The Theory of the Manipulation of Molecules with Laser Beams

Manipulation of the Spontaneous Emission Rate in Diatomic Molecules

Diploma Thesis – http://www.ub.uni-konstanz.de/kops/volltexte/2002/896/

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Overview

➤ Introduction

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➤ Diatomic molecules + radiation

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➤ The master equation

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➤ Time evolution
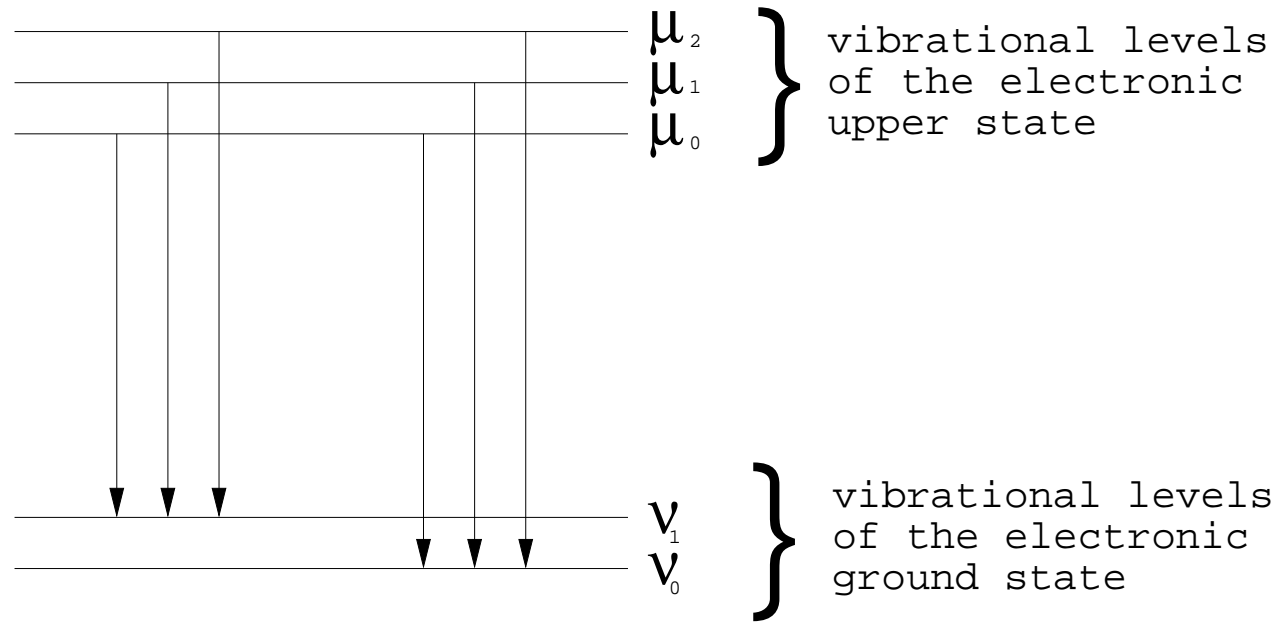
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➤ The master equation

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➤ Numerical examples

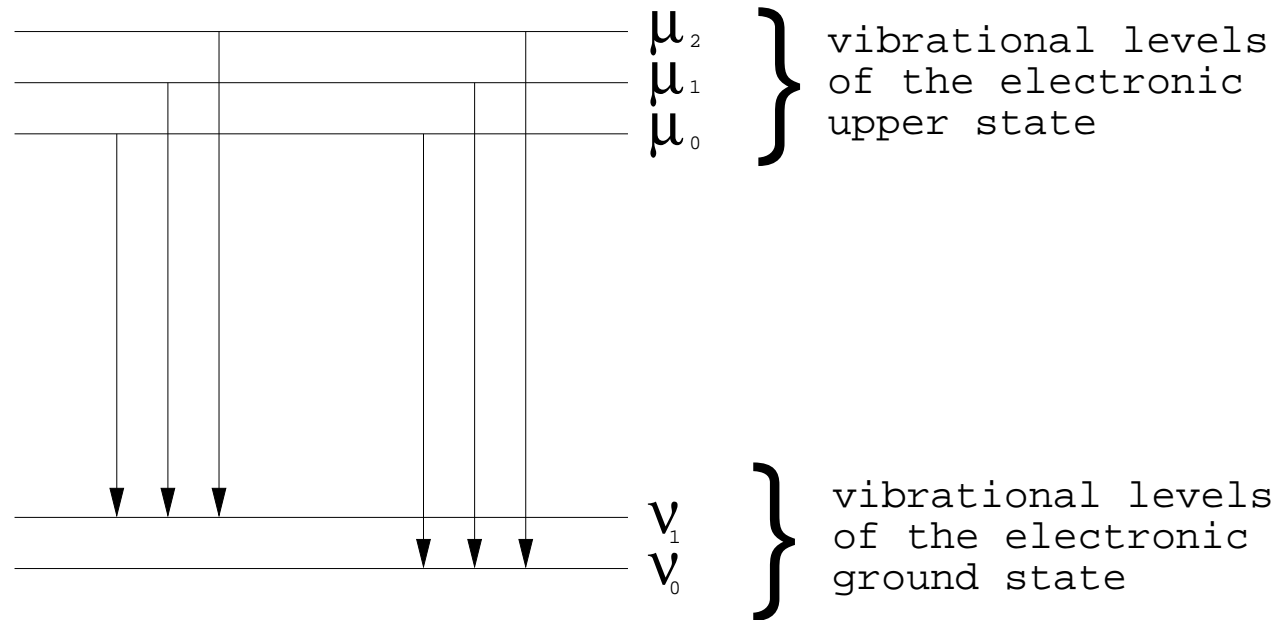➤ Time evolution

➤ Summary

Principle
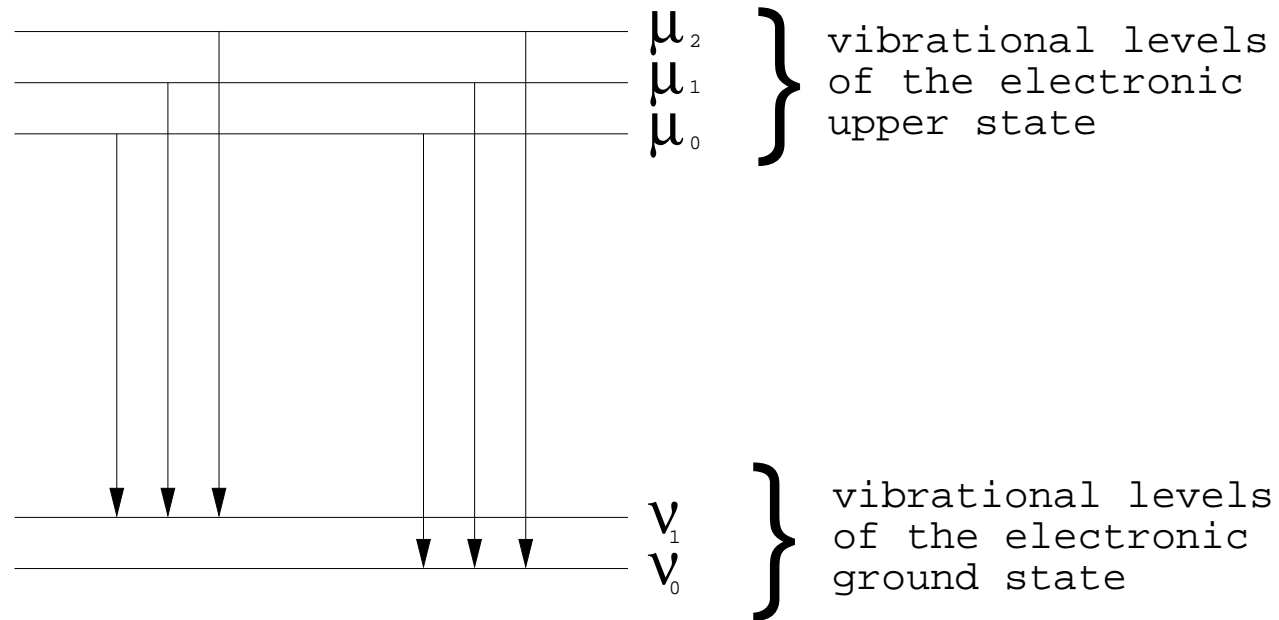
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☞ Effectively, this can result in a modification of the spontaneous emission rate.

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✌ Modification of the spontaneous emission rate could make cyclic processes like laser cooling of molecules feasable.

Coupling to the electromagnetic field

Born-Oppenheimer approximation in molecules

$$\Psi = \psi_{\mathrm{e}}(\vec{r}; R)\chi(R, \vartheta, \varphi) = \psi_{\mathrm{e}}(\vec{r}; R)P(R)\Phi(\vartheta, \varphi)$$

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Dipole matrix element

$$\vec{M}_{\mathrm{fi}} = \int \mathrm{d}^{3n}r\, \mathrm{d}^3 R\; \psi_{\mathrm{ef}}^*(\vec{r}, R)\chi_{\mathrm{f}}^*(\vec{R})(\vec{d} + \vec{D})\psi_{\mathrm{ei}}(\vec{r}, R)\chi_{\mathrm{i}}(\vec{R})$$

$$= \int \mathrm{d}\Omega \int \mathrm{d}R\, P_{\mathrm{f}}^*(R)\Phi_{\mathrm{f}}^*(\vartheta, \varphi) \overbrace{\left(\int \mathrm{d}^{3n}r\; \psi_{\mathrm{ef}}^*\, \vec{d}\, \psi_{\mathrm{ei}}\right)}^{\vec{M}_{\mathrm{fi}}^{\mathrm{e}}(R; \vartheta, \varphi)} \Phi_{\mathrm{i}}(\vartheta, \varphi)P_{\mathrm{i}}(R)$$

$$+ \int \mathrm{d}^3 R\, \chi_{\mathrm{f}}^*\, \vec{D}\, \chi_{\mathrm{i}} \underbrace{\int \mathrm{d}^3 r\; \psi_{\mathrm{ef}}^*\psi_{\mathrm{ei}}}_{=0}$$

The Franck Condon Integral

When $\vec{M}_{\mathrm{fi}}^{\mathrm{e}}(R_0 + x; \vartheta, \varphi) \approx \vec{M}_{\mathrm{fi}}^{\mathrm{e}}(R_0; \vartheta, \varphi)$:

$$\vec{M}_{\mathrm{fi}} = f_{\mathrm{fi}} \underbrace{\int \mathrm{d}\Omega \, \Phi_{\mathrm{f}}^*(\vartheta, \varphi) \vec{M}_{\mathrm{fi}}^{\mathrm{e}}(R_0; \vartheta, \varphi) \Phi_{\mathrm{i}}(\vartheta, \varphi)}_{\Rightarrow \text{selection rules of the rotational levels}}$$
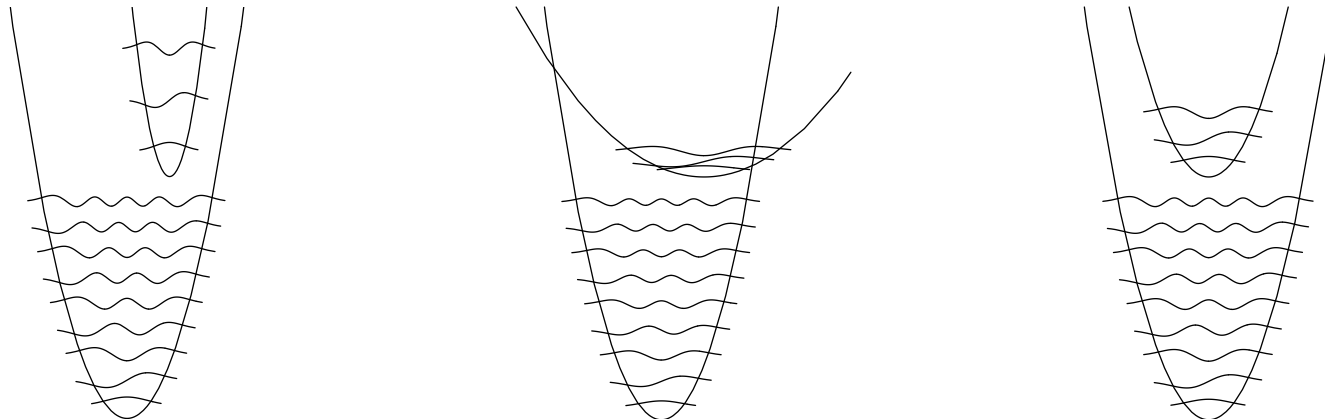
$$f_{\mathrm{fi}} := \int \mathrm{d}R \, P_{\mathrm{f}}^*(R) P_{\mathrm{i}}(R) \quad \text{Franck Condon Integral}$$
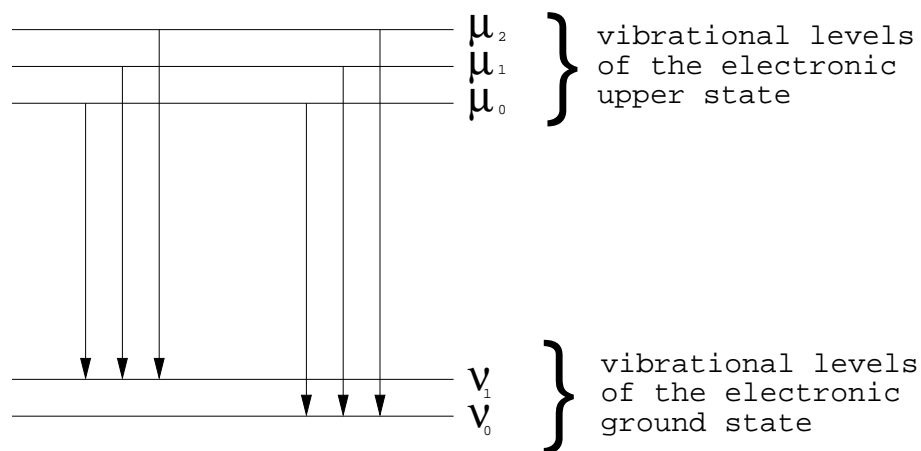
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$$f_{\mathrm{fi}} := \int \mathrm{d}R\, P^*_{\mathrm{f}}(R) P_{\mathrm{i}}(R) \quad \text{Franck Condon Integral}$$

Example
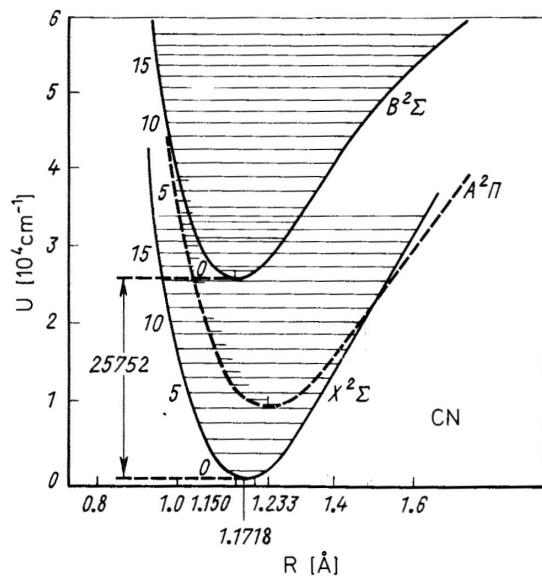
The adiabatic potential curves for the lowest electronic states of *CN* . The graph is taken from A. A. Radzig and B. M. Smirnov. *Reference Data on Atoms, Molecules, and Ions*. Springer-Verlag, Berlin, 1985.

In general possible:

Vibrational levels of the ground state that are energetically higher than levels of the first excited state

The Master Equation

Master equation in the Schrödinger picture:

$$\dot{\sigma}(t) = -i\mathcal{L}_{\text{mol}}\sigma(t) - \frac{\text{Tr}_{\text{R}}([V, \int_0^t d\tau e^{-i\tau\mathcal{L}_0}[V', |0_{\text{R}}\rangle\langle 0_{\text{R}}|\sigma(t-\tau)]])}{\hbar^2}$$

$$V := V_0 \sum_{\vec{k},s} \sum_{\mu} \sum_{\nu} \sqrt{\omega_k} a_{\vec{k}s} \vec{\epsilon}_{\vec{k}s} \vec{d}_{\mu\nu} |\mu\rangle\langle\nu| + \text{H.C.}$$

$$\mathcal{L}_{\text{mol}} := \frac{1}{\hbar}[H_{\text{mol}}, \cdots] := [\sum_{\mu} \mu|\mu\rangle\langle\mu| + \sum_{\nu} \nu|\nu\rangle\langle\nu|, \cdots]$$

$$\mathcal{L}_0 := \mathcal{L}_{\text{mol}} + \sum_{\vec{k},s}[\omega_{\vec{k}} a_{\vec{k}s}^\dagger a_{\vec{k}s}, \cdots]$$

The Master Equation (2)

$$\dot{\sigma}_{\mu_A\mu_B} = -i(\mu_A - \mu_B)\sigma_{\mu_A\mu_B} - \frac{|\vec{d}_{\text{eg}}|^2}{6\pi^2\hbar\epsilon_0 c^3}\Big\{\sum_{\mu,\nu}(r^{\mu\nu*}_{\mu_A\nu}\sigma_{\mu\mu_B} + r^{\mu\nu}_{\mu_B\nu}\sigma_{\mu_A\mu})$$

$$-\sum_{\nu,\nu_1}(r^{\nu_1\mu_B}_{\nu\mu_A} + r^{\nu\mu_A*}_{\nu_1\mu_B})\sigma_{\nu\nu_1}\Big\}$$

$$\dot{\sigma}_{\nu_A\nu_B} = -i(\nu_A - \nu_B)\sigma_{\nu_A\nu_B} - \frac{|\vec{d}_{\text{eg}}|^2}{6\pi^2\hbar\epsilon_0 c^3}\Big\{\sum_{\nu,\mu}(r^{\nu\mu*}_{\nu_A\mu}\sigma_{\nu\nu_B} + r^{\nu\mu}_{\nu_B\mu}\sigma_{\nu_A\nu})$$

$$-\sum_{\mu,\mu_1}(r^{\mu_1\nu_B}_{\mu\nu_A} + r^{\mu\nu_A*}_{\mu_1\nu_B})\sigma_{\mu\mu_1}\Big\}$$

$$r^{\mu_1\nu_1}_{\mu\nu} := \Theta(\mu_1 - \nu_1)\Theta(\mu - \nu)f^*_{\mu\nu}f_{\mu_1\nu_1}(\mu_1 - \nu_1)^3$$

Maximization at a fixed time point

$$\dot{\sigma}_{\nu_A\nu_B} = -i(\nu_A - \nu_B)\sigma_{\nu_A\nu_B} + \frac{|\vec{d}_{\text{eg}}|^2}{6\pi^2\hbar\epsilon_0 c^3}\underbrace{\left(\sum_{\mu,\mu_1}(r^{\mu_1\nu_B}_{\mu\nu_A} + r^{\mu\nu_A*}_{\mu_1\nu_B})\sigma_{\mu\mu_1}\right)}_{\text{to be maximized}}$$

Assumption: pure state

Goal: maximization of the spontaneous emission rate into one special lower level

Method: method of Langrangian multipliers

Maximization 2

Def.:

$$\chi_\mu^{\mu_1} := \chi_{\mu\nu_A}^{\mu_1\nu_B} := r_{\mu\nu_A}^{\mu_1\nu_B} + r_{\mu_1\nu_B}^{\mu\nu_A *}$$

Aussumption:

$$\sigma_{\mu\mu_1} = c_\mu c_{\mu_1}^*$$

To be maximized:

$$\sum_{\mu\mu_1} \chi_\mu^{\mu_1} \sigma_{\mu\mu_1} + \lambda(\sum_\mu \sigma_{\mu\mu} - 1)$$

Result:

$$\sum_\mu \chi_\mu^\alpha c_\mu + \lambda c_\alpha = 0$$

Results so far

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➤ The effect of maximization depends strongly on the involved Franck Condon factors.

Numerical example: CN molecule

Lennard-Jones potential fit.
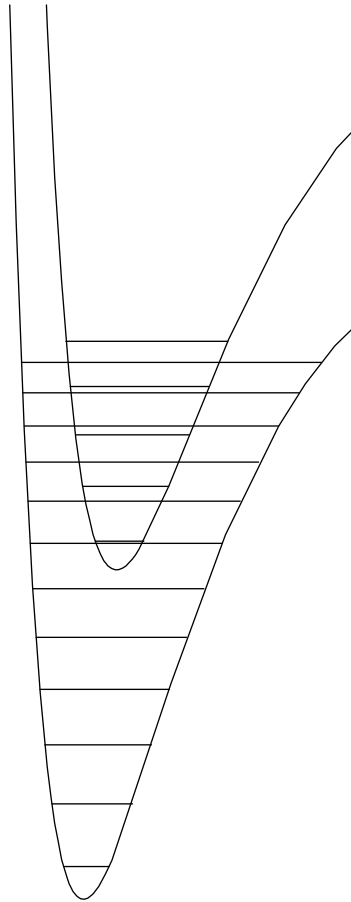
Relative transition rate:

$$\mu_0 \rightarrow \nu_0 : 0.56$$

$$\Sigma(\mu_0 \cdots \mu_4) \rightarrow \nu_0 : 0.94$$
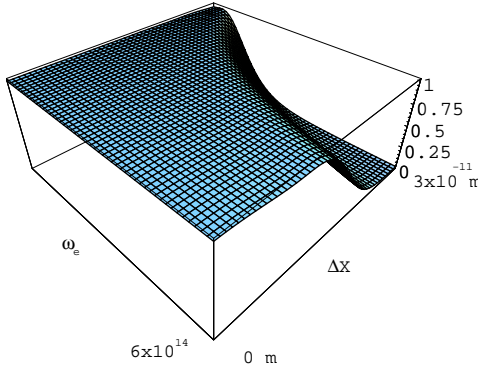
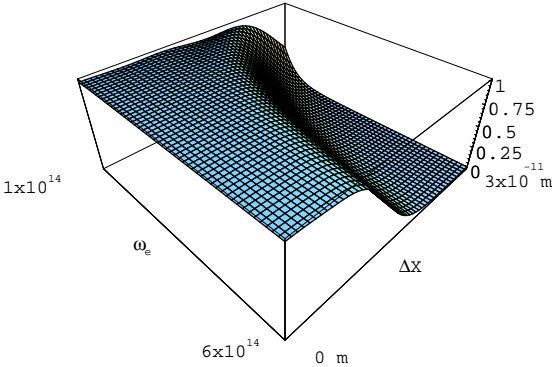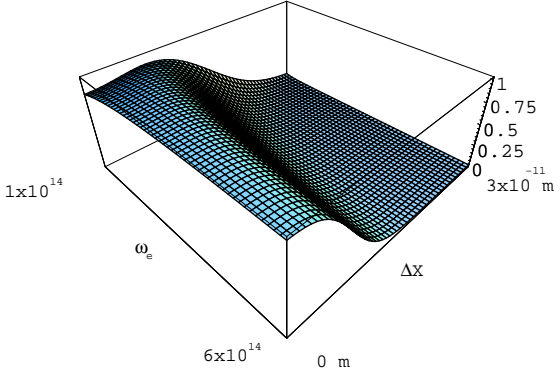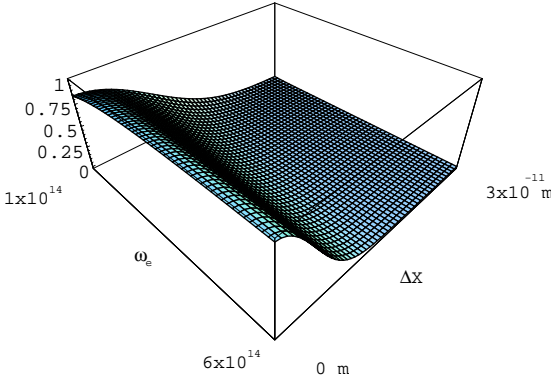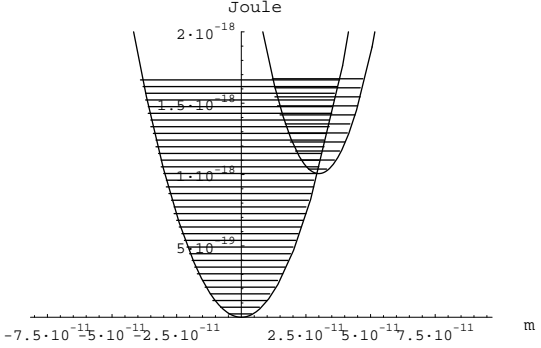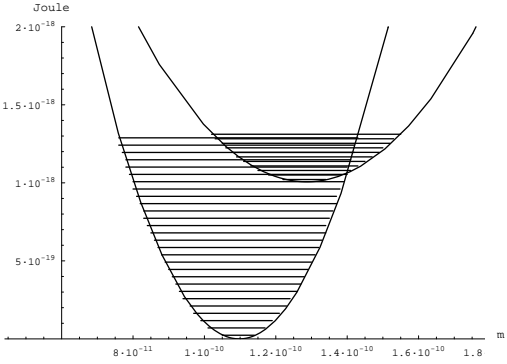# Numerical example: N_2 -like molecule
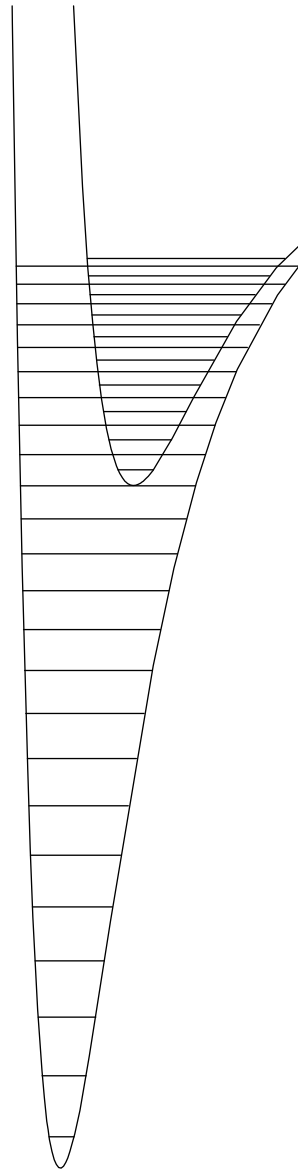
Relative transition rate:

$$\mu_0 \longrightarrow \nu_0 : 4.0 \times 10^{-5}$$

$$\Sigma(\mu_0 \cdots \mu_9) \longrightarrow \nu_0 : 1.5 \times 10^{-2}$$

Num. example: Harmonic potentials

A simple picture

Condition for maximum: $\quad \sum_\mu \chi_\mu^\alpha c_\mu + \lambda c_\alpha = 0$

with $\quad \sigma_{\alpha\alpha_1} = c_\alpha c_{\alpha_1}^*$

$$\chi_\mu^{\mu_1} = r_{\mu\nu_0}^{\mu_1\nu_0} + r_{\mu_1\nu_0}^{\mu\nu_0*}$$

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$$\chi_\mu^{\mu_1} = f_{\mu\nu_0}^* f_{\mu_1\nu_0} (\mu_1 - \nu_0)^3$$
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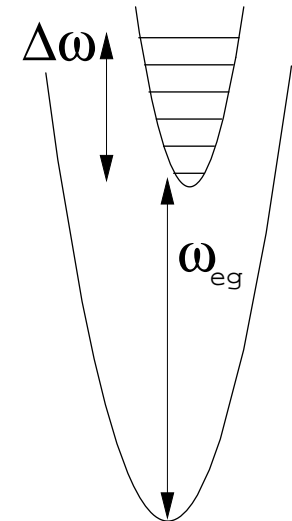Condition for maximum: $\sum_{\mu} \chi_{\mu}^{\alpha} c_{\mu} + \lambda c_{\alpha} = 0$

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$\omega_{\text{eg}} \gg \Delta\omega :$ $\chi_{\mu}^{\mu_1} \approx 2\omega_{\text{eg}}^3 f_{\mu_1\nu_0} f_{\mu\nu_0}^{*} \stackrel{\wedge}{=} 2\omega_{\text{eg}}^3 |f_{\nu_0}\rangle\langle f_{\nu_0}|$

This is true for real Franck Condon integrals.

Discussion of the simple picture

In this limit it is very easy to determine the optimal superposition:

The coefficients of the superposition are simply the overlap (scalar product) of the upper nuclear radial wave function of concern ($\mu = 0 \ldots n$) and the lower nuclear radial wave function (here ν_0).

$$c_\alpha \propto f_{\alpha \nu_0}$$

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and the maximal spontaneous emission rate is

$$\Gamma_{\text{max}} = \frac{|\vec{d}_{\text{eg}}|^2}{3\epsilon_0 \pi \hbar^2 c^3} \omega_{\text{eg}}^3 \left(\sum_\alpha |f_{\alpha\nu_0}|^2 \right)$$

Time evolution

Problem: The different energies of the upper vibrational eigenstates cause the eigenfunctions to de-phase and do destroy the superposition.
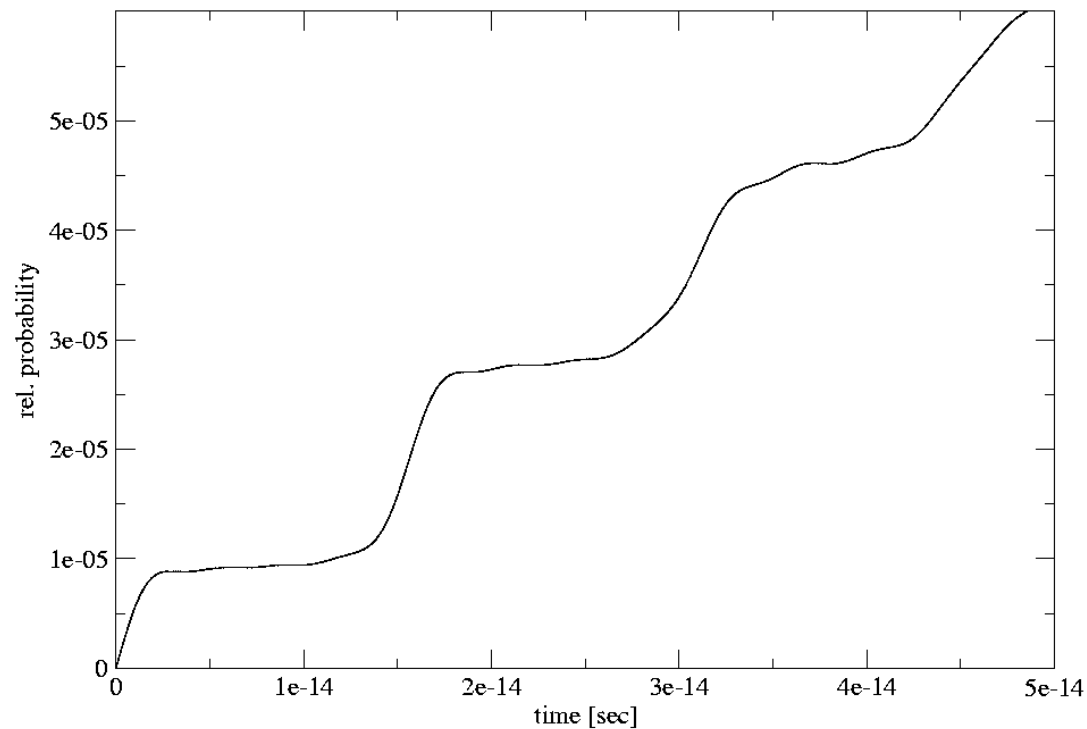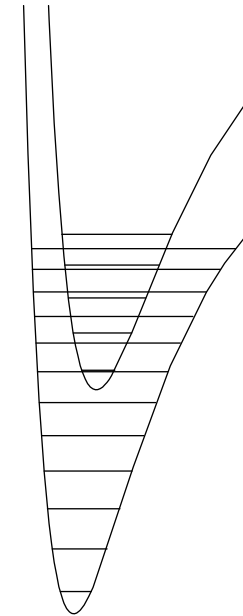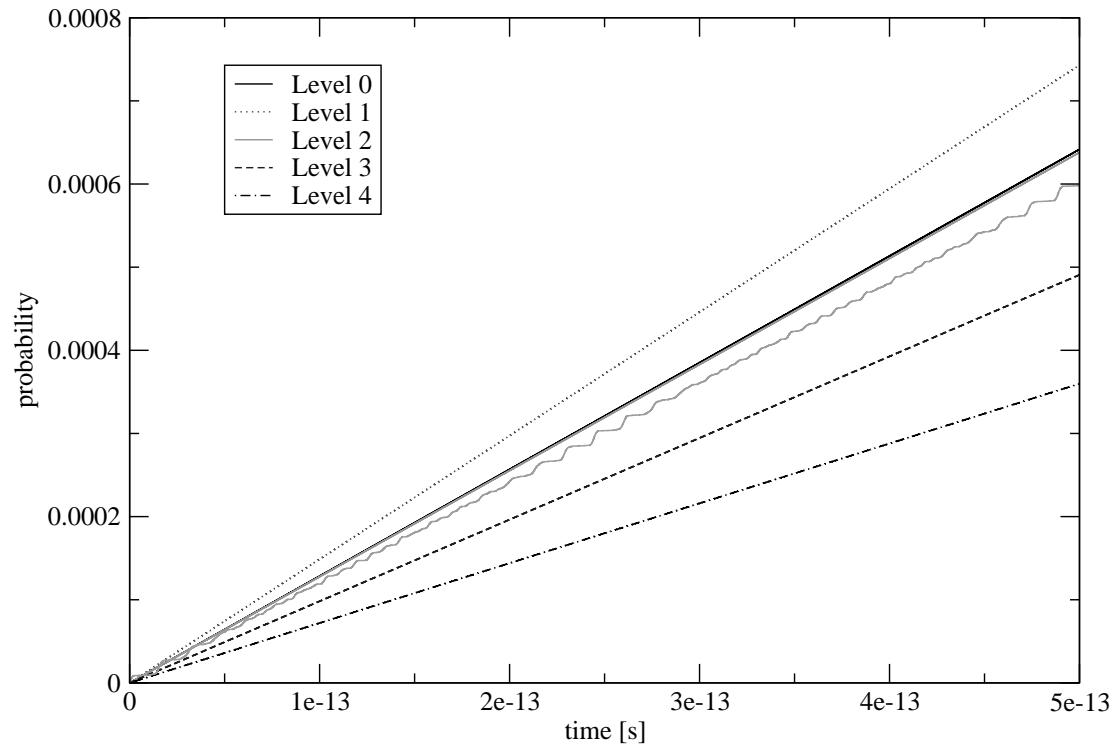
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Does this weaken the effect?

The population of ν_0 of CN for $t \in (0\text{s}, 5 \times 10^{-14}\text{s})$. Superposition of 5 upper levels.

Time evolution (2)

The population of level ν_0 of CN for $t \in (0\text{s}, 5 \times 10^{-13}\text{s})$. The straight lines stand for the population if the molecule initially is in state $\mu \in [0, 4]$. In this case, there is no interference and the time evolution of the population is just like $1 - e^{-\Gamma^{\mu}_{\nu_0} t}$.

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➤ A method to calculate the optimal superposition has been found.

➤ The maximal spontaneous emission rate depends crucially on the involved Franck Condon factors.

➤ Unfortunately the energy separation of the levels of the excited electronic state leads to de-phasing and does destroy the superposition.

➤ The effect is limited by a time $\tau_{\mathrm{vib}} \approx \pi/\Delta\omega = \pi\hbar/\Delta E$. After this time the spontaneous emission rate starts to rise again due to de-phasing.

Improvements?

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- Strong continuous wave laser

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➤ Coupling of strong lasers:

  • Pulsed laser with very high repetition rate $(\approx 10^{14} 1/\text{sec})$

  • Strong continuous wave laser

➤ Only use two upper levels and make use of the periodic change of the spontaneous emission rate.