

## Lorentzian line shape due to an inhomogeneous size distribution without relaxation

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In this paper, it is demonstrated that a Lorentzian line shape is predicted for a resonance interacting with a bath of equally spaced levels, even in the sparse, low density of states limit, if one performs an inhomogeneous average over the position of the bath states relative to the bright state. The implication for the spectroscopy of molecules in helium nanodroplets and possibly other samples with a significant size distribution is that coupling of excitations to phonons can lead to Lorentzian shaped transitions entirely from inhomogeneous broadening with no population relaxation in the sample. © 2007 American Institute of Physics. [DOI: 10.1063/1.2408416]

There is a long history of inferring aspects of intramolecular dynamics from the shape of spectroscopic transitions. In atomic and molecular physics, it is widely assumed that a Lorentzian line shape is evidence of “lifetime broadening” according to the Heisenberg uncertainty principle.<sup>1</sup> A Gaussian line shape is often taken as evidence of static inhomogeneous broadening, such as the classic case of Doppler broadening in a low pressure gas.<sup>1</sup> It is well established that one can have a purely homogeneous Gaussian line shape, such as in the transition from the ground state to a repulsive state that has an approximately equal energy slope over the Franck-Condon region.<sup>2</sup> Formally, the linear absorption spectrum can be calculated by the Fourier transform of the dipole correlation function<sup>3</sup> and as such only really gives information on the decay of the molecular coherence between the optically coupled states. This decay can occur because of homogeneous decoherence, an inhomogeneous spread of resonance frequency in the sample, or some combination of the two. When one considers cases with spectral diffusion, such that the dynamics sample different local environments or states responsible for inhomogeneous broadening, the distinction between homogeneous and inhomogeneous broadening breaks down and becomes rather meaningless when  $\Delta\omega\tau \sim 1$ .<sup>4</sup> ( $\Delta\omega$  is the spread of instantaneous transition frequencies sampled in a thermal system and  $\tau$  is a correlation time that characterizes the time required to “lose memory” of the initial value of the inhomogeneous state of the absorber.) When  $\Delta\omega\tau \ll 1$ , one has strong motional narrowing and typically a Lorentzian line shape whose width decreases (i.e., whose coherence time increases) as  $\tau$  is further reduced in size.<sup>4</sup> This case is usually classified as homogeneously broadened because each absorber is ergodically sampling the possible states or local environments and thus each is equivalent except for a time translation.

In this note, we would like to present a simple model for a mesoscopic system that leads to a prediction of a Lorentzian broadened line shape that arises from an inhomogeneous size distribution of the elements of the system. In order to make the discussion more concrete, we will present the model in the context of rovibrational absorption of a mol-

ecule in a helium nanodroplet. We believe that similar situations could naturally arise in other spectroscopic studies of nanoscale materials, where one can have a coupling to a discrete bath of phonon or electron excitations, but the size distribution in the same washes out the structure in that density of states. We note that inhomogeneously broadened Lorentzian line shapes are already known in other systems, such as the spectra of impurities in solids with dislocation defects and those of dilute ensembles of spins coupled by dipole-dipole interactions.<sup>5</sup> The present model is perhaps more widely applicable, at least in the spectroscopy of nanoscale objects, than these earlier models for which the Lorentzian line shape resulted from a particular functional form for the interactions of the optical dipole with its environment.

Consider a rotationally excited molecule, such as CO, in a helium nanodroplet. Because of the anisotropic solvation around the molecule, the rotating molecule will in principle couple to the phonon/roton elementary excitations of the helium and this could lead to the decay of the excited rotational state via phonon emission.<sup>6</sup> For a molecule imbedded in bulk helium, the phonons are continuous and one could use Fermi’s golden rule to calculate the rate of population decay of the excited rotational state due to phonon emission. In this case, the homogeneous absorption line shape will be Lorentzian with a half width at half maximum of  $\Delta E = \pi\rho(E)V(E)^2$ , where  $\rho(E)$  is the density of phonon states at the energy difference of the molecular relaxation and  $V(E)$  is the coupling matrix element of the excited molecule state with the state with the molecule deexcited and a phonon created. This is perfectly analogous to spontaneous emission of an atom or molecule, and it is well known that such an excited state decays exponentially with time constant  $\tau = \hbar/(2\Delta E)$ , i.e., the textbook example of lifetime broadening. If one considers a finite, but very large system, such that  $\Delta E\rho(E) \gg 1$  [or equivalently such that  $\rho(E)V(E) \gg 1$ ], then one will have a discrete spectrum, but as has been long known, the dynamics are essentially the same except for recurrences at long time.<sup>7,8</sup> As the size of the system is reduced, one passes through the intermediate case,  $\rho(E)V(E)$

$\approx 1$ , to the low density limit, defined by  $\rho(E)V(E) \ll 1$ . In the low density limit, almost always, one eigenstate of the system is completely dominated by the bright state and thus there is no homogeneous relaxation. In the unlikely case that a phonon happens to have the same energy as the molecular excitation [to within on the order of  $\approx V(E)$ ], one will have an isolated perturbation which will give an absorption spectrum consisting of only two transitions with a splitting of  $\geq V(E)$ . In the time domain, this implies that if we impulsively excite the molecule population of the excited state would oscillate in a two state quantum beat, again without relaxation. As we increase the size of the system (the droplet radius  $R$  in this case) we expect the density of coupled phonons to scale linearly with  $R$  (i.e., those of a fixed value or range of values of angular momentum). However, the amplitude of any phonon wave function decreases<sup>9</sup> as  $R^{-1/2}$  and thus also will the coupling matrix element  $V(E)$ , assuming it is dominated by local interactions, such as in the first solvation shell.<sup>10</sup> Thus  $\Delta E$  and thus  $\tau$  are expected to be independent of the size of the system *as long as one is in the large molecule limit*.

An attractive analytical model for studying the evolution through these cases is the Bixon-Jortner model<sup>11</sup> introduced to model nonradiative relaxation in an isolated molecule. One assumes that there is a unique “bright state” that contains all the absorption strengths in a given spectral region. This state is coupled to a bath of “dark states” which are assumed to be equally spaced with density  $\rho$  ( $\epsilon = 1/\rho$  is the level spacing) and that the bright state is coupled to all the dark states with constant matrix element  $V$ . The dark states have no direct interaction between them. Thus, the Hamiltonian matrix is diagonal except for one row and column, coupling the dark states to the single bright state. Since only the bright state has a nonzero transition moment from the ground state, the absorption intensity of any eigenstate of the system is proportional to the population of the bright state in that eigenstate. In the case we are considering, the bright state is the pure excitation of the molecule and the dark states are states where the molecule is deexcited (either partially or completely) and a phonon has been created. The change in molecular energy will include a change in kinetic energy due to the recoil momentum of the emitted phonon. The matrix element  $V$  arises from the anisotropic helium solvation density in the rotating frame of the molecule, which leads to the coupling of the rotation with the helium phonons. Zillich and Whaley have developed a method to estimate such coupling, based upon the use of bulk phonons for the solvated molecule and helium density near the molecule calculated using the diffusion Monte Carlo method,<sup>12</sup> and this was applied to the case of CO by von Häftten *et al.*<sup>6</sup>

The assumptions of a constant coupling matrix element and level spacing are questionable for the cases of intersystem crossing, internal conversion, and intramolecular vibrational relaxation for which the Bixon-Jortner model is widely used. However, these are likely reasonably good assumptions in the case of coupling of a rotational excitation to phonons in a helium droplet, at least as long as the phonon has energy below the roton energy and thus is located in the approximately linear region of the phonon dispersion curve. In that

case, the density per unit energy of phonons of fixed angular momentum is constant and neighboring dark states differ only slightly in their wave number. We take the energy of the bright state (before interaction with the dark states) to be  $E_b^0$  and the energy levels of the dark states as  $E_i^0 = E_b^0 - \alpha + i\epsilon$ ,  $i = 0, \pm 1, \pm 2, \dots$ . By this choice of index  $i$ ,  $\alpha$  is defined to be in the domain  $[-1/2, 1/2]\epsilon$ . Bixon and Jortner showed that this problem has an analytical solution if we allow the range of  $i$  to extend to  $\pm\infty$ . We will now recap this derivation.

With the above assumptions, the Hamiltonian matrix has a bright state diagonal element  $E_b^0$  with off-diagonal matrix elements  $V$  on the row and column intersecting with the diagonal element. All other off-diagonal elements (between dark states) are zero. The diagonal elements corresponding to the dark states are  $E_i^0$ . It is easily shown that  $E_n$  will be an eigenvalue of this matrix if it satisfies the following equation:

$$E_b^0 - E_n + V^2 \sum_i (E_n - E_i^0)^{-1} = 0. \quad (1)$$

Using the abbreviation  $\gamma_n = (E_n - E_b^0 + \alpha)\rho$ , the sum in the eigenvalue equation can be written as

$$\sum_i (E_n - E_i^0)^{-1} = \rho \sum_i (\gamma_n - i)^{-1} = \pi \rho \cot(\pi \gamma_n). \quad (2)$$

The last equation uses the assumption that  $i$  extend to  $\pm\infty$ .<sup>13</sup> (The Bixon-Jortner paper had a sign error in front of this sum, as easily established by numerically checking the sum.) Substituting this into Eq. (1) and substituting for  $\gamma_n$ , we get

$$E_b^0 - E_n + (\pi \rho V^2) \cot(\pi \rho (E_n - E_b^0 + \alpha)) = 0. \quad (3)$$

There is one solution for this equation between every pair of bath level and thus the density of eigenstates is the same as that of the bath. Each eigenstate shares in the population of the bright state by a fraction,

$$b_n(E_n)^2 = V^2 [(E_n - E_b^0)^2 + V^2 + (-\pi \rho V^2)^2]^{-1}. \quad (4)$$

This has a Lorentzian line shape, but with a width,  $\sqrt{V^2 + (\pi \rho V^2)^2}$ , that is wider than the golden rule width,  $\pi \rho V^2$ , increasingly so as one passes to the low density of states limit  $\rho V \ll 1$ . For fixed  $\alpha$  the spectrum is a series of sharp lines whose intensities follow this Lorentzian envelope.

We will now assume that we have an inhomogeneous distribution of the position of the dark states relative to the bright state, i.e., we have a distribution of values of  $\alpha$  such that all allowed values of  $\alpha$  are equally likely. This is to model the effect of the excitation energy of phonons shifting, with droplet size, through resonance with the deexcitation energy from the bright state. To calculate the expected average absorption at an energy  $E$ , we need to multiply the above  $b_n(E)^2$  by the probability of having an eigenvalue,  $E_n$ , at energy  $E$ . This probability density is  $P_E(E) = P_\alpha(\alpha) |d\alpha/dE_n|_E$ . The latter is easily calculated from differentiation of Eq. (3) with respect to  $E_n$ , holding  $\rho$ ,  $V$ , and  $E_b^0$  constant. This gives the result

$$\frac{d\alpha}{dE_n} = - \frac{V^2 + (\pi\rho V^2)^2 + (E_n - E_b^0)^2}{(\pi\rho V^2)^2 + (E_n - E_b^0)^2}. \quad (5)$$

We now used the assumption of a uniform distribution of  $\alpha$ , i.e.,  $P_\alpha(\alpha) = \rho$  on the interval  $[-\epsilon/2, \epsilon/2]$ . The inhomogeneous absorption profile is obtained by averaging the spectrum for each  $\alpha$ ,  $\sum_n \delta(E - E_n) b_n^2(E_n)$ , over  $\alpha$  with weight  $P_\alpha(\alpha)$ ,

$$\begin{aligned} I(E) &= \int_{-\epsilon/2}^{\epsilon/2} d\alpha P_\alpha(\alpha) \sum_n \delta(E - E_n) b_n^2(E_n) \\ &= \sum_n \int_{E_n^{(l)}}^{E_n^{(u)}} dE_n \frac{d\alpha}{dE_n} \rho \delta(E - E_n) b_n^2(E_n) \\ &= \left. \frac{d\alpha}{dE_n} \right|_E \rho b_n^2(E), \end{aligned} \quad (6)$$

where we used the fact that there is exactly one solution,  $E_n$ , between the integration bounds  $E_n^{(l)}$  and  $E_n^{(u)}$ . Using Eqs. (4) and (5) we get

$$I(E) = \frac{\rho V^2}{(E - E_b^0)^2 + (\pi\rho V^2)^2}. \quad (7)$$

This is exactly the same Lorentzian line shape as for the large system, high density of state limit, i.e., the expected line shape is expected to be independent of  $\rho(E)$  not only in the high density limit but through the entire range of density of states if one has a sufficiently large inhomogeneous size broadening to allow equal sampling of all values of the registration of the phonons with the deexcitation energy of the resonant state that is being relaxed.

The assumption of a broad distribution of droplet sizes of radii  $R$  can be expected to lead to a broad distribution of  $\rho$ , assumed constant above, because  $\rho \propto R$ . The Bixon-Jortner model assumes that the lowest energy dark state of energy  $E_i^0$  is far below the energy of the bright state,  $E_b^0$ , and then takes the limit of infinitely many levels of energies  $E_i^0$ ,  $i = 0, \pm 1, \pm 2, \dots$ , below and above  $E_b^0$ . If we take  $-M$  to be the index of the lowest energy dark state, the use of the Bixon-Jortner model implies  $M \gg 1$ . Thus, a small fractional change (on the order of  $1/M$ ) in the droplet size, and thus density of phonons, will lead to a sampling of the full range of the cyclic function  $\alpha$ . We can thus separate the inhomogeneous size distribution into sections, each having one droplet size for each allowed value of  $\alpha$ . Given the scaling discussed above, we expect  $\rho V^2$  to be approximately constant for each of these sections of the inhomogeneous distribution, and thus, in the limit  $M \gg 1$ , that each section of the inhomogeneous distribution will produce the same Lorentzian line shape. Thus, the above analysis should provide at least a fair approximation except perhaps if the bright state is in resonance with one of the very lowest energy phonons. Zillich and Whaley<sup>14</sup> have extended their earlier calculations<sup>6</sup> for the interaction of CO in  $J=1$  in helium to include finite size effects by replacing the integral over bulk phonons by a discrete sum over phonon wave numbers allowed in the liquid

droplet model. The resulting spectrum was then averaged over a droplet size distribution, and a Lorentzian line shape was predicted.

Thus, we reach the perhaps paradoxical conclusion that the prediction of a Lorentzian line shape based upon a golden rule calculation of the rate of population relaxation by coupling to a continuum of excitations (e.g., phonons) can, at least in some cases, correctly predict the observed line shape (including width) even when the density of the states of the system is far too low for the golden rule calculation to be valid. This may be the case for the  $R(0)$  transition of CO in helium nanodroplets,<sup>6</sup> where an observed Lorentzian line shape for the  $R(0)$  transition was interpreted as due to population decay of the  $J=1$  CO level by phonon emission. Other examples can be cited, of which one is the study of C-H stretching spectrum of various isotopic forms of acetylene by Nauta and Miller,<sup>15</sup> where the observation of Lorentzian line shapes was taken as an "indication that lifetime effects dominate the overall shape and width of the transitions."

However, though the Lorentzian line shape is insensitive to the density of phonon states, i.e., the mean size of the system, the physical meaning of that broadening is completely different in the large and sparse molecule limits. In the former, we have exponential population decay of the excited state population with lifetime as predicted by the uncertainty relation. In the latter, we have no population decay. The spectral line shape arises entirely of inhomogeneous broadening due to distribution of cluster sizes which leads to a distribution of shifts of the molecular excited state by usually off-resonance coupling to discrete phonon states. However, if the phonon states are dense enough, the size dependence will not be evident by changes in the size distribution unless it becomes sufficiently narrow that the assumption of an equal distribution of the phonon detuning,  $\alpha$  breaks down. It is almost like the molecule, though frustrated from relaxation by the finite level density, still presents the bulk limit in its spectrum as long as there is an inhomogeneous distribution of levels to do so.

Experimentally, it should be possible to determine whether the excited state does or does not relax if one has sufficient laser intensity to induce at least a partial saturation of the signal. Two color double resonance experiments would be the most powerful. Continuous wave IR/IR double resonance experiments, such as have recently been developed by Merritt *et al.*,<sup>16</sup> could be used and the observation of a "Bennet hole" would be an unambiguous evidence that the line shape was inhomogeneous. More powerful yet would be time resolved pump/probe experiments that would allow the population in a particular rovibrational level in helium to be followed in time. Such measurements would be largely immune from complications of spectral diffusion that plagued some earlier continuous wave double resonance experiments in helium<sup>17-19</sup> and should directly give the population relaxation times of the states probed and possibly the relaxation pathways if intermediate states could be probed. A perhaps simpler experimental method, though more limited, is to measure the one color signal strength versus intensity to determine the saturation curve. The shape of the saturation curve is qualitatively different for the homogeneous and in-

homogeneous linewidth cases,<sup>1</sup> which has already been used to establish that line shapes of some transitions of HCN (Refs. 20 and 21) and HCCCN (Ref. 17) in helium nanodroplets are inhomogeneously broadened. Given a knowledge of the IR transition strength (which should be weakly perturbed by the helium) and experimental conditions, the saturation intensity<sup>1</sup> could be used to determine the product of  $T_1 T_2$  for the transition, which should equal to  $(2\pi^2 \Delta\nu^2)^{-1}$  for a homogeneous Lorentzian line shape with full width at half maximum of  $\Delta\nu$ .

We believe that the present result should be a warning that interpretation of Lorentzian line shapes as implying population relaxation is particularly hazardous in the case of spectroscopy on mesoscopic systems with the possibility of essentially continuous inhomogeneous size distributions. In the case of the rovibrational spectroscopy of molecules in helium nanodroplets, there have been several such assignments of population relaxation times based upon observed Lorentzian line shapes, and the present results call such interpretations into question unless they are supported by additional evidence.

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<sup>8</sup>The overlap of the time evolving wave function,  $\psi(t)$ , with its initial value  $\psi(0)$  is given by  $\sum_n |b_n|^2 \exp(iE_n t/\hbar)$ , where  $b_n$  is the overlap of  $\psi(0)$  with the  $n$ th energy eigenstate. If one has evenly spaced levels, it is easily shown that there are exact recurrence, i.e.,  $|\langle \psi(t) | \psi(0) \rangle|^2 = 1$ , at times that are multiples of  $h\rho(E)$ , where  $\rho(E)$  is the density of states. For a harmonic oscillator, this is just the classical period. For the Bixon-Jortner model in the large molecule limit, to be discussed below, the levels are almost equally spaced and thus there is a strong recurrence at this same time.

<sup>9</sup>In the liquid drop model (Ref. 22), a phonon with wave number  $k$  has amplitude  $A(R)j_l(kr)$ , where  $R$  is the droplet radius. Since  $j_l(kr) \sim r^{-1} \sin(kr - l\pi/2)$  for large  $r$  (Ref. 23), it is clear that the normalization integral of  $A(R)^2 \int_0^R j_l^2(kr) r^2 dr \sim A(R)^2 R$ . Therefore the normalization and thus amplitude at fixed  $r, k$  of the phonon mode is proportional to  $R^{-1/2}$ .

<sup>10</sup>As discussed by Zillich *et al.* (Ref. 24), the coupling of the molecular rotation and the phonons arises from the anisotropic helium density that rotates with the molecule, which acts as a time dependent drive of the phonons. This anisotropy is localized near the molecule since far from the molecule the helium assumes the bulk value.

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