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Photoinduced Cooling of Polyatomic Molecules in an Electronically Excited State in the Presence of Dushinskii Rotations†

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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 generally diminish the cooling effect, 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 by 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 and co-workers[7,8] showed that, at low photoexcitation energy, increasing the pressure of the buffer gas caused a decrease in the fluorescence lifetime, which suggested that, initially, the molecular vibrations in the excited state were cold and the collisions would heat the molecule, leading to a faster decay. This interpretation was shown to be consistent with ab initio computations for the naphthalene molecules, and it showed that, indeed, cooling of the excited-state vibrations does occur when the photoexcitation frequency is close to or to the red side 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 the the topic of rather-heated debate, because of 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 cooling typically will occur 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, however, 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[2,15]

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

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where H_g is the ground-state Hamiltonian and

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

may be called the frequency-dependent partition function. The parameter 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

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

As was shown in ref 2, the average energy of the excited state may be calculated via the relation

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

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

$$\langle E_g\rangle(\beta) = -\frac{\partial}{\partial\beta}\ln\,(\mathrm{Tr}[\mathrm{e}^{-\beta H_g}]) \tag{2.5}$$

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. Thus, the ground-state Hamiltonian is 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} and 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} and 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, which defines the projection amplitude of the jth ground-electronic-state normal-mode coordinate on the ith 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 vector–matrix notation, we may rewrite eq 2.9 as

$$\underline{q}_e = \boldsymbol{S}\underline{q}_g + \underline{D} \tag{2.10}$$

where $\boldsymbol{S}$ is the orthogonal rotation matrix and $\underline{D}$ is the vector of equilibrium position shifts of the excited state, relative to the ground state. Note: Throughout this paper, we will denote (column) vectors by an underline, row vectors will be denoted by an additional superscript "T", and matrixes 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

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

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

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

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 two complete sets of excited-electronic-state coordinates $\underline{x}'$ and $\underline{y}'$, we may express eq 2.12 as

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

The off-diagonal matrix element $\langle x|\mathrm{e}^{-i\tau H}|y\rangle$ for a harmonic Hamiltonian $H = {}^1/_2(p^2 + \omega^2 q^2)$ is known[16] to be

$$\langle x|\mathrm{e}^{-i\tau H}|y\rangle = \sqrt{\frac{a(\tau)}{2\pi i\hbar}}\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}b(\tau)(x^2 + y^2) - a(\tau)xy\right]\right\} \tag{2.14}$$

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

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

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

The inner product between the ground- and excited-electronic-state coordinates $\langle\underline{x}'|\underline{x}\rangle$, using eq 2.10, is given by

$$\langle\underline{x}'|\underline{x}\rangle = \delta(\underline{x}' - (\boldsymbol{S}\underline{x} + \underline{D})) \tag{2.16}$$

where the δ function of a vector is defined as the product of the individual δ functions of its components. Therefore, the correlation function (eq 2.13) may be integrated over $\underline{x}'$ and $\underline{y}'$ and expressed as

$$\chi(\tau_g,\tau_e) = \mathrm{e}^{-i\tau_e\Delta E}\sqrt{\frac{\det(\boldsymbol{a}_g)}{(2\pi i\hbar)^N}}\sqrt{\frac{\det(\boldsymbol{a}_e)}{(2\pi i\hbar)^N}} \\ \int\int \mathrm{d}\underline{x}\,\mathrm{d}\underline{y}\,\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}(\underline{x}^{\mathrm{T}}\boldsymbol{b}_g\underline{x} + \underline{y}^{\mathrm{T}}\boldsymbol{b}_g\underline{y}) - \underline{x}^{\mathrm{T}}\boldsymbol{a}_g\underline{y}\right]\right\} \\ \exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}(\underline{x}'^{\mathrm{T}}\boldsymbol{b}_e\underline{x} + \underline{y}'^{\mathrm{T}}\boldsymbol{b}_e\underline{y}) - \underline{x}'^{\mathrm{T}}\boldsymbol{a}_e\underline{y}\right]\right\} \tag{2.17}$$

where $\boldsymbol{a}_{\mathbf{g}}$, $\boldsymbol{b}_{\mathbf{g}}$ and $\boldsymbol{a}_{\mathbf{e}}$, $\boldsymbol{b}_{\mathbf{e}}$ are defined as in eq 2.15 for the ground and excited states, respectively, and $\underline{x}'$, $\underline{y}'$ represent $(\boldsymbol{S}\underline{x} + \underline{D})$, $(\boldsymbol{S}\underline{y} + \underline{D})$, respectively, according to eq 2.16.

We further define the following matrixes:

$$\boldsymbol{A}(\tau_{\mathrm{g}},\tau_{\mathrm{e}}) = \boldsymbol{a}_{\mathbf{g}}(\tau_{\mathrm{g}}) + \boldsymbol{S}^{\mathbf{T}}\boldsymbol{a}_{\mathbf{e}}(\tau_{\mathrm{e}})\boldsymbol{S} \tag{2.18}$$

$$\boldsymbol{B}(\tau_{\mathrm{g}},\tau_{\mathrm{e}}) = \boldsymbol{b}_{\mathbf{g}}(\tau_{\mathrm{g}}) + \boldsymbol{S}^{\mathbf{T}}\boldsymbol{b}_{\mathbf{e}}(\tau_{\mathrm{e}})\boldsymbol{S} \tag{2.19}$$

$$\boldsymbol{G}(\tau_{\mathrm{g}}) = \boldsymbol{b}_{\mathbf{g}}(\tau_{\mathrm{g}}) - \boldsymbol{a}_{\mathbf{g}}(\tau_{\mathrm{g}}) \tag{2.20}$$

$$\boldsymbol{E}(\tau_{\mathrm{e}}) = \boldsymbol{b}_{\mathbf{e}}(\tau_{\mathrm{e}}) - \boldsymbol{a}_{\mathbf{e}}(\tau_{\mathrm{e}}) \tag{2.21}$$

This allows us to rewrite eq 2.17 as

$$\chi(\tau_{\mathrm{g}},\tau_{\mathrm{e}}) = \mathrm{e}^{-i\tau_{\mathrm{e}}\Delta E}\sqrt{\frac{\det(\boldsymbol{a}_{\mathbf{g}})}{(2\pi i\hbar)^{N}}}\sqrt{\frac{\det(\boldsymbol{a}_{\mathbf{e}})}{(2\pi i\hbar)^{N}}}\int\int \mathrm{d}\underline{x}\,\mathrm{d}\underline{y}$$
$$\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}(\underline{x}^{\mathrm{T}}\boldsymbol{B}\underline{x} + \underline{y}^{\mathrm{T}}\boldsymbol{B}\underline{y}) - \underline{x}^{\mathrm{T}}\boldsymbol{A}\underline{y} + \underline{D}^{\mathrm{T}}\boldsymbol{E}\underline{D} + \underline{D}^{\mathrm{T}}\boldsymbol{E}\boldsymbol{S}(\underline{x} + \underline{y})\right]\right\} \tag{2.22}$$

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

$$\chi(\tau_{\mathrm{g}},\tau_{\mathrm{e}}) = \mathrm{e}^{-i\tau_{\mathrm{e}}\Delta E}\sqrt{\frac{\det(\boldsymbol{a}_{\mathbf{g}})\det(\boldsymbol{a}_{\mathbf{e}})}{\det(\boldsymbol{B})\det(\boldsymbol{B} - \boldsymbol{A}\boldsymbol{B}^{-\mathbf{1}}\boldsymbol{A})}}$$
$$\exp\left\{\frac{i}{\hbar}[\underline{D}^{\mathrm{T}}\boldsymbol{E}\boldsymbol{S}(\boldsymbol{B} - \boldsymbol{A})^{-1}\boldsymbol{G}\boldsymbol{S}^{\mathrm{T}}\underline{D}]\right\} \tag{2.23}$$

and $\chi(\tau,\beta)$ is obtained by setting $\tau_{\mathrm{e}} = \tau$ and $\tau_{\mathrm{g}} = \beta - i\tau$ in eq 2.23.

Equation 2.23 gives the two-state correlation function, including rotation and displacement in closed form (see also the derivation in ref 15). Fourier transforming the correlation function numerically gives the "frequency-dependent partition 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, which is defined more generally as

$$\omega_{00} \equiv \sum_{i}(\omega_{\mathrm{e}_i} - \omega_{\mathrm{g}_i}) \tag{3.1}$$

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, however, 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, because it simply sets the scale of frequencies for the photoexcitation laser, so it will be set to zero. For convenience, the average energy will always be scaled to $\langle E\rangle(\omega,\beta) - \langle E_{\mathrm{g}}\rangle(\beta)$, so that a positive average energy implies heating and a negative average energy implies cooling. We will also define an effective temperature parameter for the excited state by looking for that temperature at which a Boltzmann 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

$$\langle E_{\mathrm{e}}\rangle = -\frac{\partial}{\partial\beta_{\mathrm{eff}}}\ln\mathrm{Tr}[\mathrm{e}^{-\beta_{\mathrm{eff}}H_{\mathrm{e}}}] \tag{3.2}$$

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 ranges 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$-$45. The off-diagonal elements of R will be kept small, so that $S^{\mathrm{T}}RS$ is a diagonal matrix with eigenvalues close to the integers 1$-$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 and 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 that 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 ensures 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}), because, for a zero-width pulse, the spectrum is a δ function that demands an infinite time integration. Figure 1a 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 ($R_{i>1} = 0$). Figure 1b shows the average energy in the excited state, as a function of the excitation frequency. In all cases, the temperature of the ground electronic state is 300 K.

As may be expected, the spectrum broadens under rotation; however, 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

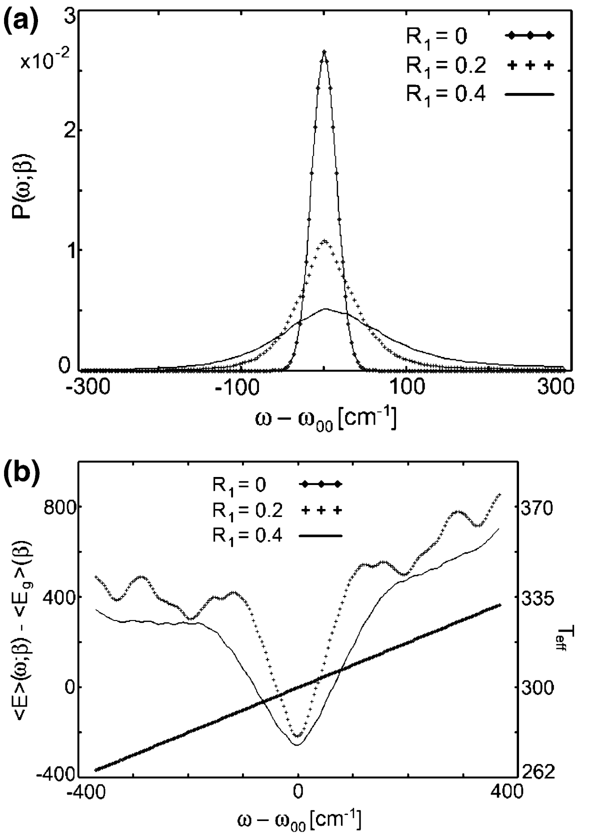

Figure 1. (a) Absorption spectrum and (b) average energy in the excited state, under conditions where the frequencies are the same in the ground and excited states and there are no position shifts. Panel a shows the absorption spectrum for three different values of the rotations, whereas panel b shows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

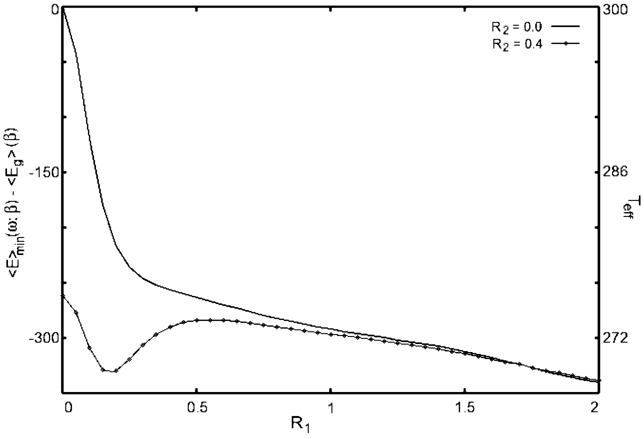

Figure 2. Minimal average energy and effective temperature in the excited state, as a function of rotation, under conditions where the frequencies in the excited and ground state are the same and there are no position displacements. Note that cooling is more extensive when $R_2 \neq 0$.

as $\hbar\omega$ increases. Cooling appears only when rotation is present. The results of Figure 1b thus show that Dushinskii rotations may induce cooling. To examine the extent of the cooling, we plot the maximal possible cooling as a function of the magnitude of the rotation in Figure 2. Although cooling is possible, it is not very large. Interestingly, however, cooling increases as the magnitude of the rotation increases. Thus, the maximal cooling when $R_2 = 0.4$ is always larger than when $R_2 = 0.2$.

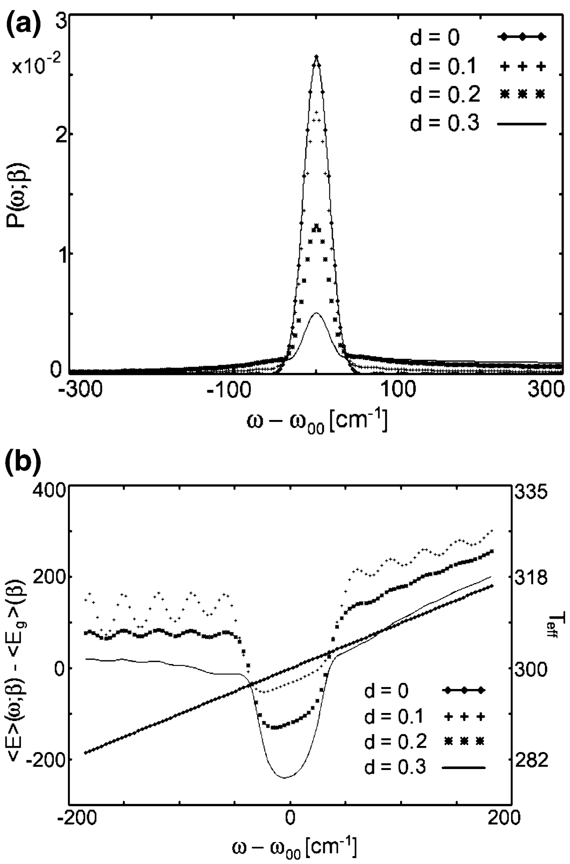

Figure 3. (a) Absorption spectrum and (b) average energy in the excited state under conditions where the frequencies are the same in the ground and excited states and there are no rotations. Panel a shows the absorption spectrum for four different values of the position shifts and panel b shows the average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

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 D to be nonzero only for the 15 modes with low frequencies. The 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 Figure 3a, we first consider the effect of displacement without rotation. Figure 3a displays the spectrum obtained for displacement values of 0, 0.1, 0.2, and 0.3, and Figure 3b 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, as well as 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 have a tendency to broaden the spectrum and decrease the overall absorption probability. The average energy and effective temperature of the excited state is shown in Figure 4b, as a function of excitation frequency; the figure shows that cooling increases

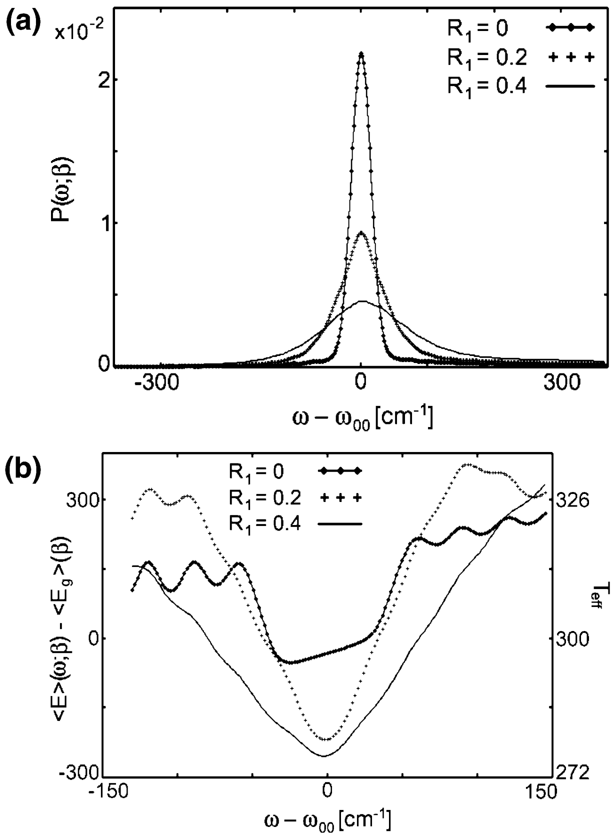

Figure 4. (a) Absorption spectrum and (b) average energy in the excited state under the conditions where the frequencies are the same in the ground and excited states and the position shift is $d = 0.1$. Panel a shows the absorption spectrum for three different values of the rotations and panel b shows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

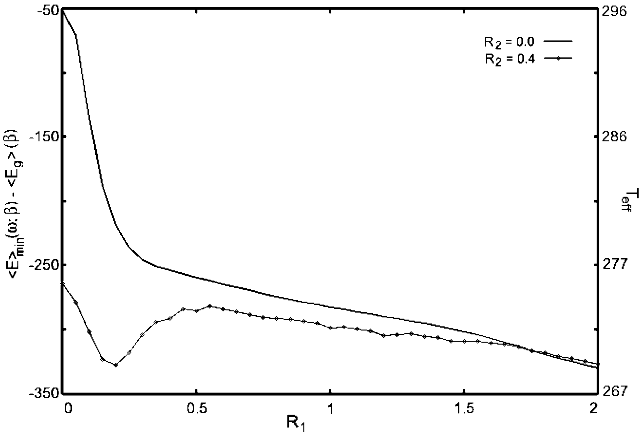

Figure 5. Minimal average energy and effective temperature in the excited state, as a function of rotation, under conditions where the frequencies in the excited and ground state are the same and the position shift is $d = 0.1$.

as rotation increases. However, as mentioned previously, the extent of cooling is not very large. In Figure 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 Figure 2, except for the fact that, for no rotation, there is some cooling, whereas, for large rotations, there is less cooling. We find that both rotation and displacement reduce the maximal heating and increase the temperature at the maximal cooling.

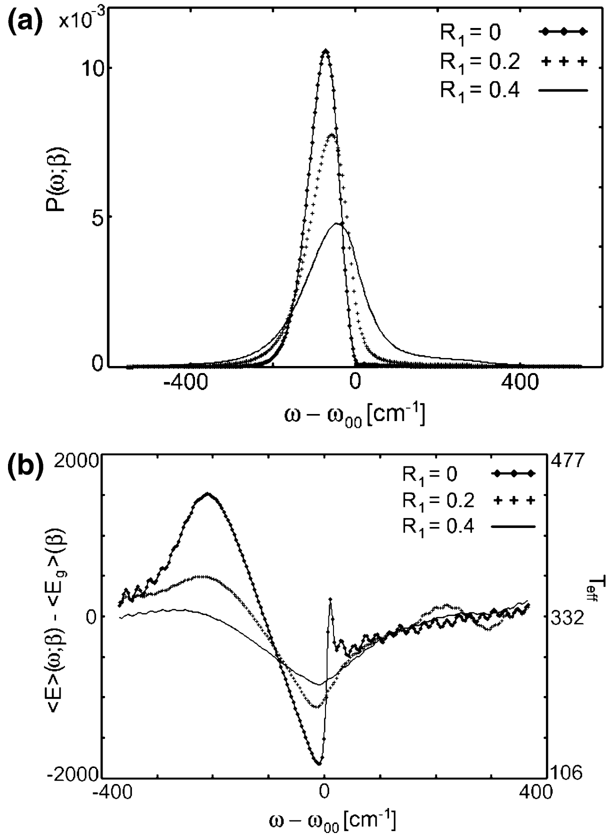

Figure 6. (a) Absorption spectrum and (b) average energy in the excited state, under conditions where the frequencies in the excited state are lower than those of the ground state but there are no position shifts. Panel a shows the absorption spectrum for three different values of the rotations and panel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

D. Case 4: Frequency Shifts and Rotations Only. As already mentioned previously, 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, those in the medium-frequency group are multiplied by 0.98, and those in the high-frequency group are multiplied by 0.99.

In Figure 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 Figure 6b. As known from our previous investigations and as shown in the figure, frequency shifts can lead to extensive cooling. Dushinskii rotation has a tendency 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.

Figure 7 shows a plot of the maximal cooling observed, 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, approaches a constant value; that is, the average energy is reduced to approximately -800 cm^{-1}.

E. Case 5: Position, Frequency Shifts, and Rotations. It has already been shown in previous work[2] that, without

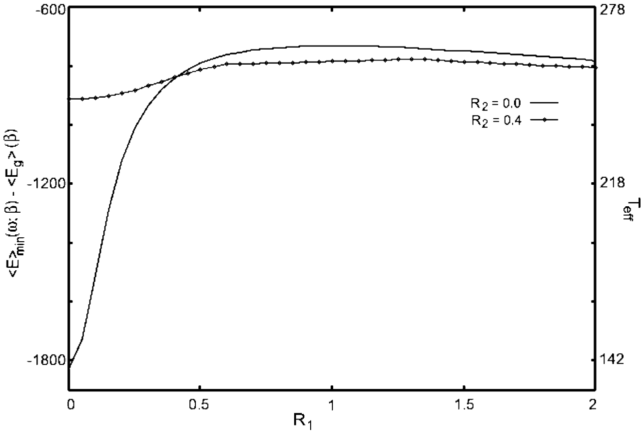

Figure 7. Minimal average energy and effective temperature in the excited state, as a function of rotation, under conditions where the frequencies in the excited state are lower than in the ground state and there are no position shifts.

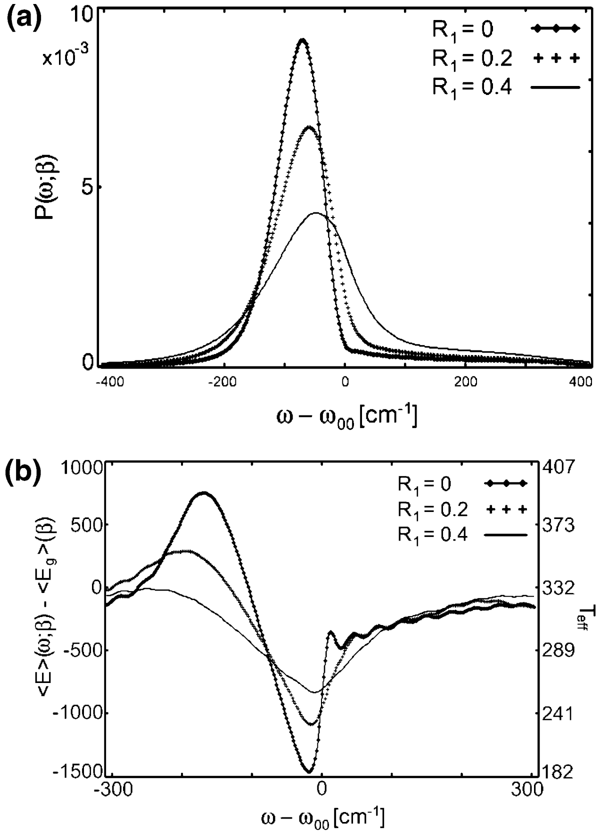

Figure 8. (a) Absorption spectrum and (b) average energy in the excited state, under conditions where the frequencies in the excited state are lower than in the ground state and the equilibrium positions in the excited state are shifted by a position shift of $d = 0.1$. Panel a shows the absorption spectrum for three different values of the rotations and panel b shows the average energy, each as a function of the excitation frequency.

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 reduce the absorption probability. The displacement also leads to increased structure in the absorption spectrum.

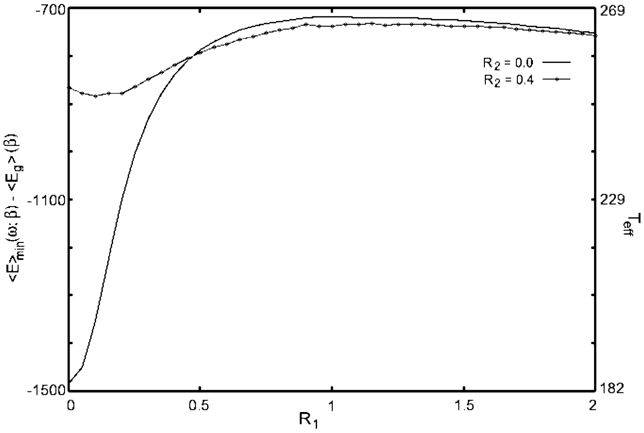

Figure 9. Minimal average energy and effective temperature in the excited state, as a function of rotation, under conditions where the frequencies in the excited state are lower than those in the ground state and the position shift is $d = 0.1$.

The average energy and effective temperature in the excited states is plotted in Figure 8b. The lowest average energy is observed at -1480 cm^{-1} and is obtained without rotation. This value is higher than that found without displacement, as can be seen by inspection of Figure 6b. However, we find that, generally, the maximal cooling is not necessarily found when there is no rotation. This is shown in Figure 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 as R_1 increases but decreases slightly in the region of $R_1 > 1$. 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 reducing the vibrational frequencies in the excited state leads to the possibility of cooling, whereas displacement and rotations have a tendency to mitigate the effect but do not destroy it completely. In this work, we have presented 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 nonuniform 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 observed, provided that the displacement and rotations are not “too strong”.

Does this mean that the cooling phenomenon generally can be ignored? We do not believe that this can be done, for several 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. However, we do note 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.[12,13] 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] have shown that non-Condon terms do not destroy the cooling phenomenon.

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