Quantum molecular dynamics study of the pressure dependence of the ammonia inversion transition

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The mechanism of the shift, broadening, and quenching of the ammonia inversion frequency with gas pressure has been a problem of lively interest for over 70 years. A simple quantum model of the ammonia molecule perturbed by collisions with ideal gas molecules displays the essential features of the experimental data for NH_3 and for ND_3. The model does not display the behavior expected from theories of environmental decoherence. On the other hand, models of perturbed classical oscillators do display behavior similar to our model and to experimental data. The quenching of the ammonia inversion transition cannot therefore be interpreted as spatial localization of the wave function.

INTRODUCTION

In chemistry, molecules have structures that can be described classically in terms of the spatial localization of the atoms. This is clearest in the case of enantiomorphic molecules which may be separated into *dextro* and *laevo* forms. In contrast, in quantum mechanics, the ground states of molecules are eigenstates of energy which are, in general, superpositions of spatially defined states [1]. How the chemical molecular states arise is an example, and perhaps the most acute example, of the problem of the emergence of the classical world from quantum theory, or the problem of measurement. While there is no rigorous explanation of this emergence, so that it is still best expressed without explanation by von Neumann's measurement or collapse axiom, decoherence mechanisms are perhaps the most popular of putative explanations of the appearance of classical behavior (for reviews see Refs. [2–4]). Be that as it may, any explicit model of measurement, collapse, or the emergence of the classical world requires testing. The ammonia molecule is often used for this, as it is light enough to display the *inversion transition* between the quantum ground and first excited states at low pressure, while at higher pressures the inversion transition broadens, shifts to lower frequency, and then quenches (the frequency goes to zero). This quenching might be considered as a direct observation of quantum decoherence or even quantum localization due to interaction with the environment [2–4]. In this paper, we show that interaction with the environment quenches the inversion transition for what might be described as "classical" reasons. The broadening, shift, and quenching of the inversion transition are simply consequences of impacts and may be described within the framework of a classical oscillator subject to noise from the environment. There is no evidence for localization onto spatial eigenstates.

Since the early days of microwave spectroscopy, the inversion transition of the ammonia molecules NH_3 and ND_3 has been extensively studied experimentally and theoretically. The ammonia molecule has two spatial eigenstates $|L\rangle$

and $|R\rangle$ with the nitrogen atom on one side or the other of the plane of hydrogen atoms, and its energy ground and first excited states $|0\rangle$ and $|1\rangle$ are the symmetric and antisymmetric quantum superpositions of the spatial eigenstates (ignoring rotational and vibrational states). The ammonia maser is based upon the transition between the energy eigenstates, which may also be described as the Rabi oscillation between the spatial eigenstates and which is a quantum phenomenon with no classical analog.

BACKGROUND

At low pressures in the gas phase, the transition between the energy eigenstates is observed near 24 GHz (0.8 cm^{-1}) in NH_3 [5]. In ND_3 [6] the transition is near 1.6 GHz (0.053 cm^{-1}). In NH_3, broadening is observed at pressures above a few mm of mercury, with a shift to lower frequency, and quenching is complete at about 1.7 bar. In ND_3, pressures about 15 times lower yield the same effects, in proportion to the inversion transition frequency.

The first explanation of the shift and broadening of the ammonia inversion transition frequency was given by Anderson [7] in terms of perturbation by the electric dipole-dipole interaction between ammonia molecules. Anderson's discussion was only qualitative. Margenau investigated the quantum states of two ammonia molecules coupled by their dipole-dipole interaction in more detail [8]. He showed that the interaction leads to the splitting of the transition into a higher frequency component with reduced strength and a lower frequency with increased strength. While this accounts for the initial shift to lower frequency, it fails to account for the quenching of the inversion transition at a higher pressure. More recently, the existence of a phase transition to a superposition of localized states has been suggested using a dipole-dipole interaction model treated by a quantum mean-field approximation as well as the coupling to a radiation field. This model also yields a frequency shift and quenching in the limiting case of infinitely many photons of the radiation field, at pressures for NH_3 and ND_3 in good agreement with experiment [9,10]. Further work shows the existence of stable localized states when dissipation is included [11–13].

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The standard theory of line-broadening by impact is given by Van Vleck and Weisskopf [14]. It predicts a line-shape function

$$f(\nu) = \frac{1}{1 + b^{-2}(\nu - \nu_0)^2} + \frac{1}{1 + b^{-2}(\nu + \nu_0)^2}, \quad (1)$$

where the width b is given by $1/2\pi\tau$ for strong impacts occurring at a mean interval of τ, and therefore proportional to the pressure. The theory does not predict any peak shift: ν_0 is a constant, the natural frequency of the oscillator. Anderson developed the theory further and obtained a shift of ν_0 to lower frequency equal to the width b [15]. Fano recast the problem of pressure broadening in the Liouville representation and obtained a shift to lower frequency independent of the broadening [16]. Ben-Reuven used the Fano theory to show that the ammonia spectra can be well-fitted with a related expression but with three independent parameters proportional to the pressure. Two of them express the effects of elastic collisions on the width and on the frequency shift as in Eq. (1), and the third parameter expresses the effect of inelastic collisions [17].

We are interested in a dynamical theory of the transition and of quenching and localization. It is important to know if the dipole-dipole interaction of ammonia molecules is crucial to the quenching, or if it merely influences the collision cross section. In a dynamical model, one might also hope to observe decoherence or localization. Accordingly, we have set up a molecular dynamics simulation in which the quantum nature of the ammonia molecule is explicitly taken into account. We find that the model accounts for the shift, broadening, and quenching of the inversions transition purely in terms of perturbation by collision with ambient gas molecules, without any quantum localization.

AMMONIA QUANTUM MOLECULAR DYNAMICS MODEL

We model the problem in one dimension. The model is described in more detail in Ref. [18]. The ammonia molecule is represented by a double-well potential, with the two time-dependent spatial wave functions Ψ_L and Ψ_R. With a weak coupling between the wells the Hamiltonian in the spatial basis is

$$\mathbf{H} = \begin{pmatrix} \omega_0 & \frac{1}{2}\omega_1 \\ \frac{1}{2}\omega_1 & \omega_0 \end{pmatrix}. \quad (2)$$

Diagonalizing the Hamiltonian, the ground and first excited states of the system are found to be Ψ_0 and Ψ_1 with a frequency splitting of ω_1. The general state of the system is a superposition, with

$$\Psi = a\Psi_0 + b\Psi_1,$$

$$|a|^2 + |b|^2 = 1. \quad (3)$$

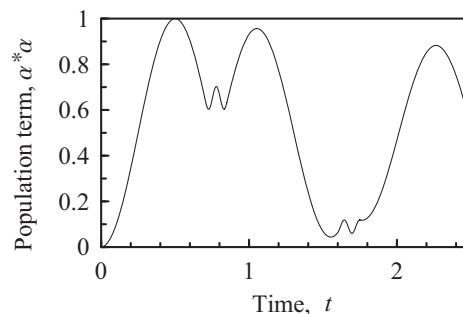Expanding this in the spatial basis set Ψ_L and Ψ_R, we have time-varying coefficients,

FIG. 1. The evolution of the occupancy of the left-hand well is shown with two perturbations occurring at $t=0.7$ and 1.6. The units of time are chosen so that the Rabi angular frequency ω_1 is 2π. The perturbation is $\omega_P=60$. The initial wave function is given by $a=b=1/\sqrt{2}$; after the two perturbations the values are $a=0.54-0.73i$, and $b=0.36+0.22i$.

$$\Psi = \alpha(t)\Psi_L + \beta(t)\Psi_R \quad (4)$$

so that the amplitude of the wave function beats or oscillates between the two wells. The squared amplitude $|\alpha(t)|^2 = \alpha\alpha^*$ oscillates at the frequency ω_1 and with a beat amplitude that depends on the initial values of a and b, from zero for, e.g., $a=1$, $b=0$ to a maximum amplitude of unity for, e.g., $a=b=1/\sqrt{2}$. This oscillation is the inversion transition or Rabi oscillation of the molecule.

We model impacts, or interactions with the environment, by a term which is diagonal in the spatial representation. That is, we suppose that the double well is tilted during an impact. If a gas atom coming in from the left raises the energy of the left-hand well, the Hamiltonian during impact is

$$\mathbf{H}' = \begin{pmatrix} \omega_0 + \omega_P & \frac{1}{2}\omega_1 \\ \frac{1}{2}\omega_1 & \omega_0 \end{pmatrix}. \quad (5)$$

Diagonalizing and expanding in the spatial basis set as before, we obtain the normalized eigenvectors $\mathbf{u}$ and $\mathbf{v}$ of $\mathbf{H}'$. Equations (3) and (4) become

$$\Psi' = a_P\Psi'_0 + b_P\Psi'_1 = \alpha'(t)\Psi_L + \beta'(t)\Psi_R. \quad (6)$$

The Rabi oscillation is now at a much higher frequency and a much smaller amplitude (for $\omega_P \gg \omega_1$). In reality, the perturbation rises and falls continuously in an impact, but we approximate with a top-hat function, so that ω_P is switched on at a time t_0 and switched off again at t_1. At these times, we match the coefficients in the spatial basis, using $\alpha'(t_0) = \alpha(t_0)$ and $\beta'(t_0) = \beta(t_0)$ to solve for a_P and b_P at the onset of the perturbation, and then the new $\alpha(t_1) = \alpha'(t_1)$, $\beta(t_1) = \beta'(t_1)$ to solve for the new a and b at the end of the perturbation. These boundary conditions ensure that the amplitude and phase of the wave function in each well do not change discontinuously at the beginning and end of the perturbation. The resulting time evolution of the occupancy or population term $\alpha\alpha^*$ is illustrated in Fig. 1.

To model NH_3 and ND_3, we can choose the units of time so that the Rabi frequency is unity ($\omega_1 = 2\pi$). The strength of the perturbation is of the order of k_BT, which at room tem-
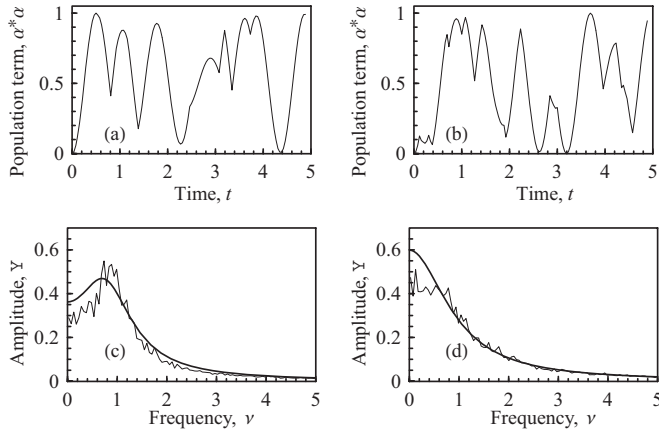
FIG. 2. The occupation of the left-hand well, $y(t) = \alpha^* \alpha$, is plotted against time as in Fig. 1, with the NH_3 parameters, for (a) $p = 3.5$ impacts per cycle, below the quenching, and (b) $p = 7.5$ impacts per cycle, above the quenching. The Fourier transforms $Y(\nu)$ are shown in (c) and (d), respectively, together with the fits using Eq. (1).
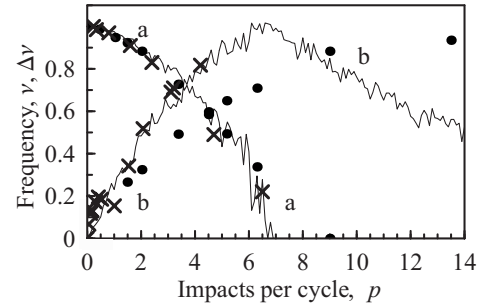

FIG. 3. The solid curves show (a-a) the peak frequency and (b-b) the broadening for NH_3 as a function of the number of impacts per cycle as described in the text. The data points show (a-a) the peak frequency and (b-b) the broadening reported by Bleaney and Loubser [19] for NH_3 (solid circles), and (a-a) the peak frequency and (b-b) the broadening reported by Birnbaum and Maryott [6] for ND_3 (crosses) with both data sets scaled as described in the text.

perature is 208 cm^{-1}. For NH_3, therefore, we take $\omega_P = 208\omega_1/0.8 = 260\omega_1$ and for ND_3, $\omega_P = 208\omega_1/0.0.053 = 3925\omega_1$. The duration $\Delta t = t_0 - t_1$ of an impact is hard to estimate. However, inspection of Fig. 1 shows that to achieve a strong impact (in the sense of Van Vleck and Weisskopf [14]), we need something of the order of one cycle of the perturbed Rabi oscillation, i.e., $\omega_P \Delta t \sim 2\pi$, while larger values will have no extra effect. We therefore take values of Δt from a random distribution over the range 0 to $2\pi/\omega_P$. The average frequency of impacts corresponds to the gas pressure. We require an impact cross section to relate the frequency of impacts to the gas pressure quantitatively. Bleaney and Loubser [19] and other authors obtain impact cross sections from the pressure-broadening of the transition, assuming strong impacts and using $b = 1/2\pi\tau$. We shall see below that such estimates are unreliable, and therefore in our simulation we use the measure p impacts per Rabi cycle instead of pressure, and we vary p over a wide range.

We calculate the values of $\alpha^* \alpha$ at discrete time intervals δt with $\Delta t < \delta t \ll 1$. At each time interval we have a probability $\delta t / \tau$ of having an impact, so that there are $p = 1/\tau$ impacts per cycle. If there is an impact, we use $\alpha'(t_0) = \alpha(t_0)$ and $\beta'(t_0) = \beta(t_0)$ to solve for a_P and b_P at the onset of the perturbation, and then calculate the new $\alpha(t_1) = \alpha'(t_1)$, $\beta(t_1) = \beta'(t_1)$ to solve for the new a and b at the end of the perturbation. Then the calculation of the list of values is resumed. Examples are shown in Fig. 2 for medium (a) and high (b) values of p. The numerical Fourier transforms of the lists are calculated, shown in Figs. 2(c) and 2(d), and fitted with $Af(\nu)$ of Eq. (1), with b, ν_0, and amplitude A as fitting parameters. Our interest here is in the fitted values of b and ν_0 as functions of p. In Fig. 3 these are compared with the experimental data for NH_3 [19] and ND_3 [6] with the constant of proportionality between p and pressure (corresponding to the impact cross section) as a free parameter.

The NH_3 data is plotted using the conversion factor of a pressure $P = 1$ bar being equivalent to $p = 4.5$ impacts per cycle. For ND_3, the data fits equally well but with $p = 4.5$

equivalent to the pressure $P = 1/15$ bar, consistent with the 15 times lower inversion frequency in ND_3 given the same impact parameter. In both cases, full quenching is observed at about 6.5 impacts per cycle. The model presented here accounts remarkably well for the shift and quenching of the ammonia inversion transition peak. It accounts less well for the broadening, which occurs initially at the rate $b \sim 0.25p$ in the simulation and in the ND_3 data while the broadening occurs only at $b \sim 0.18p$ in the NH_3 experimental data. Above the quenching pressure the NH_3 experimental broadening continues to increase while the model broadening decreases. To gain a better understanding of this behavior, we investigate how a simple classical oscillator behaves under similar perturbations.

CLASSICAL PERTURBED HARMONIC OSCILLATOR

A classical oscillator may be perturbed by collision in a large variety of well-defined ways. We evaluate two perturbations here. We calculate the values of a sinusoid of frequency $\nu = 1$ at discrete time intervals $\delta t \ll 1$. At each time interval we have a probability $\delta t / \tau$ of having an impact, so that there are $p = 1/\tau$ impacts per cycle. If there is an impact, the sinusoid is modified accordingly, and then the calculation of the list of values is resumed. The numerical Fourier transform is calculated and we find that $Af(\nu)$ of Eq. (1) fits well for a variety of definitions of the impacts, over a very wide range of p, with b, ν_0, and A as fitting parameters. Our interest here is in the fitted values of b and ν_0 as functions of p.

The strongest perturbation possible (in the sense of Van Vleck and Weisskopf [14]) is a collision that destroys all memory of position and speed (or amplitude and phase). To model this, at impact we pick the new amplitude A of the sinusoid $A \cos(2\pi\nu t + \varphi)$ at random from the range 0 to 1 and the new phase φ at random from the range 0 to 2π. In this model, the peak is shifted to *higher* frequency, shown in Fig. 4(a), before decreasing again. Then quenching occurs, i.e., the frequency collapses to zero. The width continues to increase at still higher values of p, Fig. 4(c). This is a stronger
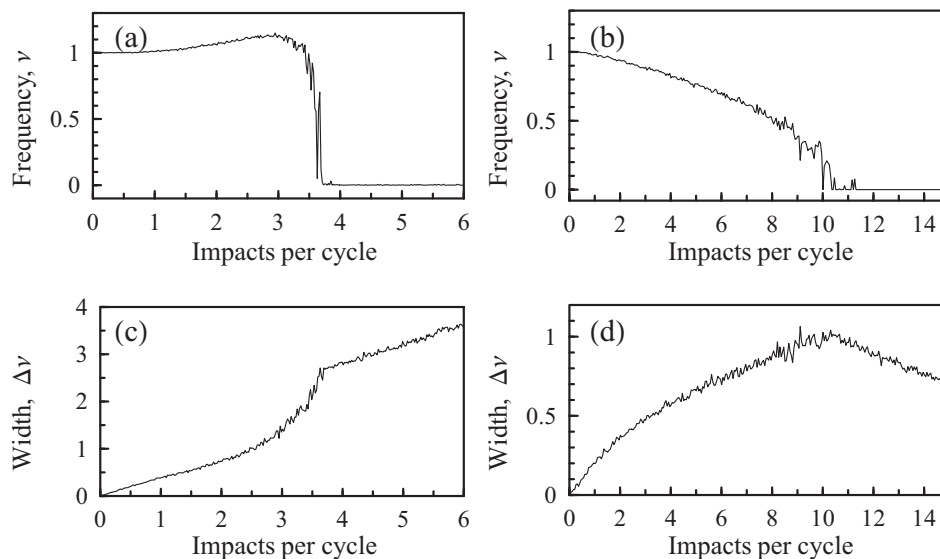
FIG. 4. The peak frequency and the peak width are plotted for the broken sinusoids with unity frequency as described in the text. In (a) the peak frequency is shown for the strongest possible impact, with phase and amplitude completely randomized by the impact. In (b) the peak frequency is shown for the weaker impact in which the boundary condition at impact keeps the sinusoid continuous but changes the phase and amplitude at random within that constraint. The corresponding peak widths are shown in (c) and (d), respectively

impact than the impacts on the ammonia molecule, for the quenching occurs at $p = 3.5$ impacts per cycle and the initial slope of the broadening is given by $b \sim 0.5p$. It is interesting to compare with the broadening assumed by Van Vleck and Weisskopf for strong impacts of $b = 1/2\pi\tau$, equivalent to b $= 0.16p$.

In an alternative definition of impact which is in closer accordance with the ammonia model and Fig. 1, we define the impact at t_0 by taking the position $x(t_0)$ as unchanged by the impact, the new amplitude A as random in the range $x(t_0)$ to 1, and the new phase φ such that the speed $\dot{x}(t_0)$ is a random variable in the range consistent with the new amplitude. In this model, the peak shift in Fig. 4(b) and width in Fig. 4(d) behave in very much the same way as the ammonia results of Fig. 3, with the initial broadening $b \sim 0.2p$. However, the impact is weaker than in the ammonia model, for quenching occurs at $p = 10.5$ impacts per cycle. Above quenching, b decreases again.

RESULTS AND DISCUSSION

Figure 4 shows that the details of the peak shift and the broadening are very sensitive to the exact nature of the boundary conditions between the periods of unperturbed free oscillation. A more complete description of the impact (including, for example, inelastic collisions as in Ben-Reuven [17]) might well account for the discrepancies between data and model in Fig. 3. However, we do not know of any way to predict the initial slope of $b(p)$, nor its functional form below and above the quenching, from a specification of the boundary conditions. Neither the mathematics of the noisy oscillator (see, e.g., the book by Gittenberg [20]) nor of the classical kicked rotor appear to answer this question.

The key result is that the ammonia model (Fig. 3) and even the broken sinusoid of Fig. 4(c) both show the Rabi

oscillation frequency shifting to lower frequency, broadening, and quenching—going to zero frequency—as the impact rate is increased, in agreement with experiment. Although the model is only one-dimensional, the generality of the behavior seen in Fig. 4 implies that a more complete three-dimensional model would behave in the same way. It is important to note that the state vector shows no evidence of localization. In Fig. 5 we plot the time-dependence of a diagonal and an off-diagonal element of the single-molecule
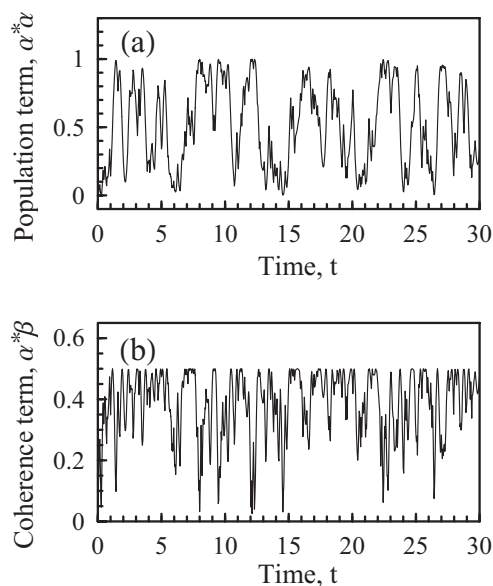

FIG. 5. Two elements of the NH_3 single-molecule density matrix calculated as for Fig. 2 are plotted against time under a high impact rate $p = 12$, well above the quenching impact rate. In (a), the diagonal term, $\alpha^* \alpha$, varies randomly between 0 and 1. In (b), the off-diagonal element $\alpha^* \beta$ varies randomly between 0 and 0.5.

density matrix for our model for an impact rate well above quenching. The decoherence program predicts that the off-diagonal elements of the density matrix will decay or relax to zero. We do not observe that in Fig. 5(b). Of course, the decoherence program describes an ensemble of possible evolutions, and the vanishing of the diagonal elements is the result of an averaging over those possible histories. In our model such an averaging would always yield zero and it is not clear what events would be required to set up a nonzero average. Then the question of what would bring about the vanishing of the off-diagonal terms is therefore left open. Quantum state diffusion [21] predicts that the state vector will diffuse to one or the other of the spatial eigenstates because the interaction with the environment here depends on the spatial configuration of the ammonia molecule. This predicts that either $\alpha^*\alpha$ or $\beta^*\beta$ will tend towards unity while

the other elements of the single-molecule density matrix should tend to zero. We do not observe that in either Figs. 5(a) and 5(b). It remains open what changes to the model would induce this.

We have presented a dynamical model describing the evolution of an individual wave function according to standard quantum mechanics. It shows that the ammonia shift and quenching are fully accounted for in terms of a perturbed oscillator, and should not therefore be cited as an experimental observation of either decoherence or quantum localization.

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