

Adiabatic quantum approach to optical line shapes in the condensed phase

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It is shown that absorption line shapes in the condensed phase can be well described with an adiabatic quantum model. This model reproduces the results of other line-shape models and includes spectral-diffusion and motional-narrowing effects. The motional narrowing is described in a purely quantum-mechanical manner and is found to result from the delocalized character of the wave functions of the low-frequency modes to which the optically active mode is coupled. In many line-shape models it is assumed that an increase in the rate of spectral diffusion automatically leads to motional narrowing of the absorption line. However, this assumption is no longer correct if the low-frequency motion is affected by a change in the quantum state of the high-frequency mode. It is demonstrated that this quantum effect can easily be accounted for in the adiabatic quantum model and that this effect leads to different dependencies of motional narrowing and spectral diffusion on the low-frequency motion. [S0163-1829(99)01134-0]

I. INTRODUCTION

In the condensed phase, absorption lines of high-frequency modes are predominantly broadened as a result of the interactions with low-frequency degrees of freedom. These interactions do not lead to an energy transfer to the low-frequency modes but to a (stochastic) modulation of the transition frequency of the high-frequency mode. Hence these interactions are denoted as quasielastic interactions. The broadening that results from these interactions is often referred to as pure dephasing. Pure dephasing has been studied and described for many different physical systems and is often modeled with semiclassical approaches in which the low-frequency mode is explicitly described in a classical manner.¹⁻⁵ In these models the frequency fluctuations of the high-frequency mode are calculated in a molecular-dynamics simulations using a potential-energy term that accounts for the interaction between the high- and low-frequency modes.^{4,5} With increasing temperature the amplitudes of most modes will increase, leading to a stronger frequency modulation. As a result, a broadening of the absorption line shape with temperature is expected. However, in the late 1940s it was found in nuclear-magnetic-resonance (NMR) studies that for some inhomogeneous systems the line shape actually became *narrower* with increasing temperature.^{6,7} To understand this narrowing it is important to realize that the absorption line shape is not only determined by the frequency distribution that results from the quasielastic interactions with the low-frequency degrees of freedom, but also by the *dynamics* of the frequency modulation. This dynamics can result both from an exchange of the excitation between different sites or from a change in the surroundings of the excited oscillator. The frequency fluctuations will lead to an averaging of the oscillator frequencies over the spectral distribution so that all oscillators effectively acquire the central frequency of this distribution. As a result, the observed absorption line will become narrower than the spectral distribution. This effect is denoted as motional narrowing.

Several line-shape models were developed that account for the effect of motional narrowing.⁸⁻¹⁵ These models al-

ways contain a spectral distribution function and a characteristic spectral modulation process, often characterized by a coupling or a correlation time constant for the frequency of the oscillator. In some models, like the exchange model,^{9,10} the spectral distribution peaks at a few well-defined frequencies⁹⁻¹² whereas in other models the spectral distribution is assumed to be Gaussian.¹³⁻¹⁵ In the so-called Gauss-Markov stochastic modulation model the fluctuations form a Gaussian process and the autocorrelation function of the detuning decays exponentially (Markov approximation) with time constant τ_c . When τ_c decreases, which corresponds to an increased rate of spectral modulation, the linear absorption spectrum evolves from a broad Gaussian to a much narrower Lorentzian. This model has been widely applied to describe the line shapes obtained in different optical spectroscopic experiments.¹⁶⁻²⁰

In modeling the absorption line shape it is often assumed that the excitation of the high-frequency mode does not affect the low-frequency motion. The independence of the low-frequency motion on the quantum state of the high-frequency mode is referred to as zero back reaction (ZBR). Almost all line-shape models and molecular-dynamics simulations of the optical line shape assume ZBR. This assumption was even used in some recent advanced molecular-dynamics simulations in which the low-frequency motion leads to strong nonadiabatic changes of the quantum state of the high-frequency mode.²¹⁻²³ An important consequence of assuming ZBR is that an increase of the rate of frequency fluctuation always leads to a motional narrowing effect. In the limit that the frequency fluctuation becomes infinitely fast, the linewidth becomes equal to zero.

There are also line-shape models that do not assume ZBR. In, for instance, the Brownian oscillator model it is assumed that the excitation of the high-frequency mode results in a change of the equilibrium position of the harmonic low-frequency motion.²⁴⁻²⁶ Also in some recent classical molecular-dynamics simulations^{27,28} the change of the intermolecular interactions due to the excitation of the high-frequency mode is incorporated. Hence in this treatment the low-frequency motion is allowed to be different for the

ground and excited state of the high-frequency mode. An important consequence of not assuming ZBR is that an increase in the rate of the frequency fluctuations may only lead to a partial narrowing of the absorption line or even no narrowing at all, depending on the precise character of the low-frequency motion in the ground and excited state of the high-frequency mode. For instance, in case the low-frequency modes in the ground and excited state of the high-frequency mode are formed by two displaced harmonic oscillators, an increase of the oscillation frequency of the low-frequency mode will lead to a more rapid spectral modulation but has no effect at all on the absorption linewidth.

The intermediate situation of partial narrowing is rather difficult to model since it requires a distinction between frequency fluctuations that lead to an averaging over the spectral distribution and thus to a narrowing effect and frequency fluctuations that do not lead to a narrowing of the absorption line. In this paper we will show that such a distinction and thus a correct description of partial motional narrowing can easily be obtained when both the high-frequency mode and the low-frequency mode are quantum mechanically described using an adiabatic model. This model has been successfully used to describe the broadening of the O-H stretching vibration due to hydrogen bonding.^{29–31} However, motional narrowing and spectral diffusion have never been discussed before in the context of this model. It will be shown that the adiabatic quantum model includes both these effects and can be quite generally applied to describe optical line shapes in the condensed phase.

This paper is organized as follows. In Sec. II the adiabatic quantum model is presented. The results obtained with this model for two different types of spectral distributions are presented in Sec. III. In Sec. IV these results are discussed and compared to the results of other line-shape models. Finally, Sec. V brings the conclusions.

II. THEORETICAL MODEL

We consider a set of high-energy degrees of freedom like electronic excitations, molecular vibrations, and optical phonons with coordinates $\{R\}$ and a manifold of low-frequency states like acoustic phonons and translational degrees of freedom with coordinates $\{l\}$. The Schrödinger equation of this system has the following form:

$$\left\{ \sum_R \frac{\hbar^2}{2m_R} \nabla_R^2 + \sum_l \frac{\hbar^2}{2m_l} \nabla_l^2 + V_h(\{R\}) + V_l(\{l\}) + V_{hl}(\{R\}, \{l\}) \right\} \Psi(\{R\}, \{l\}) = E \Psi(\{R\}, \{l\}), \quad (2.1)$$

with m_R and m_l the mass of the quasiparticles in the coordinates R and l , respectively.

This Schrödinger equation can be simplified using an adiabatic approach in which the (high-frequency) motion in coordinates $\{R\}$ can be separated from the motion of the (low-frequency) degrees of freedom with coordinates $\{l\}$. This is a good approximation if the motion in the high-frequency coordinate is much faster than that in the low-frequency coordinate. Then the wave function Ψ can be

written as $\psi(\{R\}; \{l\}) \phi(\{l\})$ (Born-Oppenheimer approximation). The function $\psi(\{R\}; \{l\})$ represents the wave function in the high-frequency coordinates that depends parametrically on the low-frequency coordinates $\{l\}$. This type of adiabatic treatment is well known and can be found in many textbooks.³² The adiabatic treatment forms a good approximation if the terms $\nabla_{\{l\}} \psi(\{R\}; \{l\})$ and $\nabla_{\{l\}}^2 \psi(\{R\}; \{l\})$ are negligible, that is when the character of the high-frequency wave functions $\psi(\{R\}; \{l\})$ do not strongly change as a function of the low-frequency coordinate l .

In the following, only a single high-frequency coordinate R and a single low-frequency coordinate l will be considered. For each high-energy state $\psi_i(R; l)$ there exists a manifold of functions $\phi_{ia}(l)$ that are the solutions of the following simple one-dimensional Schrödinger equation:

$$\left(\frac{\hbar^2}{2m_l} \frac{\partial^2}{\partial l^2} + V_l(l) + E_i(l) \right) \phi_{ia}(l) = E_{ia} \phi_{ia}(l). \quad (2.2)$$

The state of the system is given by $\sum_{i,a} C_{ia} \psi_i(R; l) \phi_{ia}(l)$. The time dependence (modulation) of the transition frequency results from the fact that many low-frequency states $\phi_{ia}(l)$ of different energy will be thermally occupied leading to quantum interference effects. The phase relation between ϕ_{1a} will affect the quantum interference of the transitions from the ϕ_{1a} states to a particular ϕ_{2a} state and thus the transfer of population to this state. The initial phase relation of each oscillator in the system will be different and thus each single oscillator will have a different time-dependent absorption spectrum. In the following, we will only address the ensemble- and time-averaged linear absorption spectrum, but the treatment can easily be extended to describe nonlinear optical experiments like spectral-hole burning and photon-echo spectroscopy in which the time dependence of the absorption spectrum of an individual oscillator can be measured.

The absorption line is given by an electric-dipole transition between the occupied $\psi_1 \sum_a C_{1a} \phi_{1a}$ and the set $\psi_2 \sum_b \phi_{2b}$. For the ensemble- and/or time-averaged absorption spectrum the phase relations of the ϕ_{1a} states will average out so that the shape of this line is only determined by the thermal occupation of these states and the cross sections of the transitions from these states to the manifold of ϕ_{2b} states:

$$W \approx \sum_{a,b} |C_{1a}|^2 |\langle \psi_2 \phi_{2b} | R | \psi_1 \phi_{1a} \rangle|^2 = |\langle \psi_2 | R | \psi_1 \rangle|^2 \sum_{a,b} |C_{1a}|^2 |\langle \phi_{2b} | \phi_{1a} \rangle|^2. \quad (2.3)$$

It follows from this expression that the broadening is given by the matrix elements $\langle \phi_{2b} | \phi_{1a} \rangle$, representing the projection of each state ϕ_{2b} on the complete set $\{\phi_{1a}\}$. The shape and width of the distribution of transition frequencies thus depends on the difference between ϕ_{2b} and ϕ_{1a} , which is determined by the difference between the potentials $E_2(l)$ and $E_1(l)$. If these potentials strongly differ, the transitions between the manifolds $\{\phi_{2b}\}$ and $\{\phi_{1a}\}$ are accompanied by the emission or absorption of a large number of energy quanta in the low-frequency coordinates $\{l\}$.

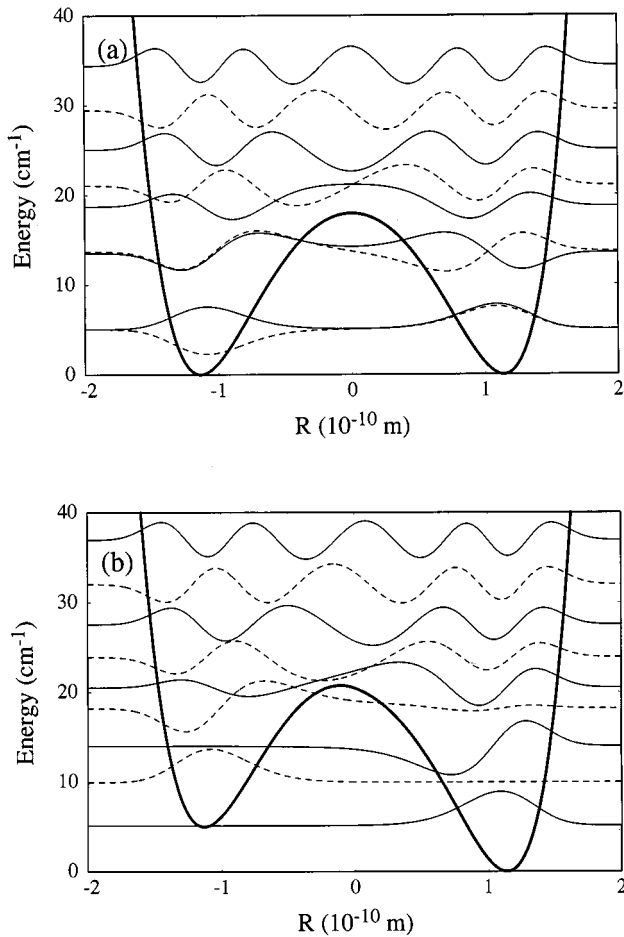


FIG. 1. Potential-energy curves used to calculate the absorption line shape for a doubly peaked spectral distribution. Also shown are the lowest nine vibrational wave functions calculated using a mass of 50 amu ($1 \text{ amu} = 1.66054 \times 10^{-27} \text{ kg}$). (a) $V_1 = 4.2l^6 - 21l^2$; (b) $V_2 = 4.2l^6 - 21l^2 - 2.8[l/|l|][1 - e^{-2|l|}]$, with the potential energy in cm^{-1} and the coordinate l in 10^{-10} m .

III. RESULTS

In this section the adiabatic model of the previous section is used to calculate the characteristics of the motional narrowing and spectral diffusion for two model systems.

A. Peaked spectral distribution

As described in the introduction, an absorption line shape is determined by a spectral-distribution function and the rate and character of the frequency modulation within this distribution. For some systems the spectral distribution peaks at a few distinct frequencies. Examples of these can be found in studies on optical phonons, molecular vibrations^{9,10} and proton-spin resonances (NMR).^{11,12}

The optical line shape of a doubly peaked spectral distribution can be modeled using the potentials E_1 and E_2 presented in Fig. 1. It should be noted here that the energies and shapes of these potentials are chosen arbitrarily and are not meant to describe a specific system. If there would be no dynamics (motion) in the potentials E_1 and E_2 , the possible transitions between E_1 and E_2 lead to a doubly-peaked absorption line shape for the high-frequency mode. The frequency of the high-frequency mode is determined by the

vertical displacement in energy of E_1 and E_2 . In order for the adiabatic treatment to be valid, this energy difference should be large compared to the spacing of the low-frequency levels and the height of the barriers in the potentials E_1 and E_2 . Since we are only interested in the shape of the spectra, the energy difference of E_1 and E_2 is not specified but it is assumed that this energy difference is large enough for the adiabatic treatment to be valid.

The Schrödinger equation for the low-frequency mode [Eq. (2.2)] is solved using the Numerov method. In a typical calculation of the optical line shape, the lowest 250 vibrational levels are calculated for both potentials E_1 and E_2 . The optical linewidth starting from the levels in potential E_1 is calculated using Eq. (2.3). These levels are assumed to be thermally occupied following a Boltzmann distribution.

In Fig. 2 absorption spectra are presented calculated at four different temperatures. At 1 K only the lowest states in the potential E_1 will be occupied. These states mainly have transition probability to the two lowest states in E_2 that are well localized in either one of the two wells. Hence the absorption spectrum consists of two narrow peaks. If the temperature is increased to 10 K, higher states will get occupied that have transition probability to more delocalized states in E_2 . This will lead to a broadening of the two peaks in the absorption spectrum. If the temperature is further increased to 100 K, most of the occupied states in E_1 have transition probability to delocalized states in E_2 . This delocalization leads to an averaging of the energies of the two wells of E_2 and thus the absorption will now peak at the average frequency of the two lines at low temperature. However, the wave functions just above the barrier in E_2 will still strongly differ from the thermally occupied wave functions in E_1 so that the transition will still be broad. If the temperature becomes very high, e.g., 1000 K, most of the thermally occupied states of E_1 are well above the barrier separating the two wells and have transition probability to similar states in E_2 . These high-energy states are not too strongly influenced anymore by the asymmetry in the potential and thus become quite similar to the corresponding states in E_1 . Hence the resulting absorption line will be narrow. The narrowing of the transition with increasing vibrational quantum number is illustrated in Fig. 3(a). The temperature dependence of the overall absorption can be obtained by summing over the thermally occupied vibrational states. In Fig. 3(b) the overall width of the absorption is shown as a function of temperature, clearly illustrating the motional-narrowing effect. At low temperatures, the linewidth shows a capricious dependence on temperature due to the fact that only a limited number of low-frequency quantum states is occupied. At high temperatures, many states are occupied leading to a nearly classical behavior of the low-frequency mode and a smooth decrease of the linewidth with temperature. Also shown in Fig. 3(b) is the linewidth in the inhomogeneous limit (infinite mass). For an infinitely large mass, the kinetic energy term $(\hbar^2/2m_l)(\partial^2/\partial l^2)$ in Eq. (2.2) becomes negligible compared to the potential energy and the wave function becomes completely localized at the position where the energy of the level equals the potential energy. In this limit the absorption line will be given by the energy differences between the potentials E_2 and E_1 over the thermally occupied range of E_1 . In this inhomogeneous limit there is no exchange between dif-

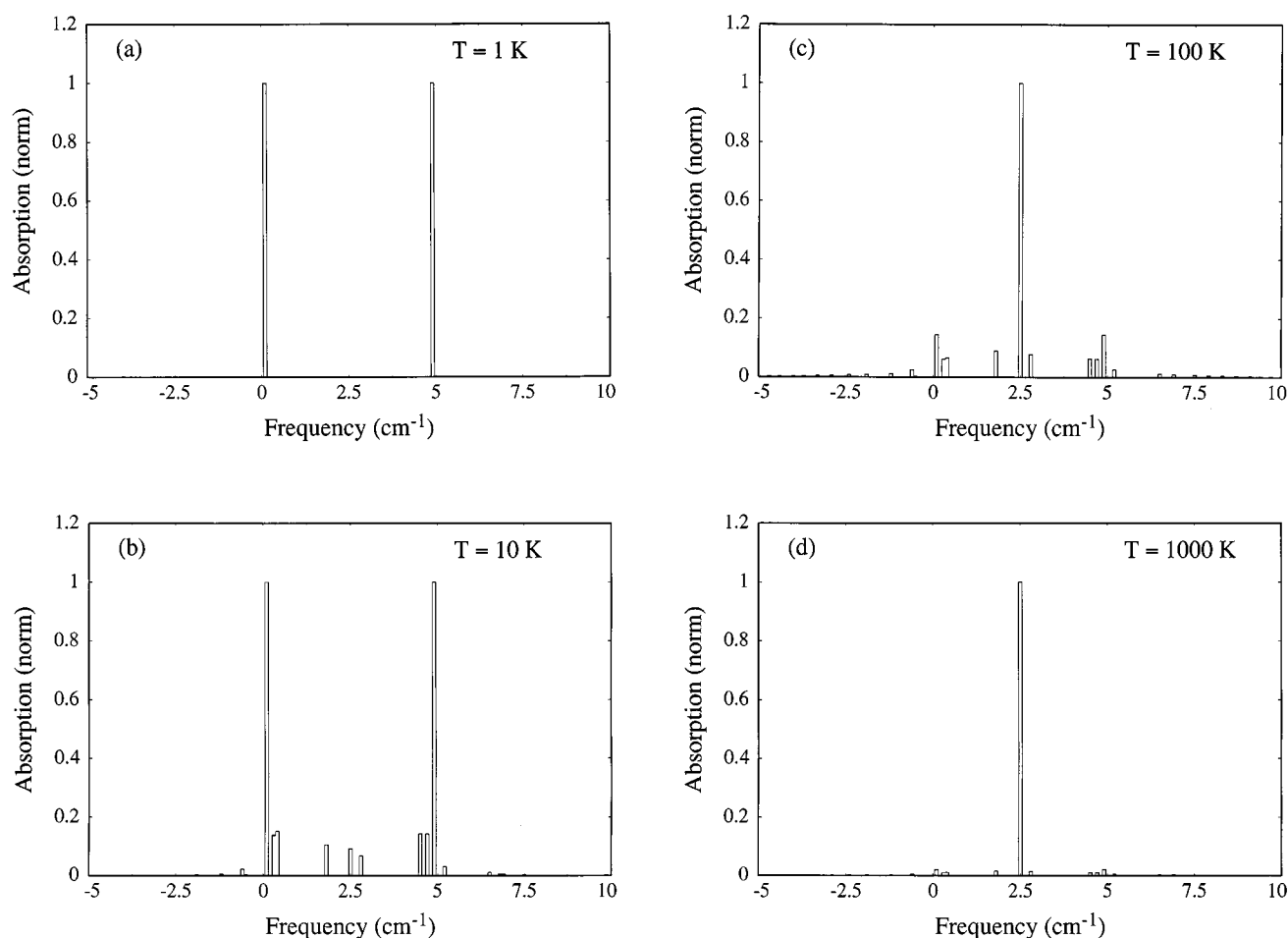


FIG. 2. Absorption spectra at four different temperatures calculated using the potentials of Fig. 1 using a mass of 50 amu.

ferent positions l and thus no fluctuation of the transition frequency. The inhomogeneous line width increases with temperature because the thermally occupied range of the potential E_1 and thus the range of energy differences with E_2 becomes larger. Hence it is clear that the motional narrowing shown in Fig. 3(b) is not the result of a decrease in the width of the spectral distribution but really the result of a more rapid fluctuation within this distribution. It is interesting to note that the absorption linewidth can never really narrow down to zero because the adiabatic description will no longer be valid if the motion in l becomes infinitely fast. If the motion in l becomes very fast, it is no longer possible to separate the time scales of the high- and low-frequency motion. As a result, the ground and excited state of the high-frequency mode are no longer decoupled which means that there will be population relaxation out of the excited state to the ground state. This population relaxation will lead to a nonzero absorption linewidth, even if the motional narrowing would lead to a complete vanishing of the linewidth.

In the conventional description of motional narrowing for a system with a peaked spectral distribution,⁹⁻¹² the absorption spectrum is described with a few coupled differential equations that each describe the time evolution of the polarization at one of the discrete frequencies of the spectral distribution. The motional narrowing results from an increase of the coupling of these equations with temperature. In the adia-

batic quantum description the narrowing results from an increase in the delocalization and the energy of the thermally occupied wave functions. Apparently the adiabatic frequency fluctuation that leads to motional narrowing is contained in the character of the wave functions, which can be understood in the following way. The delocalization of the wave function over l represents the evolution from a particular transition frequency (given by the difference between E_1 and E_2 at a particular value of l) to another frequency. This change in transition frequency is accompanied by a complementary change in the kinetic energy in l . The fact that the wave function has the same energy at all l means that the sum of the energy in the high-frequency coordinate R and the kinetic energy in l does not change in this process, as is expected for an adiabatic interaction. With increasing temperature, higher energy states get occupied that have a larger kinetic energy l which implies that the different regions of the potentials E_1 and E_2 are sampled more rapidly so that the structures of the potentials are more and more averaged out in the wave functions. As a result, the wave functions of the low-frequency mode in E_1 and E_2 will become more similar and the absorption line becomes narrower. The increase in similarity of the wave functions in E_1 and E_2 implies that the low-frequency motion becomes increasingly independent on the quantum state of the high-frequency resonance: the low- and the high-frequency mode become increasingly decoupled.

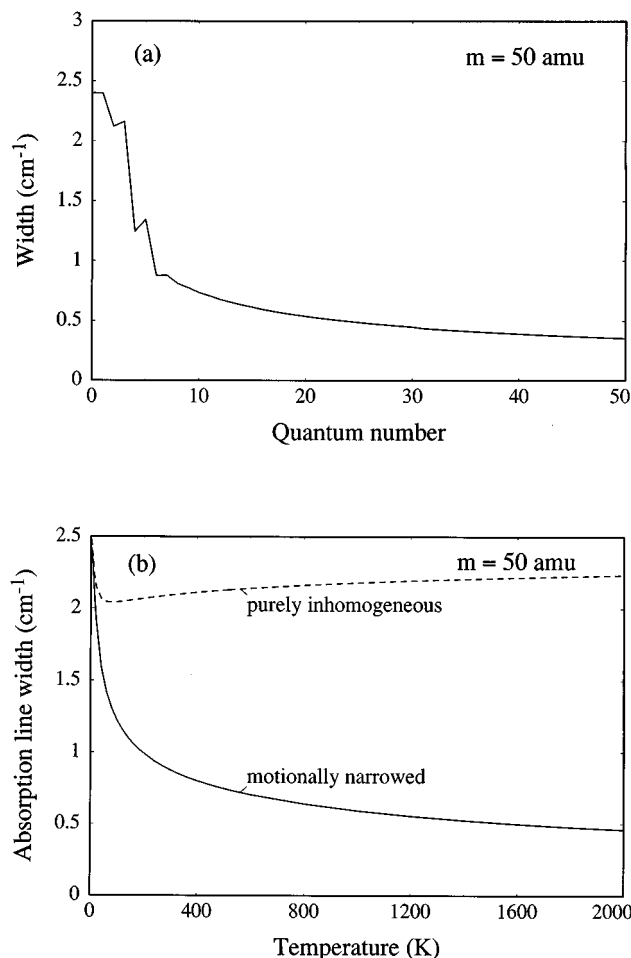


FIG. 3. Absorption linewidth for the transition between the potentials of Fig. 1 as a function of vibrational quantum number (a) and as a function of temperature (b), calculated for a mass of 50 amu. Also shown in (b) is the inhomogeneous linewidth that corresponds to the energy difference between the potentials over the thermally occupied range of the potential of Fig. 1(a).

In addition to motional narrowing, there will be a spectral-diffusion process that results from the quantum interference of the occupied states in E_1 . This interference results in an ongoing change of the upper states in E_2 that are optically coupled to the occupied states in E_1 . However, since there is no phase relation between the upper states in E_2 , this quantum interference does *not* lead to a transfer of the polarization from one frequency to another *with phase conservation* for the polarization. As a result, the quantum interference will not contribute to the motional narrowing.

B. Broad, structureless spectral distribution

For many systems, the spectral distribution is not peaked at a few well-defined frequencies but is broad and structureless. Such a spectral distribution can be obtained using potentials with different oscillatory modulations, as illustrated in Fig. 4. In Fig. 5 the absorption line shape that results from these potentials is presented as a function of vibrational quantum number and as a function of temperature. In Fig. 5(a) it is seen that at low vibrational quantum numbers the width of the absorption line strongly changes as a function of

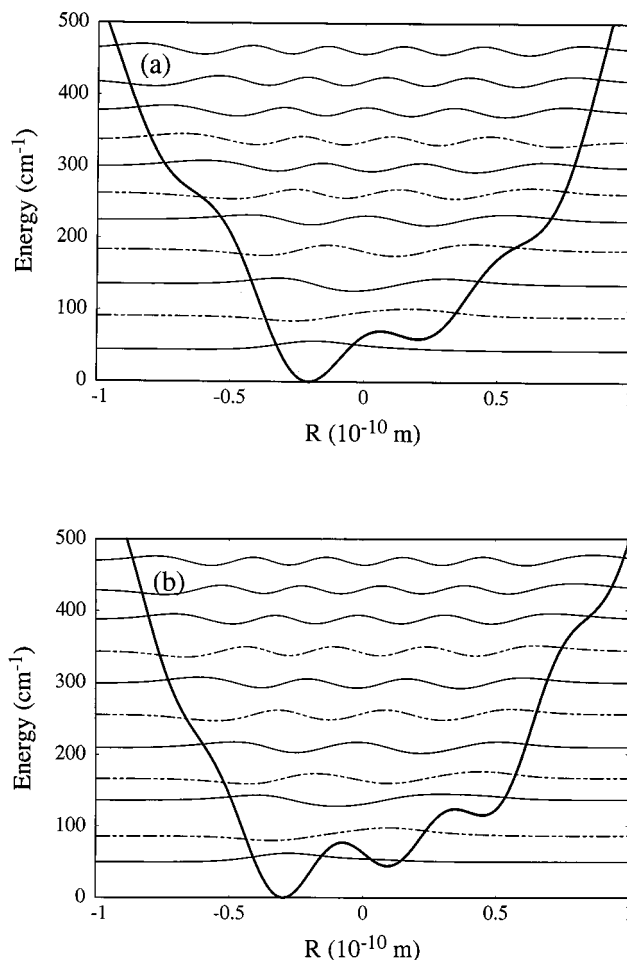


FIG. 4. Potential-energy curves used to calculate the absorption line shape for a broad continuous spectral distribution. Also shown are the lowest 11 vibrational wave functions assuming a mass of 20 amu. (a) $V_1 = 500l^2 + 30[\sin(7.5l) + \cos(12.5l)]$; (b) $V_2 = 500l^2 + 30[\sin(5l) + \cos(7.5l) - \sin(15l)]$, with the potential energy in cm^{-1} and the coordinate l in 10^{-10} m.

vibrational quantum number because the energy of the states is within the range of the modulation of the potential-energy curves. At higher energies, the linewidth is observed to decrease with increasing vibrational quantum number. With increasing temperature the occupation of these higher energy states that have narrower linewidths will increase which results in a narrowing of the absorption linewidth with temperature, as shown in Fig. 5(b).

In Fig. 6 the width of the absorption is presented as a function of temperature for different displacements of the position of the minimum of E_2 with respect to that of E_1 . It is clear from this figure that the motional-narrowing effect decreases with increasing displacement. For large displacements the linewidth even increases with temperature. This increase of the linewidth with temperature results from two effects. In the first place, for a nonzero displacement, the spectral range of transition frequencies from E_1 to E_2 will strongly increase with increasing degree of excitation in the potential E_1 . At large displacements and high temperatures the spectral width due to the displacement will dominate over the spectral width that results from the difference in the

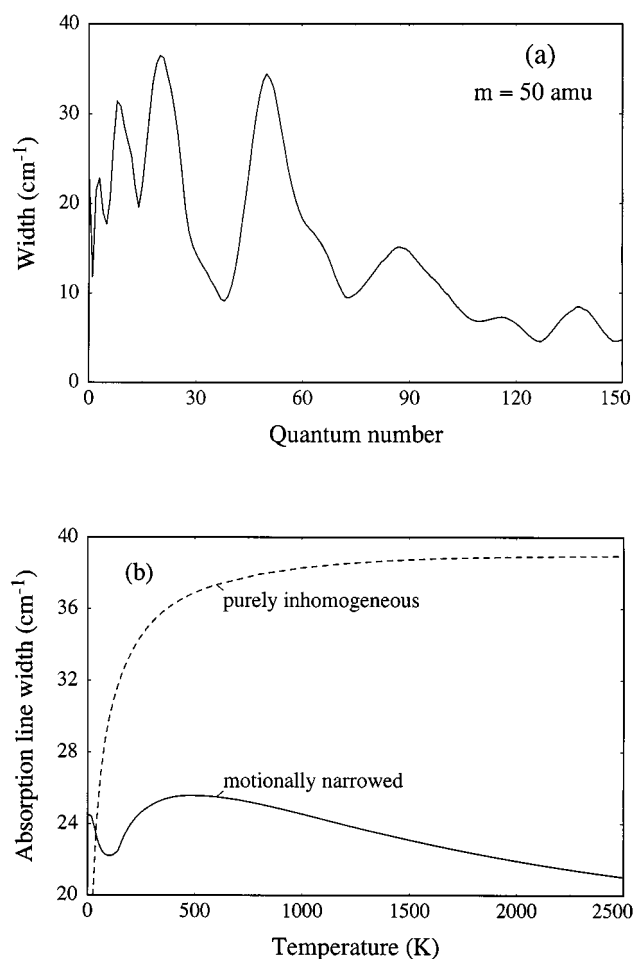


FIG. 5. Absorption linewidth of the transition between the potentials of Fig. 4 as a function of vibrational quantum number (a) and as a function of temperature (b), calculated for a mass of 50 amu. Also shown in (b) is the inhomogeneous linewidth that corresponds to the energy difference between the potentials over the thermally occupied range of the potential of Fig. 4(a).

modulation of the potentials. In this limit the linewidth has a $[\coth(\hbar\omega_l/2kT)]^{1/2}$ dependence on temperature (with $\hbar\omega_l$ the frequency spacing in the harmonic potentials), as has been found previously in other line-shape models that describe the

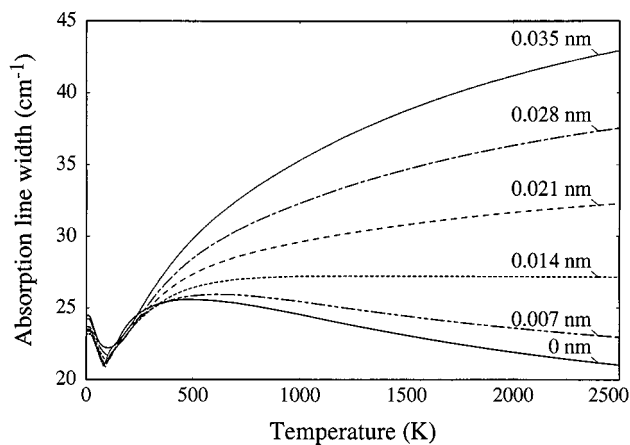


FIG. 6. Absorption linewidth as a function of temperature for six different displacements of the minima of the potentials of Fig. 4.

transition between two displaced (unmodulated) parabola.³⁰ Second, if the potentials E_1 and E_2 are displaced, there can be no complete motional-narrowing effect since there can be no averaging out of a difference in equilibrium position. Hence, even at very high degrees of excitation, the wave functions in E_1 will remain different from those in E_2 . This means that in case of a displacement there will always be a residual linewidth, even if the rate of spectral diffusion would be infinitely fast, e.g., when the mass of the quasiparticle in l becomes equal to zero. This residual linewidth is determined by the displacement of the potentials. Apparently, there can only be a complete motional-narrowing effect if the *overall* shapes of the potentials E_1 and E_2 are exactly the *same*. Hence in a quantum-mechanical picture, in which the motion in l can differ for different quantum states of the high-frequency mode, an increase in the rate of spectral diffusion does not necessarily lead to motional narrowing.

IV. DISCUSSION

In many line-shape models like the exchange model^{9,10} and the Gauss-Markov model there is only one fluctuation process that governs both the spectral diffusion of the optimum frequency at which an oscillator can be excited, and the transfer of the optically induced polarization from one frequency to another with phase and amplitude conservation. This conservation of phase and amplitude of the polarization in going from one frequency to another is essential for getting a motional narrowing effect since only then an increase in the rate of the frequency fluctuations will make the rate of phase accumulation of the polarization increasingly similar to the average frequency of the frequency distribution. If there is no conservation of phase and amplitude, an increase in the rate of the frequency fluctuations will lead to a more rapid decay of the polarization and thus to a broadening instead of a narrowing effect. Also in the semiclassical line-shape models, in which the frequency fluctuations are explicitly calculated by means of a molecular-dynamics simulation,^{4,5} it is assumed that the frequency fluctuations leading to motional narrowing have exactly the same dynamics as the spectral diffusion. This means that in all these descriptions (exchange, Gauss-Markov and semiclassical models) the absorption linewidth will become equal to zero if the spectral diffusion becomes infinitely fast.

In the previous section it was shown that in the adiabatic quantum model the spectral diffusion and motional narrowing have different origins. Spectral diffusion results from the quantum interference of the occupied low-frequency states whereas motional narrowing is contained in the delocalization of the wave functions of these states. This delocalization can have a different dependence on the degree of excitation (temperature) of the low-frequency mode than the spectral-diffusion process. As a result, an increase in the rate of spectral diffusion does not automatically imply that the amount of motional narrowing will increase. It was shown that a complete narrowing only occurs if the potentials E_1 and E_2 have exactly the same overall shape. This means that for a complete narrowing the low-frequency motion should *not* be affected by the excitation of the high-frequency mode [zero back reaction (ZBR)], as is assumed to be the case in most

line-shape models. Often the assumption of ZBR is based on the argument that the low-frequency mode behaves classically. However, the fact that the motion of the low-frequency mode behaves classically does not exclude the possibility that this motion changes upon excitation of the high-frequency mode. The assumption of ZBR will in fact only be correct if the low-frequency motion is dominated by other interactions than the interaction with the high-frequency mode or if the degree of excitation in the high-frequency mode is very high. In the latter case it can be expected that the range of l and the low-frequency motion will hardly be affected by putting in another quantum in the high-frequency mode. It should be realized here that this means that not only the low-frequency mode but also the high-frequency mode should be in a classical limit. However, in most spectroscopic studies the number of quanta in the high-frequency mode will be small and thus it can be expected that in many cases the low-frequency motion strongly depends on the quantum state of the high-frequency mode, even if the low-frequency mode itself behaves classically. If this is the case, the low-frequency motion in the ground and excited state of the high-frequency mode should be described independently in order to obtain a correct description of the optical line shape. Such an independent description is provided by the adiabatic model, irrespective whether the low-frequency motion is of quantum, classical, or intermediate character.

The (multimode) Brownian oscillator model²⁴⁻²⁶ is one of the few line-shape models that does not assume ZBR. In this model the potentials of the low-frequency mode are formed by displaced parabola and the (classical) harmonic low-frequency motion is damped due to stochastic interactions with a bath. Since the parabola in the ground and excited state have exactly the same shape, this model can neither account for a change of frequency of the low-frequency oscillator upon excitation nor for anharmonic effects in the low-frequency motion. In the adiabatic quantum model it is easy to use parabola with different curvatures for the ground and excited state and to include anharmonic effects. An even more important difference with the adiabatic quantum model is that it is assumed in the Brownian oscillator that the stochastic interactions with the bath do *not* contribute to the width of the spectral distribution and only affect the motion in the low-frequency coordinate. Due to this assumption, an increase in temperature does not lead to an increase in the rate of the frequency fluctuations in the Brownian oscillator model and thus there can be no motional narrowing of the absorption line with temperature in this model. In fact, in the Brownian oscillator model an increase in temperature will lead to a broadening of the line since the width of the spectral distribution increases following a $[\coth(\hbar\omega_l/2kT)]^{1/2}$ dependence on temperature. In contrast, in the adiabatic quantum model the stochastic interactions can contribute to the broadening of the absorption. This contribution is represented by the difference in modulation of the potentials E_1 and E_2 . An increase in temperature leads to a motional narrowing of the contribution of this difference in modulation leaving only the line broadening that results from the displacement of the potentials. As a result, the absorption line can show a partial narrowing effect, as is shown in Fig. 6.

The model of Robertson and Yarwood³³ is quite similar to the Brownian oscillator model but does not include the dy-

namic Stokes shift. As in the exchange model and the semiclassical approaches, it is assumed in this model that the low-frequency motion is *not* affected by the excitation of the high-frequency mode (ZBR) and thus predicts a complete narrowing of the absorption line if the spectral diffusion becomes infinitely fast. However, this assumption is rather strange since in view of the coupling used in this model, the excitation of the high-frequency mode in fact should lead to a change in the equilibrium position of the damped harmonic low-frequency motion.

The Gauss-Markov, the exchange and the semiclassical models on one hand and the Brownian oscillator model on the other hand represent two extremes with respect to motional narrowing. In terms of the adiabatic quantum model, the former models represent systems for which the potentials E_1 and E_2 have different modulations but exactly the same overall shape. In contrast, the Brownian oscillator represents a system for which the modulation of the potentials is the same but the overall shape of the potential differs. It is clear that the adiabatic quantum model can reproduce both extreme cases but also the intermediate situation where an increase in the rate of spectral diffusion leads to a *partial* narrowing of the absorption line. In this case both the modulations and the overall shapes of the potentials E_1 and E_2 differ. Up to now motional narrowing and spectral diffusion have not been discussed in the context of the adiabatic quantum model. This is probably due to the fact that up to now this model has only been used in the specific case where the potentials of the low-frequency mode are displaced parabola without any modulation.^{29,30} For this specific choice of potentials there will be no motional-narrowing effect.

Linear absorption spectra in the condensed phase are often very broad and structureless and thus form a very poor probe for the microscopic dynamics. Fortunately, nonlinear optical techniques like spectral-hole burning and photon-echo spectroscopy give much more information on the microscopic dynamics since these techniques are far more sensitive to the differences in the time scales and spectral ranges of the spectral-diffusion and motional-narrowing processes. These techniques are also capable of distinguishing the motional-narrowing and spectral-diffusion effects. A great advantage of the adiabatic quantum model is that it provides an independent microscopic description of motional-narrowing and spectral-diffusion effects. Hence it is expected that especially for the modeling of these nonlinear experiments the adiabatic quantum model will have significant advantages over conventional approaches like the Gauss-Markov and the Brownian oscillator model.

V. CONCLUSIONS

We presented an adiabatic quantum description for the broadening of optical line shapes that results from the quasi-elastic interactions with lower frequency modes. In this model the microscopic origins of motional narrowing and spectral diffusion are different. Spectral diffusion results from the quantum interference of the wave function of the low-frequency mode. This quantum interference leads to a modulation of the optimum transition frequency without phase conservation for the polarization. Hence this process

does not contribute to the motional narrowing. Instead, the motional narrowing results from the delocalized character of the wave functions of the low-frequency mode. Due to this delocalization, the differences in the shape and modulation of the potentials that describe the low-frequency motion in the ground and excited state of the high-frequency mode are averaged out, which leads to a narrowing of the absorption line shape. It is shown that the calculation of the wave functions of the low-frequency mode presents a simple and straightforward method to account for motional narrowing effects, that can be used for all possible shapes of the potentials of the low-frequency mode.

In case the potentials have the same overall shape for the ground and excited state of the high-frequency mode, the adiabatic quantum model will give the same results as line-shape models in which it is assumed that the frequency fluctuations that lead to motional narrowing have exactly the same dynamics as the spectral diffusion of the optimum transition frequency. However, this assumption is only correct if the excitation of the high-frequency mode does not lead to a change in the overall shape of the potential that governs the low-frequency motion [assumption of zero back reaction (ZBR)]. In many spectroscopic studies the degree of excitation in the high-frequency mode will be low which makes it in fact quite likely that the excitation of the high-frequency mode leads to a change in the low-frequency motion, even if

the low-frequency mode itself behaves classically. Such a change can easily be accounted for in the adiabatic quantum model by using different potentials for the low-frequency motion in the ground and excited state of the high-frequency mode.

In conclusion, the adiabatic quantum model forms a quite general approach to the description of optical line shapes in the condensed phase. This model can reproduce the results of other line-shape models and in addition can account for situations in which an increase of the rate of spectral diffusion leads to a partial motional-narrowing effect. It is expected that the adiabatic quantum model will be of particular use in the modeling of nonlinear experiments that sensitively probe the different characteristics of motional narrowing and spectral diffusion.

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