cos \chi - i \sin \chi) = \underline{\rho e^{-i\chi}} \end{aligned}$$

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

$$\begin{aligned} \underline{C_3 Q_x} &= \cos\left(\frac{2\pi}{3}\right) Q_x - \sin\left(\frac{2\pi}{3}\right) Q_y \\ \underline{C_3 Q_y} &= \sin\left(\frac{2\pi}{3}\right) Q_x + \cos\left(\frac{2\pi}{3}\right) Q_y \end{aligned}$$

so that

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

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  $e^{(\pm 2\pi i/3)}$ . We can express the transformation in a matrix form as

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

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:

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

(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,

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

$Q_{\pm}$  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:

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

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:

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

and also

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

with the same coefficients.

The off-diagonal matrix elements are:

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

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

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

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:

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

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

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

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

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

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:

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

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

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

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

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

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

and:

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

Then,

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

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

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:

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

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:

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

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

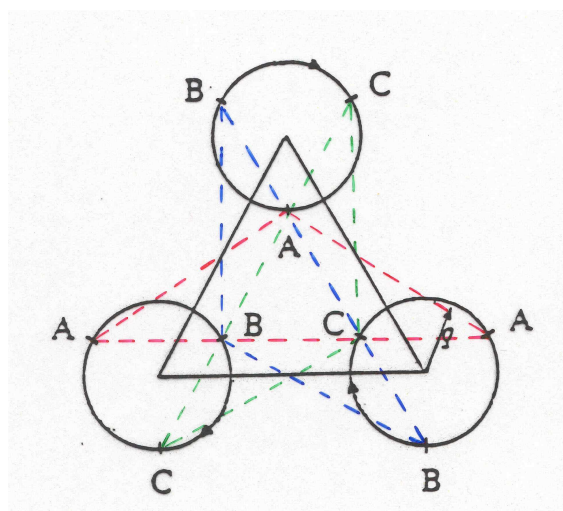
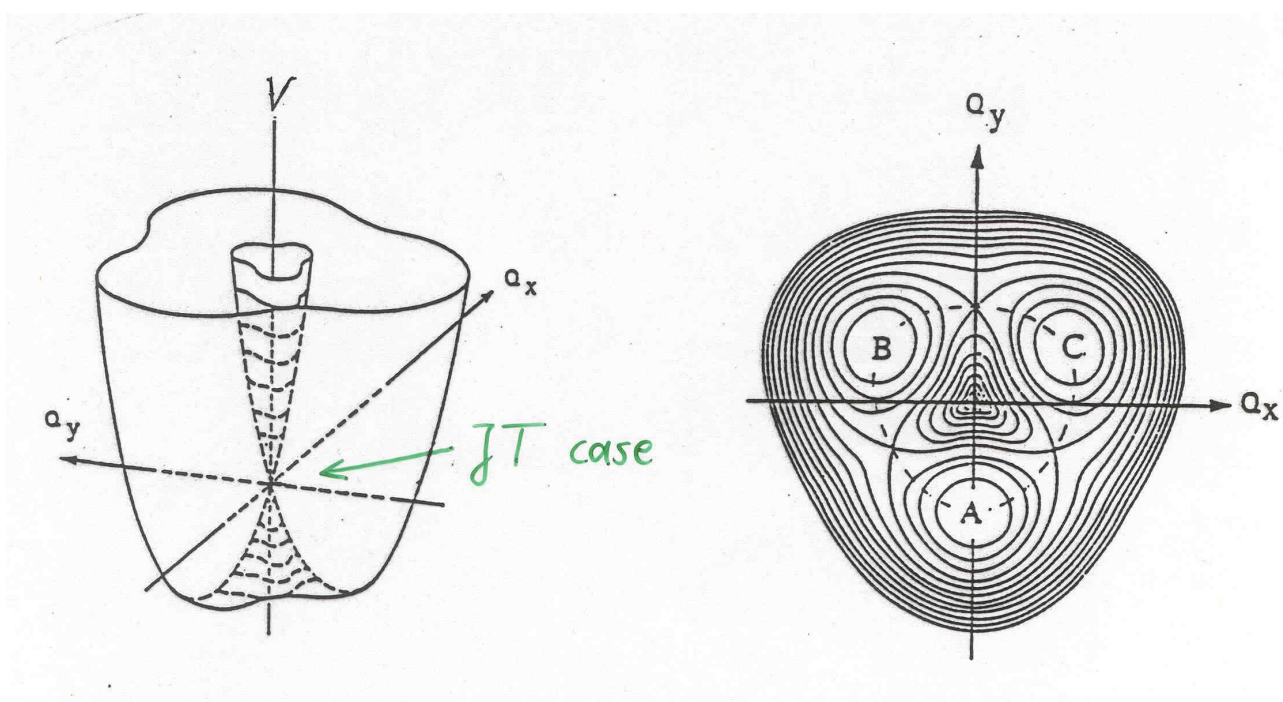
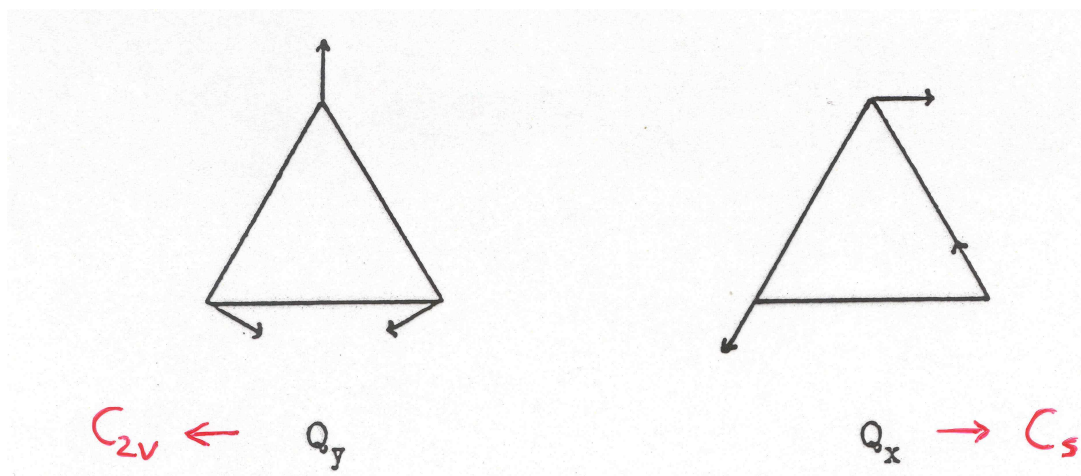
$$V_{1,2} = \frac{\omega}{2}\rho^2 \pm k\rho\sqrt{1 + \frac{g}{k}\rho\cos(3\chi)}$$

By expansion of the square root:

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

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

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

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

we get,

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

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.,

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

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

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

$$\Phi_1^{ad} = \cos\left(\frac{\chi}{2}\right)\Phi_x + \sin\left(\frac{\chi}{2}\right)\Phi_y$$

$$i \Phi_2^{ad} = -\sin\left(\frac{\chi}{2}\right)\Phi_x + \cos\left(\frac{\chi}{2}\right)\Phi_y$$

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

$$\Phi_1^{ad}(2\pi) = -\Phi_1^{ad}(0)$$

$$\Phi_2^{ad}(2\pi) = -\Phi_2^{ad}(0)$$

They transform again into themselves after a  $4\pi$ -loop. This is the 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  $-\frac{\omega}{2\rho^2}\partial^2/\partial\chi^2$ :

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

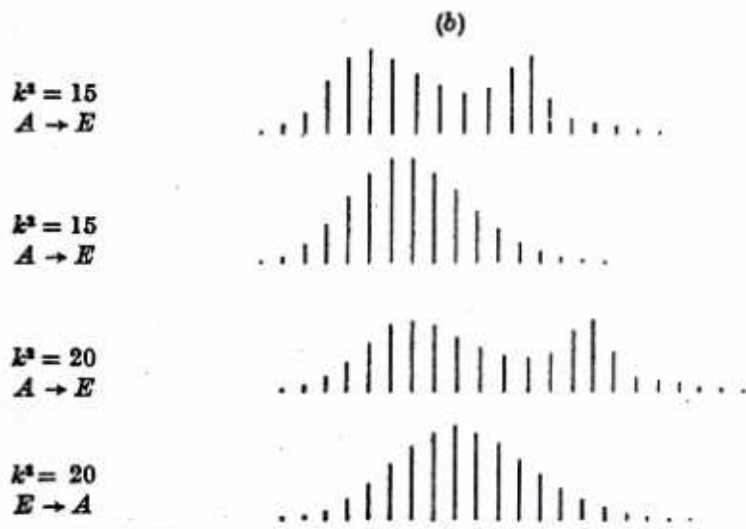
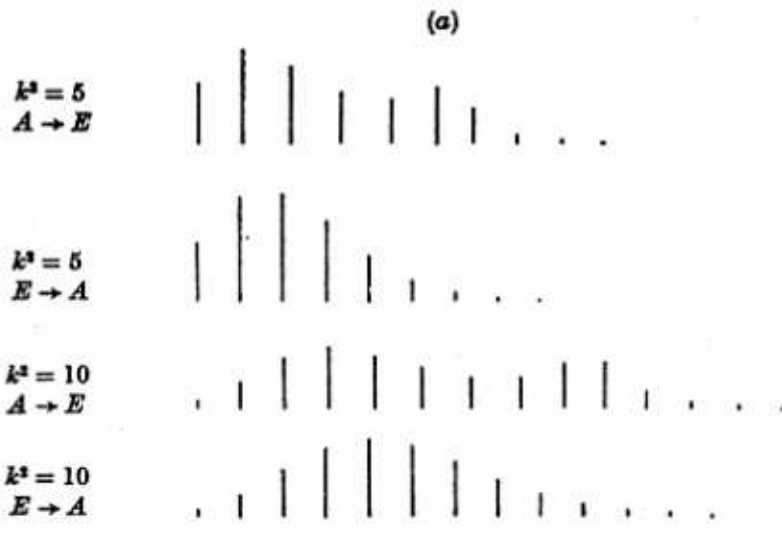
The non-adiabatic coupling operator  $\mathbf{\Lambda}$  reads:

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

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  $A_{1g} \rightarrow E_{g1}$  and  $E_{1g} \rightarrow A_{2g}, A_{2g1}$ . The 0-0 line is that on the left in each diagram.

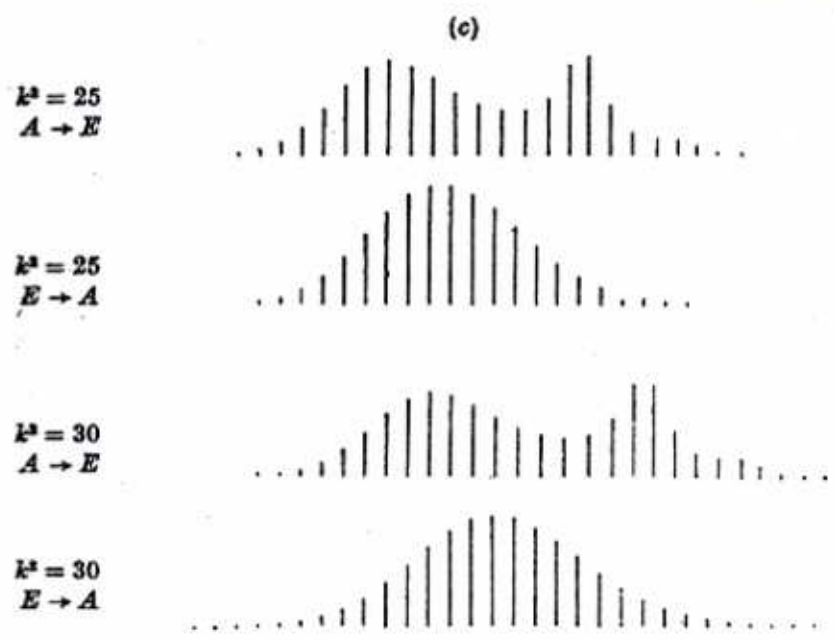
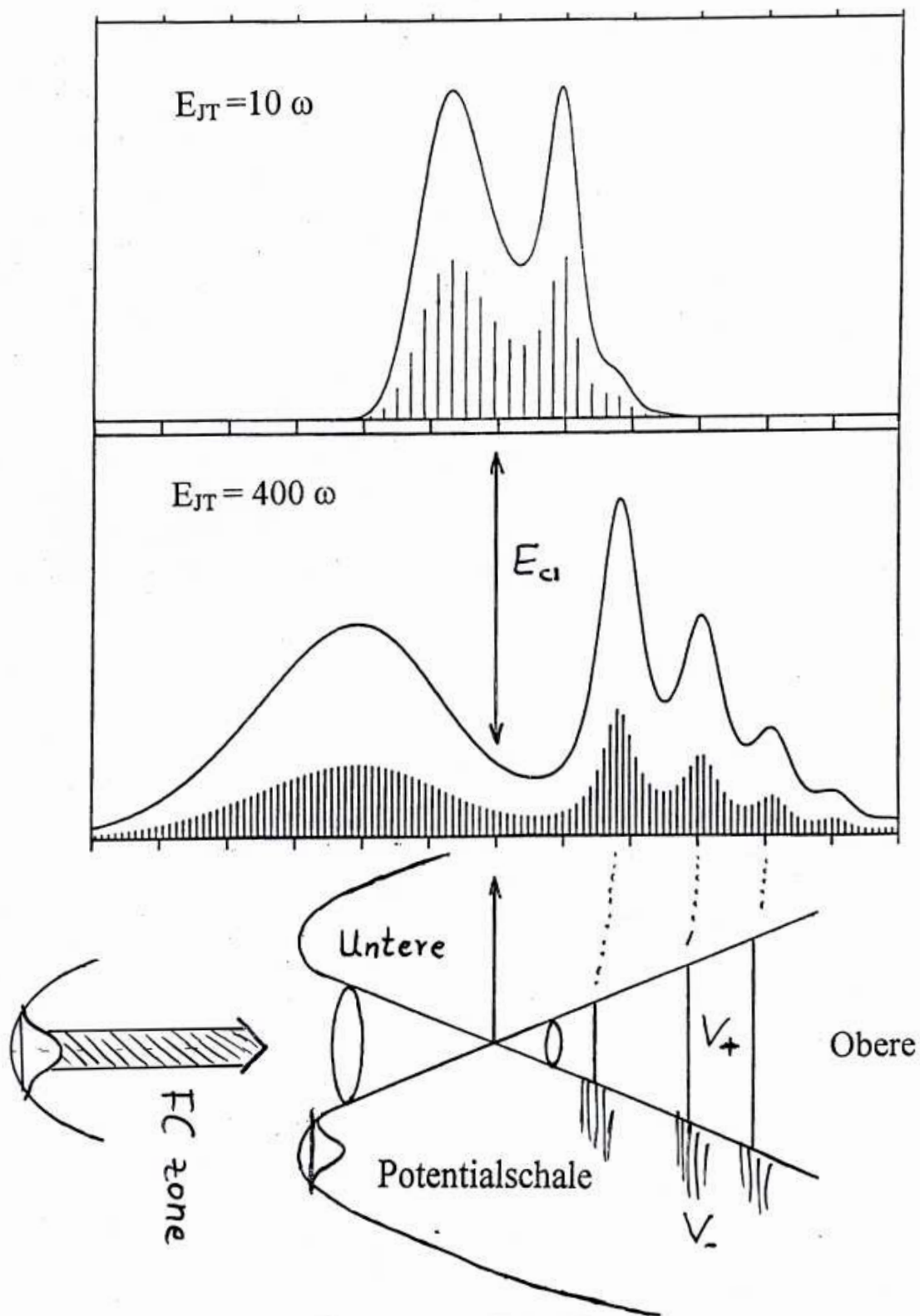


FIGURE 4c. Vibrational structure of (allowed) electronic transitions  $A_{1g} \rightarrow E_{g1}$  and  $E_{1g} \rightarrow A_{2g}, A_{2g1}$ . For large distortions the 0-0 line is no longer visible.

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



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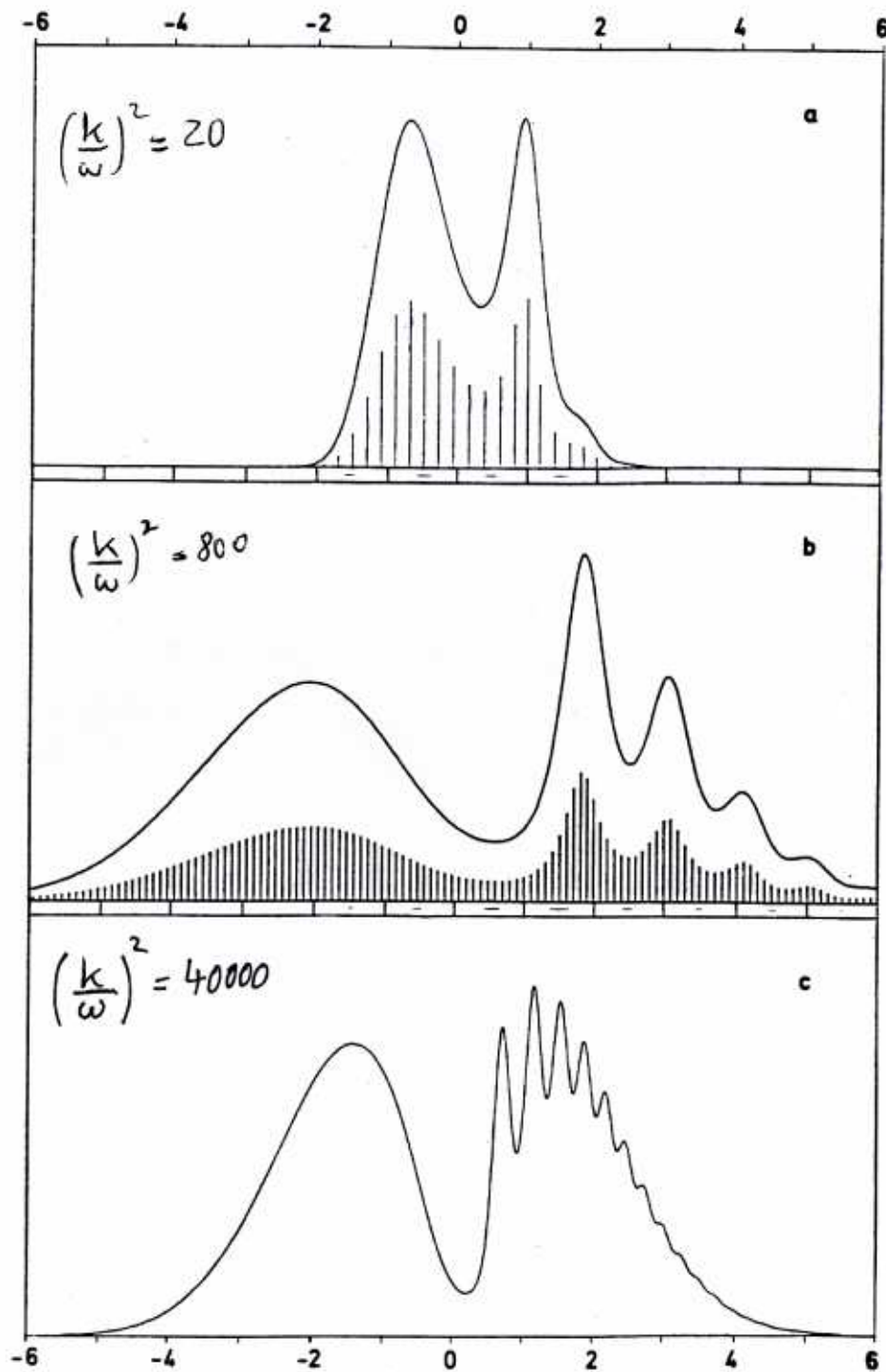


Figure 1. Exact JT line spectra and band shape curves. The band shape curves are obtained from the line spectra by convoluting them with Gaussians of width  $\gamma$ . (a)  $\omega=0.1$ ,  $\kappa=\sqrt{0.2}$ ,  $\gamma=0.1$ ; (b)  $\omega=0.1$ ,  $\kappa=2\sqrt{2}$ ,  $\gamma=0.2$ ; (c)  $\omega=0.01$ ,  $\kappa=2$ ,  $\gamma=0.1$ .

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