Photoinduced cooling of polyatomic molecules in an electronically excited state in the presence of Dushinskii rotations

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Abstract

We present a theoretical study of the effect of Dushinskii rotations on the vibrational population created in an excited electronic state through photoexcitation. Special attention is given to the effect of Dushinskii rotations on the possibility of cooling the vibrational population in the excited state, relative to the thermal distribution in the ground state. The absorption spectrum and corresponding average energy in the excited state are calculated using a closed form expression for the harmonic correlation function between the ground and excited electronic states, which includes the effects of Dushinskii rotations, equilibrium position shifts and frequency shifts between the excited and ground electronic state normal modes. We investigate numerically the separate and joint effects of rotation, position shifts and frequency shifts on the absorption spectrum and average vibrational energy in the excited electronic state. We find that although the Dushinskii rotations diminish the cooling effect in general, the effect does not disappear, and in some cases may also increase slightly.

I. INTRODUCTION

In a series of recent papers [1–6] it was shown that photoexcitation of a thermal polyatomic molecule from the ground electronic state to an excited electronic state could under favorable circumstances be accompanied with cooling of the vibrational population in the excited state. Most recently we have shown that this phenomenon accounts correctly for the measured fluorescence lifetimes of naphthalene in the S_1 state [6]. Beddard et al [7,8] showed that at low photoexcitation energy, increasing the pressure of the buffer gas caused a decrease in the fluorescence lifetime, suggesting that initially the molecular vibrations in the excited state were cold and the collisions would heat up the molecule, leading to a faster decay. This interpretation was shown to be consistent with ab-initio computations for the naphthalene molecules and that indeed cooling of the excited state vibrations takes place when the photoexcitation frequency is close or to the red of the ω_{00} transition frequency.

The phenomenon of cooling was also used to interpret the experimental finding that the isomerization lifetime of photoexcited trans-stilbene decreases when going from the gas to the condensed phase. Gershinski and Pollak [1] noted that if the molecule is initially cooled, then immersion in a liquid would reheat the molecule and thus lead to faster decay and shorter lifetimes. This explanation has been though the topic of rather heated debate, due to the uncertainty in the details of the excited state potential energy surface of stilbene [9–12].

Wadi and Pollak [2] gave an in depth study of the conditions that lead to the cooling phenomenon, in the absence of Dushinskii rotations [14]. Within the Condon approximation and using harmonic potentials for the ground and excited potential energy surfaces, they showed that it will occur typically, when the vibrational frequencies in the excited electronic state are somewhat weaker than the frequencies in the ground state. However, if the equilibrium positions of the excited state differ significantly from those of the ground state, cooling will not occur. Thus far though, nothing is known about the effect of Dushinskii rotations on the cooling phenomenon. That is, what happens to the cooling phenomenon when there is no longer a one to one correspondence between the normal modes of the ground and excited electronic states?

The central theme of this paper is to study the effects of Dushinskii rotations on the vibrational population in the excited state. We will show, that although typically the rotations reduce the cooling phenomena, they do not destroy it completely and may even at times increase it.

In Section II we present the necessary formalism for computation of the spectra and the average energy in the excited state. In Section III we consider a model harmonic molecule with 45 degrees of freedom to study numerically the different possible effects of Dushinskii rotations on the average vibrational energy in the excited electronic state. We end with a Discussion.

II. THEORY

A. General formalism

The Fermi Golden rule expression for the (normalized) absorption spectrum into the excited electronic state, obtained within the Condon approximation, using an infinitely narrow laser pulse of frequency ω is [15,2]:

$$P(\omega;\beta) = \frac{Z(\omega;\beta)}{Tr[e^{-\beta H_g}]} \tag{2.1}$$

where H_g is the ground state Hamiltonian and

$$Z(\omega;\beta) = \frac{\hbar}{2\pi}\int_{-\infty}^{\infty} d\tau e^{-i\tau(\Delta E-\hbar\omega)}\chi(\tau,\beta) \tag{2.2}$$

may be termed as the frequency dependent partition function. The value ΔE is the energy gap between the bottom of the potential of the excited state Hamiltonian H_e and the bottom of the potential of the ground state Hamiltonian H_g. The thermal cross correlation function of the ground and excited states, $\chi(\tau,\beta)$ is defined by:

$$\chi(\tau,\beta) = Tr[e^{-i\tau H_e}e^{-(\beta-i\tau)H_g}] \tag{2.3}$$

As was shown in Ref. [2] the average energy of the excited state, may be calculated via the relation

$$< E > (\omega, \beta) = \hbar\omega - \Delta E - \frac{\partial}{\partial\beta} \ln Z(\omega; \beta) \tag{2.4}$$

By definition, the vibrational population in the excited electronic state is considered to be cooled for those excitation frequencies ω, for which $< E > (\omega, \beta) \leq < E_g > (\beta)$, where the ground state average energy $< E_g > (\beta)$ is

$$< E_g > (\beta) = -\frac{\partial}{\partial\beta} \ln Tr[e^{-\beta H_g}] \tag{2.5}$$

The condition for cooling may thus be expressed as

$$\hbar\omega - \Delta E - \frac{\partial}{\partial\beta} \ln P(\omega; \beta) \leq 0 \tag{2.6}$$

B. Harmonic model

The formal results for the two state problem may be calculated (almost) analytically, provided that the ground and excited electronic state Hamiltonians are harmonic. The ground state Hamiltonian is thus a collection of N normal modes:

$$H_g = \frac{1}{2}\sum_{i=1}^{N}(p_{g_i}^2 + \omega_{g_i}^2 q_{g_i}^2) \tag{2.7}$$

where q_{g_i}, p_{g_i} are the ith mass weighted normal mode coordinate and momentum respectively.

The excited state Hamiltonian is also composed of N normal modes, but with different coordinates, momenta, frequencies and position shifts:

$$H_e = \frac{1}{2}\sum_{i=1}^{N}(p_{e_i}^2 + \omega_{e_i}^2 q_{e_i}^2) + \Delta E \tag{2.8}$$

where q_{e_i}, p_{e_i} are the ith mass weighted normal mode coordinate and momentum of the excited state Hamiltonian, respectively. The excited state coordinates q_{e_i} are assumed to be given as linear combinations of the ground state coordinates q_{g_i}:

$$q_{e_i} = \sum_{j=1}^{N} S_{ij} q_{g_j} + D_i \tag{2.9}$$

where S_{ij} is the Dushinskii [14] rotation matrix element, defining the projection amplitude of the j-th ground electronic state normal mode coordinate on the i-th excited electronic state normal mode coordinate. D_i is the equilibrium position of the ith mode in the excited state relative to the ground state.

Using a vector-matrix notation, we may rewrite Eq. 2.9 as:

$$\underline{q_e} = \mathbf{S}\underline{q_g} + \underline{D} \tag{2.10}$$

where $\mathbf{S}$ is the orthogonal rotation matrix and $\underline{D}$ is the vector of equilibrium position shifts of the excited state relative to the ground state. We will denote (column) vectors by an underline, row vectors by an additional superscript "T" and matrices will be boldface.

To obtain the absorption spectrum it is necessary to find an explicit expression for the cross correlation function Eq. 2.3. Defining

$$\chi(\tau_g, \tau_e) = Tr(e^{-i\tau_g H_g} e^{-i\tau_e H_e}), \tag{2.11}$$

and tracing over the ground electronic state coordinates, we have:

$$\chi(\tau_g, \tau_e) = \int d\underline{x} < \underline{x}| e^{-i\tau_g H_g} e^{-i\tau_e H_e} |\underline{x} > \tag{2.12}$$

where the vector $\underline{x}$ represents the ground electronic state normal mode coordinates q_{g_i}. By inserting a complete set of ground electronic state coordinates $\underline{y}$, and 2 complete sets of excited electronic state coordinates $\underline{x}'$ and $\underline{y}'$ we may express Eq. 2.12 as:

$$\chi(\tau_g, \tau_e) = \int\int\int\int d\underline{x} d\underline{y} d\underline{x}' d\underline{y}' < \underline{x}| e^{-i\tau_g H_g} |\underline{y} >< \underline{y}|\underline{y}' >< \underline{y}'| e^{-i\tau_e H_e} |\underline{x}' >< \underline{x}'|\underline{x} > \tag{2.13}$$

The off diagonal matrix element $< x|e^{-i\tau H}|y >$ for a harmonic Hamiltonian $H = \frac{1}{2}(p^2 + \omega^2 q^2)$ is known [16] to be:

$$< x|e^{-i\tau H}|y >= \sqrt{\frac{a(\tau)}{2\pi i\hbar}} e^{\frac{i}{\hbar}[\frac{1}{2}b(\tau)(x^2+y^2) - a(\tau)xy]} \tag{2.14}$$

where $a(\tau) = \omega / \sin(\hbar\omega\tau)$ and $b(\tau) = \omega / \tan(\hbar\omega\tau)$. Hence if the Hamiltonian is a collection of N independent normal modes, as defined for the ground and excited electronic state Hamiltonians (Eqs. 2.7 and 2.8) we have

$$< \underline{x}|e^{-i\tau H}|\underline{y} >= \sqrt{\frac{\det(\mathbf{a})}{(2\pi i\hbar)^N}} e^{\frac{i}{\hbar}\left[\frac{1}{2}\left(\underline{x}^T\mathbf{b}\underline{x}+\underline{y}^T\mathbf{b}\underline{y}\right)-\underline{x}^T\mathbf{a}\underline{y}\right]} \tag{2.15}$$

where $\mathbf{a}$ and $\mathbf{b}$ are diagonal matrices with elements $a_i(\tau) = \omega_i / \sin(\hbar\omega_i\tau)$ and $b_i(\tau) = \omega_i / \tan(\hbar\omega_i\tau)$ respectively, and the time dependence on $\mathbf{a}$ and $\mathbf{b}$ has been omitted for the sake of brevity.

The inner product between the ground and excited electronic state coordinates $< \underline{x}'|\underline{x} >$, using Eq. 2.10, is given by:

$$< \underline{x}'|\underline{x} >= \delta(\underline{x}' - (\mathbf{S}\underline{x} + \underline{D})) \tag{2.16}$$

where the δ function of a vector is defined as the product of the individual δ functions of its components. The correlation function Eq. 2.13 may therefore be integrated over $\underline{\mathrm{x}}$' and $\underline{\mathrm{y}}$' and expressed as:

$$\chi(\tau_g, \tau_e) = e^{-i\tau_e\Delta E} \sqrt{\frac{\det(\mathbf{a_g})}{(2\pi i\hbar)^N}} \sqrt{\frac{\det(\mathbf{a_e})}{(2\pi i\hbar)^N}} \cdot$$
$$\int\int d\underline{x}d\underline{y} e^{\frac{i}{\hbar}\left[\frac{1}{2}\left(\underline{x}^T\mathbf{b_g}\underline{x}+\underline{y}^T\mathbf{b_g}\underline{y}\right)-\underline{x}^T\mathbf{a_g}\underline{y}\right]} e^{\frac{i}{\hbar}\left[\frac{1}{2}\left(\underline{x}'^T\mathbf{b_e}\underline{x}'+\underline{y}'^T\mathbf{b_e}\underline{y}'\right)-\underline{x}'^T\mathbf{a_e}\underline{y}'\right]} \tag{2.17}$$

where $\mathbf{a_g}$, $\mathbf{b_g}$ and $\mathbf{a_e}$, $\mathbf{b_e}$ are defined as in Eq. 2.15 for the ground and excited states respectively, and $\underline{x}'$, $\underline{y}'$ represent $(\mathbf{S}\underline{x} + \underline{D})$, $(\mathbf{S}\underline{y} + \underline{D})$, respectively, according to Eq. 2.16.

We further define the following matrices:

$$\mathbf{A}(\tau_g, \tau_e) = \mathbf{a_g}(\tau_g) + \mathbf{S}^T\mathbf{a_e}(\tau_e)\mathbf{S} \tag{2.18}$$

$$\mathbf{B}(\tau_g, \tau_e) = \mathbf{b_g}(\tau_g) + \mathbf{S}^T\mathbf{b_e}(\tau_e)\mathbf{S} \tag{2.19}$$

$$\mathbf{G}(\tau_g) = \mathbf{b_g}(\tau_g) - \mathbf{a_g}(\tau_g) \tag{2.20}$$

$$\mathbf{E}(\tau_e) = \mathbf{b_e}(\tau_e) - \mathbf{a_e}(\tau_e) \tag{2.21}$$

This allows us to rewrite Eq. 2.17 as:

$$\chi(\tau_g,\tau_e) = e^{-i\tau_e \Delta E}\sqrt{\frac{\det(\mathbf{a_g})}{(2\pi i\hbar)^N}}\sqrt{\frac{\det(\mathbf{a_e})}{(2\pi i\hbar)^N}}\cdot \\ \int\int d\underline{x}d\underline{y}e^{\frac{i}{\hbar}\left[\frac{1}{2}\left(\underline{x}^T\mathbf{B}\underline{x}+\underline{y}^T\mathbf{B}\underline{y}\right)-\underline{x}^T\mathbf{A}\underline{y}+\underline{D}^T\mathbf{E}\underline{D}+\underline{D}^T\mathbf{ES}(\underline{x}+\underline{y})\right]} \tag{2.22}$$

The remaining Gaussian integrations are somewhat tedious but straightforward and one finds:

$$\chi(\tau_g,\tau_e) = e^{-i\tau_e \Delta E}\sqrt{\frac{\det(\mathbf{a_g})\det(\mathbf{a_e})}{\det(\mathbf{B})\det(\mathbf{B}-\mathbf{A}\mathbf{B}^{-1}\mathbf{A})}}e^{\frac{i}{\hbar}\left[\underline{D}^T\mathbf{ES}(\mathbf{B}-\mathbf{A})^{-1}\mathbf{GS}^T\underline{D}\right]}, \tag{2.23}$$

and $\chi(\tau,\beta)$ is obtained by setting $\tau_e = \tau$ and $\tau_g = \beta - i\tau$ in Eq. 2.23.

Eq. 2.23 gives the two state correlation function, including rotation and displacement in closed form (see also the derivation of Ref. [15]). Fourier transforming the correlation function numerically gives the "frequency dependent correlation function" as in Eq. 2.2 which also gives the normalized absorption spectrum. One then follows Eq. 2.4 to obtain the average energy in the excited state.

III. NUMERICAL RESULTS

In this section we shall use different harmonic models of a polyatomic molecule, to study numerically the effect of Dushinskii rotation and equilibrium position shifts on the thermal absorption spectrum and the average vibrational energy in the excited electronic state. If the equilibrium positions and frequencies in the excited electronic state are the same as in the ground state and in the absence of rotation, the absorption spectrum is a "δ" function centered at the ω_{00} transition frequency, defined more generally as

$$\omega_{00} \equiv \sum_i(\omega_{e_i} - \omega_{g_i}). \tag{3.1}$$

The average energy in the excited state is then identical to the average energy in the ground state, there is no cooling or heating. Our first model will therefore be one in which we have only Dushinskii rotations. Any change in the absorption spectrum and in the average energy will be in this case purely a result of the rotations.

In our second model, we introduce position shifts without rotations and without frequency shifts. Here, any change in the absorption spectrum and in the average energy will result only from the position shifts. We then also study the case of both rotation and position shifts, without frequency shifts.

Typically though, a polyatomic molecule in its excited state will have vibrational frequencies that are lower than the ground state frequencies. Electronic excitation serves to weaken vibrational bonds. If there are no equilibrium position shifts and no rotations, then one will typically observe substantial cooling of the excited state population, provided that the photoexcitation frequency is in the vicinity of the ω_{00} transition frequency. The fourth case will then be to study the effects of Dushinskii rotations when there are no equilibrium position shifts but the frequencies are shifted. Finally we will consider the case where position shifts are also included.

The energy gap ΔE between the ground and excited electronic states is unimportant, since it simply sets the scale of frequencies for the photoexcitation laser, so it will be set to 0. For convenience, the average energy will always be scaled to $< E > (\omega, \beta) - < E_g > (\beta)$, so that a positive average energy implies heating and a negative one implies cooling. We will also define an effective temperature parameter for the excited state by looking for that temperature at which a Boltzman distribution in the excited state would give the resulting average energy. More precisely, the effective (inverse) temperature is defined as the solution of the equation:

$$< E_e > = -\frac{\partial}{\partial \beta_{eff}} \ln Tr[e^{-\beta_{eff} H_e}] \tag{3.2}$$

A. Case 1. Rotations only.

Our model polyatomic molecule will have 45 degrees of freedom, divided into three groups: low, medium and high frequencies. The low frequency group ranges from 50 to 470

cm^{-1} with an equal spacing of 30 cm^{-1}, the medium frequency group ranges from 800 to 1220 cm^{-1} with the same spacing, and the high frequency group range from 2000 to 2700 cm^{-1} with an equal spacing of 50 cm^{-1}. These three groups mimic a typical frequency distribution of a polyatomic molecule.

The inverse rotation matrix S^T is synthesized by diagonalizing a symmetric matrix R, with the diagonal elements having the integer values of 1 to 45. The off-diagonal elements of R will be kept small so that $S^T RS$ is a diagonal matrix with eigenvalues close to the integers 1 to 45. The off diagonal elements of R will be chosen as identical for all first off-diagonal elements, second off-diagonal elements, etc. This means that all R_{ij} are equal for a given $k \equiv |i-j|$, where k is an integer between 1 to 44. We can thus define a vector with elements R_k, such that all elements R_{ij} of the matrix R obeying $k \equiv |i-j|$ will be equal to R_k. Thus R_k will be used as a parameter which characterizes the extent of rotation. For example, we may use R_1=0.4, $R_2 = 0.1$ and $R_k = 0$, for $k \geq 3$. This way of synthesizing a rotation matrix assures a larger rotation for low frequencies and a smaller rotation for high frequencies, as would be expected for a typical polyatomic molecule.

To simplify the numerics for this case, we will use a laser pulse with a finite frequency width ($\sigma = 15 cm^{-1}$), since for a zero width pulse the spectrum is a delta function demanding an infinite time integration. Panel (a) of Figure 1 shows the absorption spectrum without rotation, and with the two rotation values: $R_1 = 0.2$ and $R_1 = 0.4$, but with all higher order rotations set to zero ($R_{i>1} = 0$). Panel (b) shows the average energy in the excited state as a function of the excitation frequency. In all cases, the ground electronic state temperature is $300K$.

As may be expected, the spectrum broadens under rotation, but the average energy has a minimum only when rotation is present. Without rotation, each transition from a given ground state energy level, can occur only to the same excited state energy level. Therefore, the average energy increases linearly with $\hbar\omega$. Cooling appears only when rotation is present. The results of Fig. 1b thus show that Dushinskii rotations may induce cooling. To see the extent of the cooling, we plot in Fig. 2 the maximal possible cooling as a function of the magnitude of the rotation. Although cooling is possible, it is not very large. Interestingly though, cooling increases as the magnitude of the rotation increases. Thus, the maximal cooling when $R_2 = 0.4$ is always larger than when $R_2 = 0$.

B. Case 2. Position shifts only.

One typically expects significant position shifts in the excited state only for the low frequency modes. We will choose the displacement vector $\underline{D}$ to be non-zero only for the 15 modes with low-frequencies. Its normalized dimensionless value $d_i \equiv D_i\sqrt{\omega_{e_i}/\hbar}$ will be chosen as a small number between 0 and 1.

In Fig. 3a we first consider the effect of displacement without rotation. Panel (a) displays the spectrum obtained for displacement values of 0, 0.1, 0.2 and 0.3 and panel (b) displays the average energy and effective temperature in the excited state for the same cases. As expected, the spectrum becomes more and more structured, as the displacement increases. Although the displacement alone can induce cooling, it is not very significant. Displacement alone or rotations alone are insufficient for significant cooling to occur.

C. Case 3. Position shifts and rotations only.

Next we analyze the effect of rotation and displacement, by holding the displacement at the fixed value of $d_i = 0.1$. Large displacement and rotation significantly decreases the magnitude of the absorption spectrum, making the calculation increasingly difficult. There is no qualitative change in the results if the shift is increased further.

Figure 4a shows the absorption spectrum without rotation, and for the two rotation values: $R_1 = 0.2$ and $R_1 = 0.4$, with $R_{i>1} = 0$. We note that displacement and rotation tend to broaden the spectrum and decrease the overall absorption probability. The average energy and effective temperature of the excited state is shown in panel (b) of the figure as a function of excitation frequency. One sees that cooling increases with rotation. However, as before, the extent of cooling is not very large. In Fig. 5 we plot the maximal cooling found for the fixed value of the displacement as a function of the magnitude of the rotation in the first off diagonal element. The results resemble Fig. 2 except for the fact that for no rotation there is some cooling, while for large rotations there is less cooling. We find that both rotation and displacement lower the maximal heating and increase the temperature at the maximal cooling.

D. Case 4. Frequency shifts and rotations only.

As already mentioned earlier, in a typical polyatomic molecule one expects to find lower vibrational frequencies in the excited electronic state. The effect will be stronger for low frequency modes than for high frequency modes. The frequency shifts will be thus modeled as in previous work [3]. That is, frequencies of the low-frequency group are multiplied by a constant factor of 0.95, the medium-frequency group by 0.98, and the high-frequency group by 0.99.

In Fig. 6a we plot the absorption spectrum for the three cases $R_1 = 0$, $R_1 = 0.2$ and $R_1 = 0.4$, where for all cases $R_{i>1} = 0$. The resulting average energy and effective temperature in the excited state are plotted as a function of the excitation frequency in panel (b) of the Figure. As known from our previous investigations and as seen in the Figure, frequency shifts can lead to extensive cooling. Dushinskii rotation tends to broaden the absorption spectrum, reduce the absorption probability and reduce the cooling phenomenon. However the cooling is not destroyed completely, nor is the dependence on the magnitude of the rotation monotonic.

In Fig. 7 we plot the maximal cooling found as a function of the magnitude of the rotation. We note that when $R_2 = 0$ we get a sharp increase in the minimum energy as R_1 is increased. Rotation significantly limits the cooling effect. However, it does not disappear, and in the presence of large rotation tends to a constant value, that is, the average energy is lowered to approximately $-800 cm^{-1}$.

E. Case 5. Position, frequency shifts and rotations.

It has already been shown in previous work [2], that without rotations, increasing the displacement diminishes the cooling. Here we show that also in the presence of displacement, rotation also diminishes the cooling although it does not disappear completely. Figure 8a shows the absorption spectrum for the three rotation values $R_1 = 0, R_1 = 0.2$ and $R_1 = 0.4$, keeping $R_{i>1} = 0$ and the fixed value of the displacement at $d_i = 0.1$. As may have been expected from the previous cases, both displacement and rotation broaden the spectrum and lower the absorption probability. The displacement also leads to increased structure in the absorption spectrum.

The average energy and effective temperature in the excited states is plotted in Fig. 8b. The lowest average energy is at $-1480cm^{-1}$ and is obtained without rotation. This value is higher than that found without displacement, as can be seen by inspection of Fig. 6b. However, we find that in general, the maximal cooling is not necessarily found when there is no rotation. This is shown in Fig. 9, where we plot the maximal cooling as a function of the magnitude of the rotation. One notes that for $R_2 = 0$, the minimum energy sharply increases with increasing R_1 but decreases slightly in the region $R_1 > 1$. Similarly for $R_2 = 0.4$ we observe the maximal cooling at $R_1 = 0.2$.

IV. DISCUSSION

In this work we have presented a study aimed at understanding how rotations affect the average energy in the excited state. A short summary of our numerical findings is that lowering the vibrational frequencies in the excited state leads to the possibility of cooling, while displacement and rotations tend to mitigate the effect but do not destroy it completely. We have presented here results for an idealized model. Our numerical experience with other models is qualitatively similar. Although in any given molecule the rotation matrix will be more structured and non uniform than in the model we have used, our numerical experience on a variety of models and conditions shows that the overall result remains the same. Cooling of the vibrational population in the excited state may be found provided that the displacement and rotations are not "too strong".

Does this mean that the cooling phenomenon can in general be ignored? We believe that not, for a number of reasons. The previous analysis of the naphthalene molecule, presented in Ref. [8] did take rotations into account, but cooling remained rather significant when the excitation frequency was in the vicinity of ω_{00}. Dushinskii rotations are negligible for the benzene molecule, where theory has also predicted extensive cooling under the same conditions. They cannot be neglected for Stilbene. We do note though that even the latest computations of an ab-initio potential energy surface for this system have not been shown to agree with experimental thermal absorption spectra [13,12]. The final word on the importance of cooling in this intriguing system has not yet been said. In addition, the effect of anharmonicity on the cooling phenomenon remains completely unknown. For molecules such as stilbene, with low barriers to isomerization, which are accessible at room temperature, anharmonicity cannot be ignored. We also note that we have not presented a study of non-Condon effects, however our recent results on cooling in the naphthalene [6] and benzene molecules [4] do show that non-Condon terms do not destroy the cooling phenomenon.

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Figure captions

FIG. 1 Absorption spectrum and average energy in the excited state. The frequencies are the same in the ground and excited states, there are no position shifts. Panel (a) shows the absorption spectrum for three different values of the rotations, panel (b) the average energy as a function of the excitation frequency. Note the effective temperature scale on the right axis.

FIG. 2 Minimal average energy and effective temperature in the excited state as a function of rotation. The frequencies in the excited and ground state are the same and there are no position displacements. Note that cooling is more extensive when $R_2 \neq 0$.

FIG. 3 Absorption spectrum and average energy in the excited state. The frequencies are the same in the ground and excited states, there are no rotations. Panel (a) shows the absorption spectrum for four different values of the position shifts, panel (b) the average energy as a function of the excitation frequency.

FIG. 4 Absorption spectrum and average energy in the excited state. The frequencies are the same in the ground and excited states and the position shift is $d = 0.1$. Panel (a) shows the absorption spectrum for three different values of the rotations, panel (b) the average energy as a function of the excitation frequency.

FIG. 5 Minimal average energy and effective temperature in the excited state as a function of rotation. The frequencies in the excited and ground state are the same. The position shift is $d = 0.1$.

FIG. 6 Absorption spectrum and average energy in the excited state. The frequencies in the excited state are lower than those of the ground state, but there are no position shifts. Panel (a) shows the absorption spectrum for three different values of the rotations, panel (b) the average energy as a function of the excitation frequency.

FIG. 7 Minimal average energy and effective temperature in the excited state as a function of rotation. The frequencies in the excited state are lower than in the ground state. There are no position shifts.

FIG. 8 Absorption spectrum and average energy in the excited state. The frequencies and equilibrium positions in the excited states are shifted, $d = 0.1$. Panel (a) shows the absorption spectrum for three different values of the rotations, panel (b) the average energy as a function of the excitation frequency.

FIG. 9 Minimal average energy and effective temperature in the excited state as a function of rotation. The frequencies in the excited state are lower than in the ground state. The position shift is $d = 0.1$.

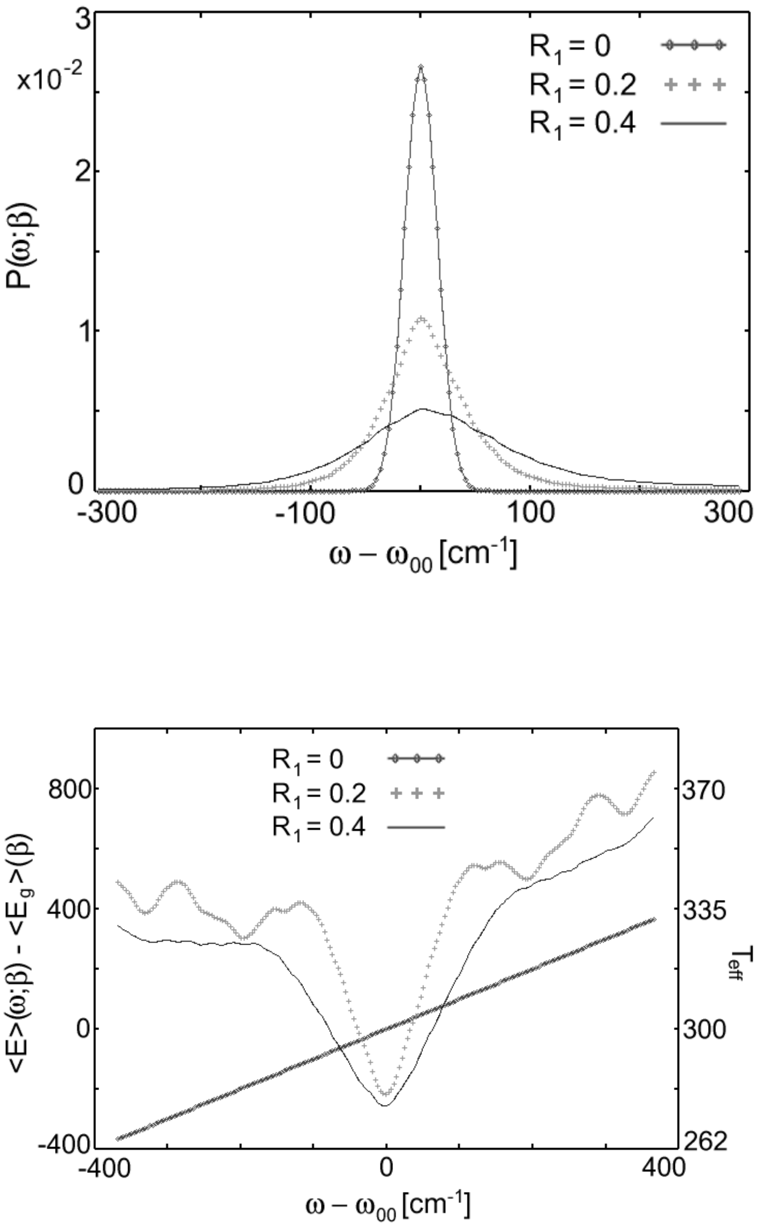


Figure 1, Ianconescu and Pollak

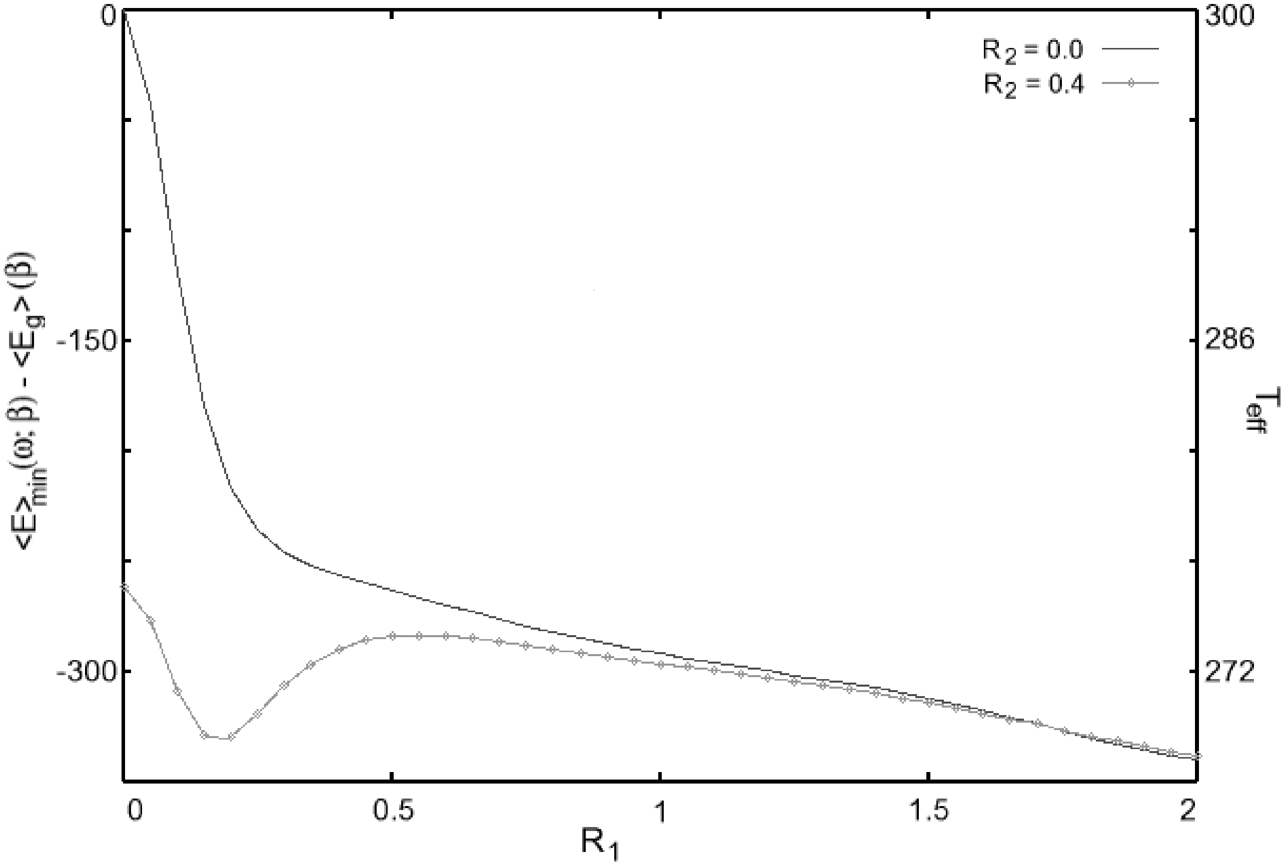


Figure 2, Ianconescu and Pollak

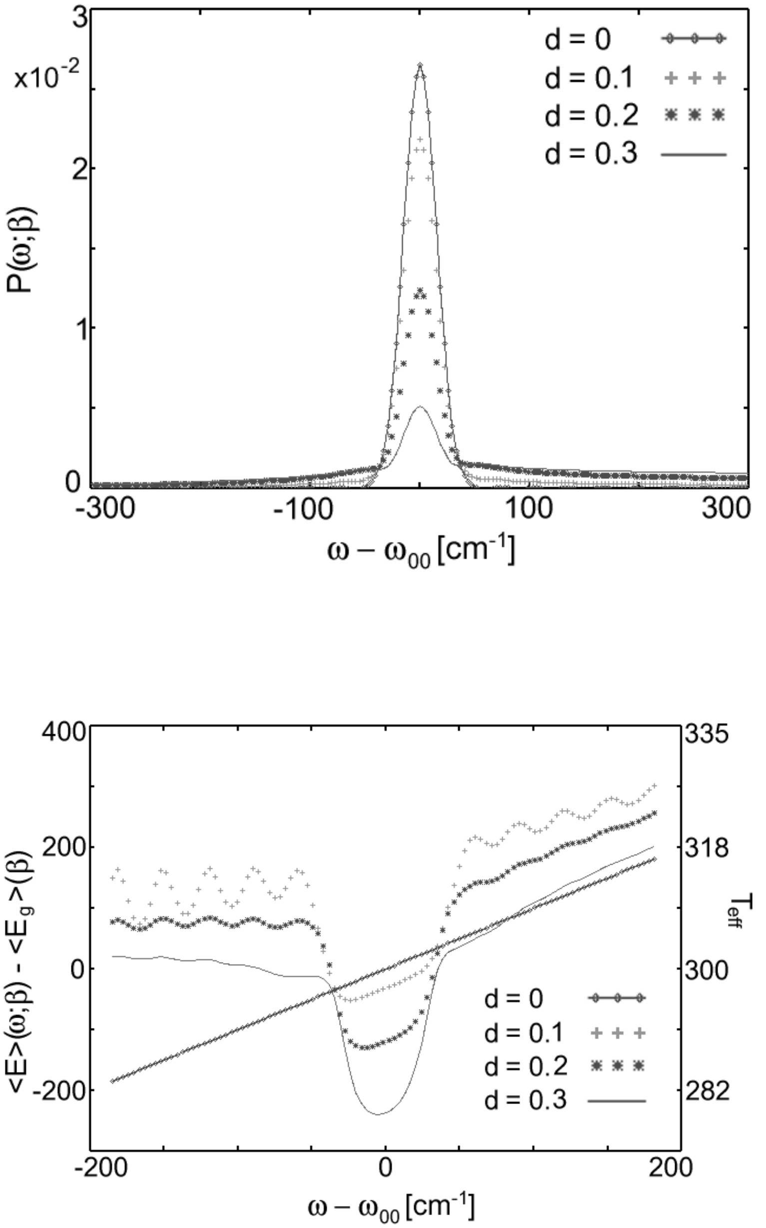
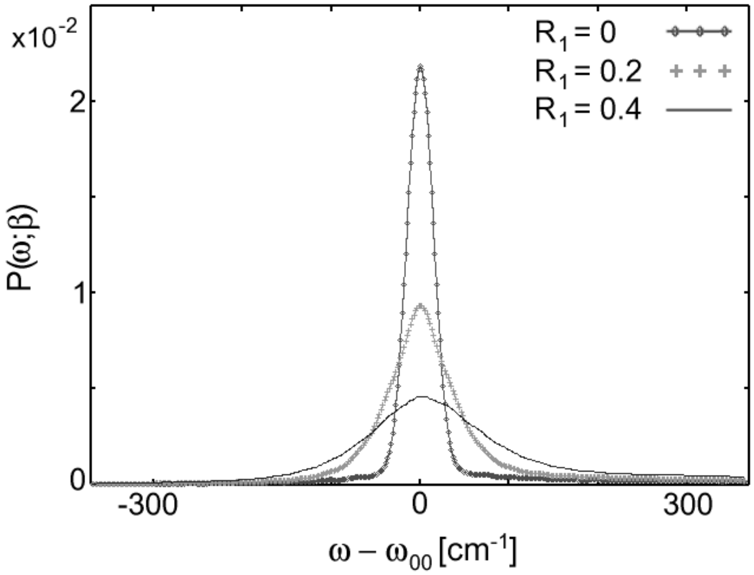


Figure 3, Ianconescu and Pollak



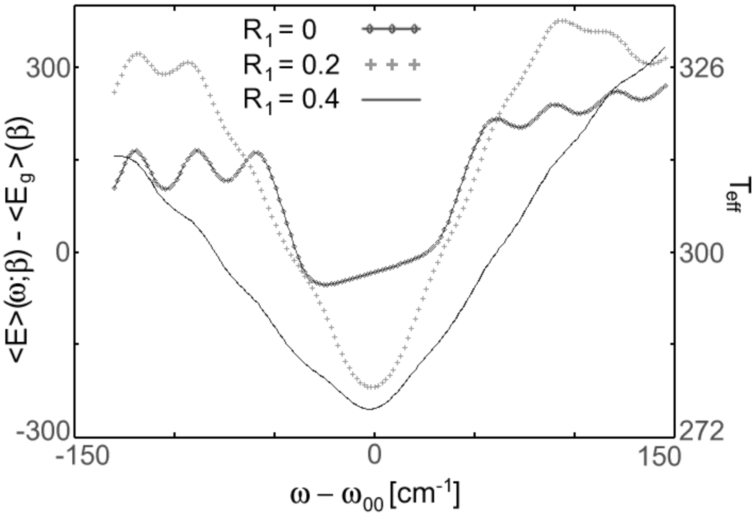


Figure 4, Ianconescu and Pollak

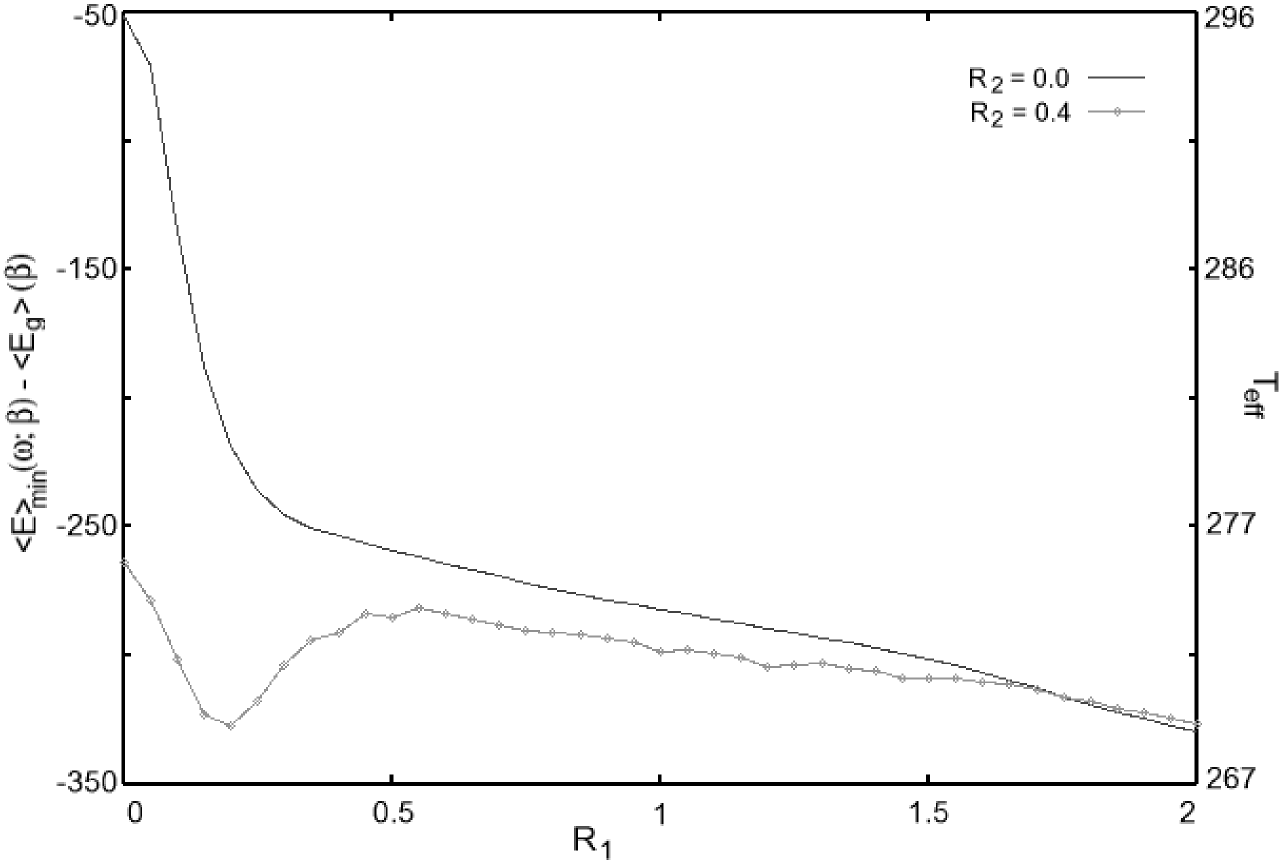


Figure 5, Ianconescu and Pollak

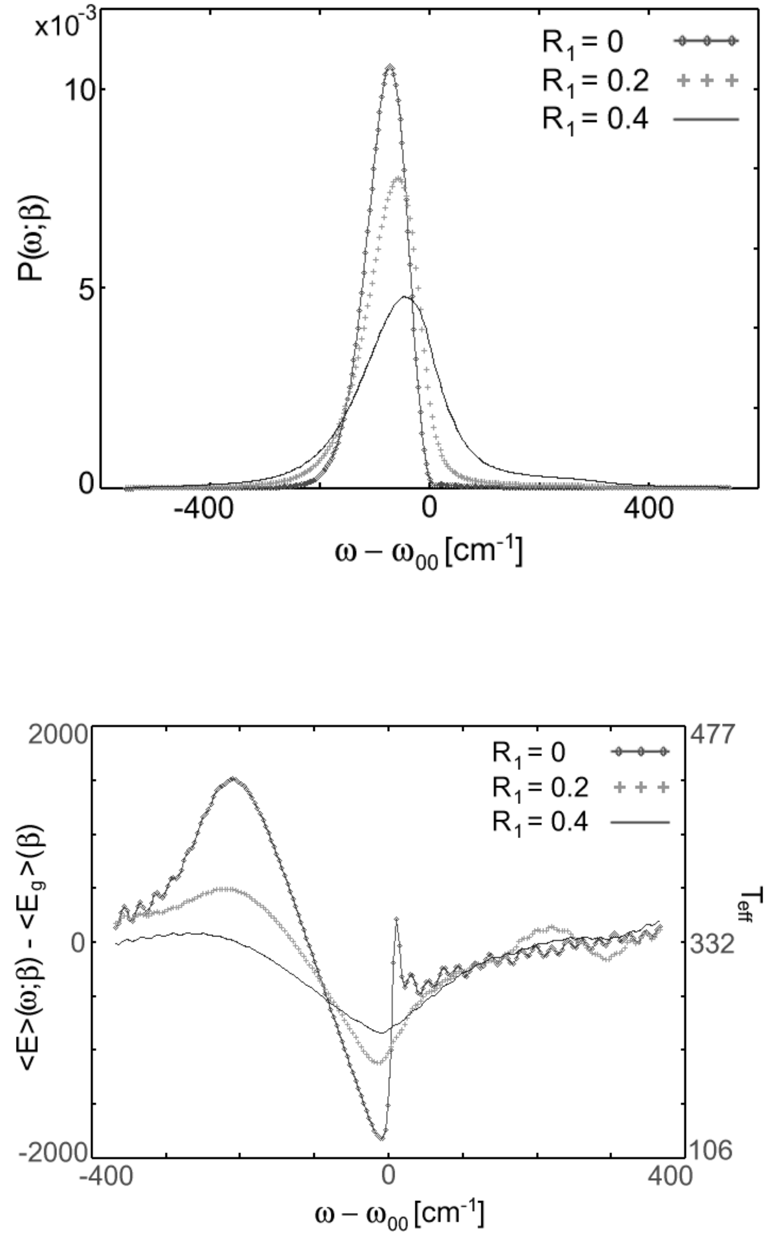


Figure 6, Ianconescu and Pollak

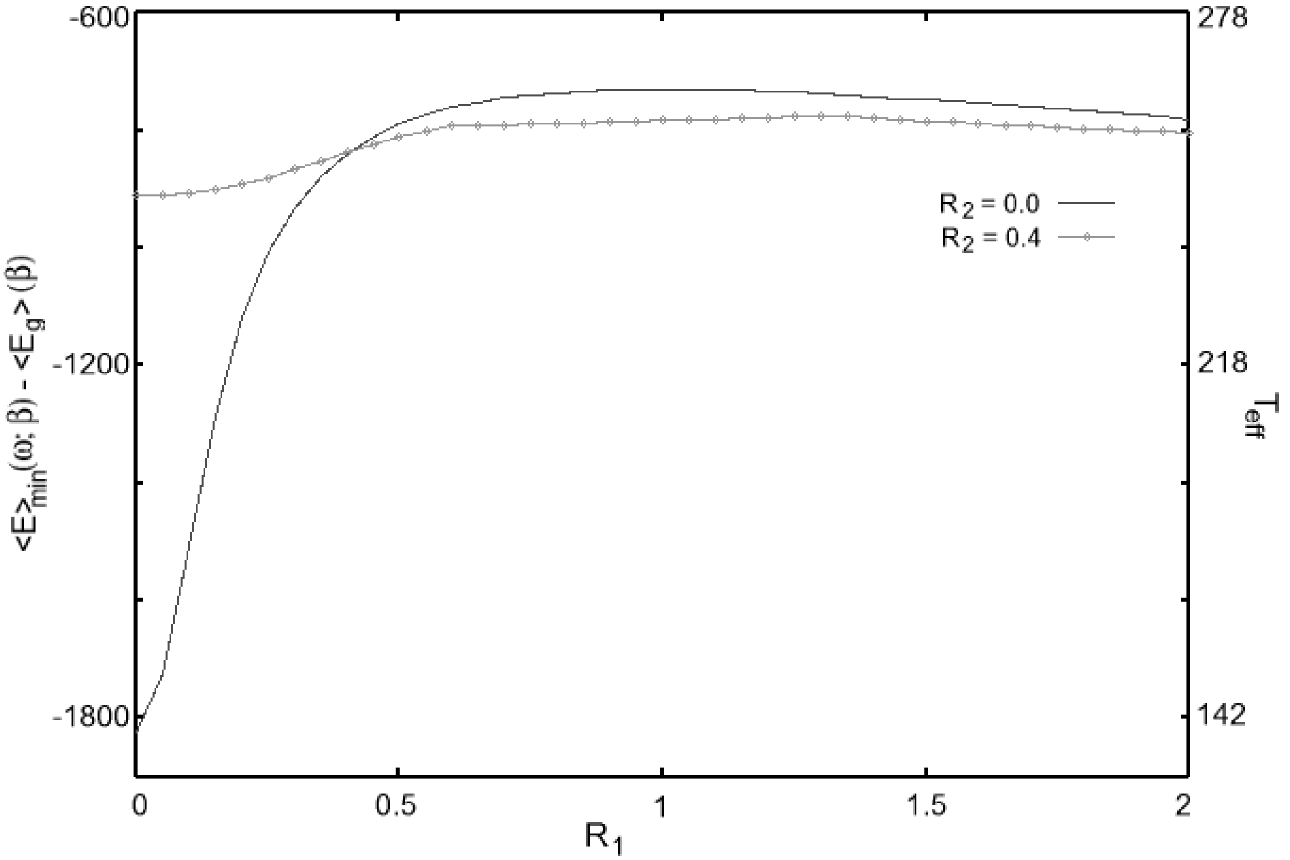


Figure 7, Ianconescu and Pollak

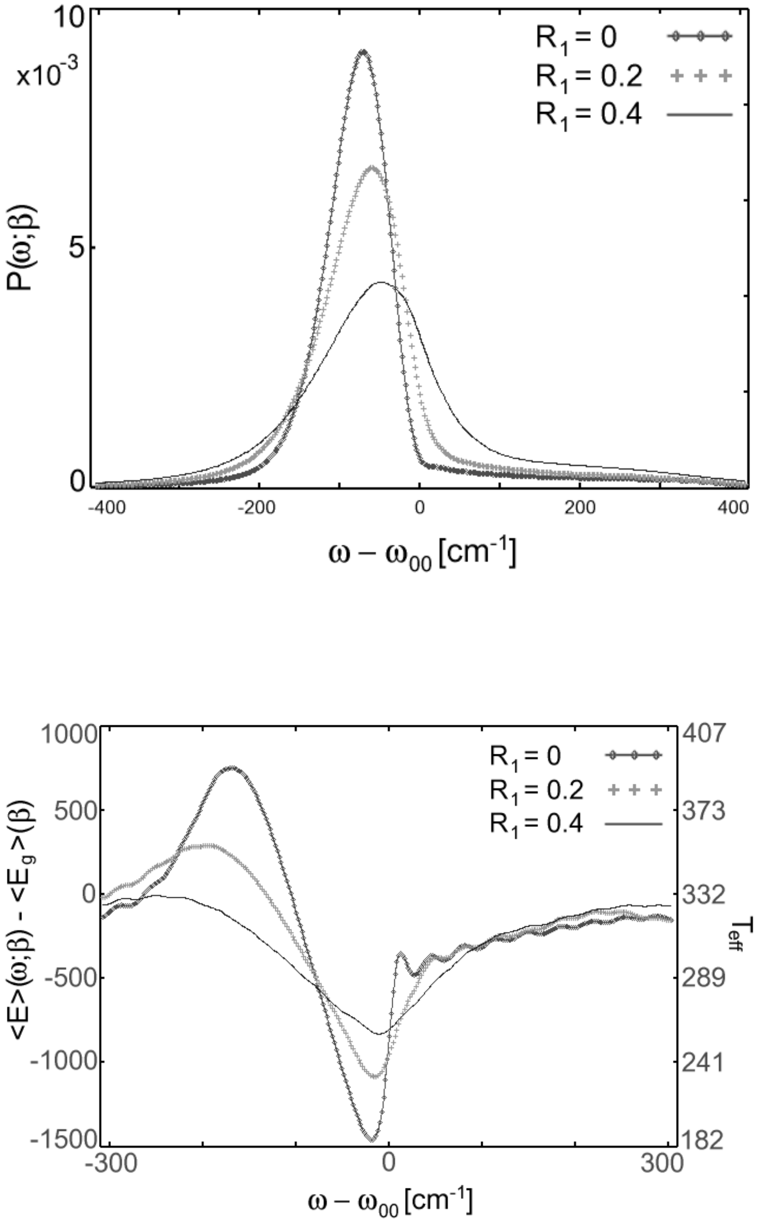


Figure 8, Ianconescu and Pollak

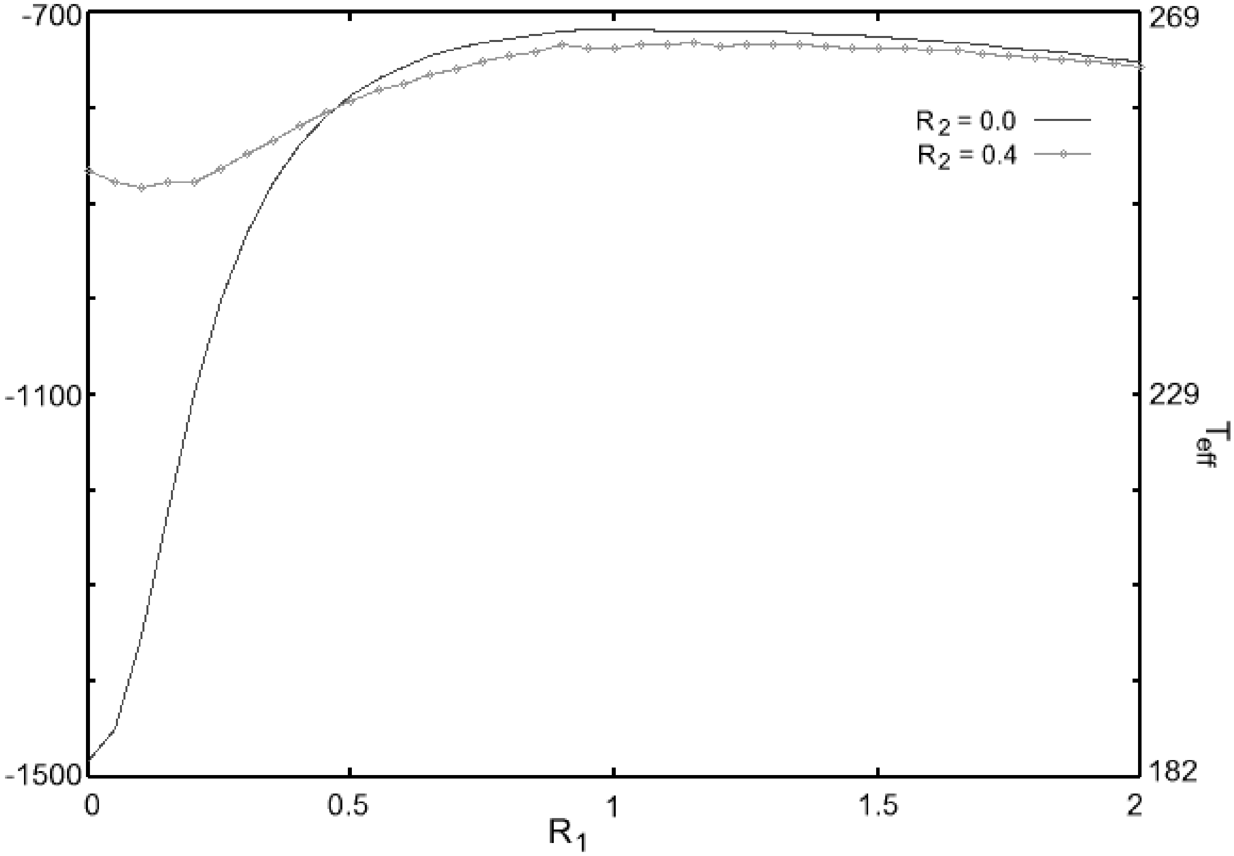


Figure 9, Ianconescu and Pollak