Chaos and incoherence in a model of multiple-photon excitation of molecular vibrations

Jay R. Ackerhalt and P. W. Milonni
Theoretical Division, Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545
(Received 11 March 1986)

We consider in detail our earlier classical model of multiple-photon excitation of molecular vibrations in an infrared laser field, wherein the observed fluence dependence of the process is associated with chaotic variations of a pumped mode. We focus our attention first on a quasicontinuum model of background vibrational modes, which provides us with a dynamical system in which the role of chaos is neatly interpretable. Then we consider a model with only a finite number of background modes in order to corroborate the conclusions drawn from the quasicontinuum model.

I. INTRODUCTION

Recently a number of papers have dealt with problems of energy deposition in driven, classically chaotic systems. An early example is the work of Casati *et al.*[1] in which the energy of a periodically kicked pendulum was found to grow, on average, linearly with time. Another interesting example was provided even earlier by Leopold and Percival,[2] who considered a classical model of a hydrogen atom in a sinusoidal electric field. Further work on this model was recently described by van Leeuwen *et al.*[3], who report excellent agreement between the classical computations and the experimental results of Bayfield and Pinnaduwage[4] on the microwave ionization of highly excited hydrogen atoms.

Earlier we described a classical model for the multiple-photon excitation (MPE) of molecular vibrations by an infrared laser field.[5] The dynamics of this model were found to be chaotic, with the consequence that the MPE process was predicted to be fluence dependent rather than intensity dependent. In particular, the energy absorbed from the field was found to grow, on average, linearly with time. Thus the model provides an interesting paradigm for two important aspects of MPE that have been observed for some time. (1) It is surprisingly easy to dissociate polyatomic molecules, in spite of the possibility of bottlenecking due to a mismatch between the field frequency and allowed transition frequencies as the excitation proceeds up the vibrational ladder. Such dissociation in laser fields of modest power was first observed in experiments of Isenor and Richardson in 1971 (Ref. 6), and raised the possibility of laser-controlled isotope separation. (2) The MPE process depends strongly on the fluence of the applied field, i.e., the total energy in a laser pulse, but not on the detailed variations of intensity within the pulse. This trend towards fluence dependence was recently corroborated in the experiments of Simpson *et al.*,[7] who found increasingly strong fluence dependence as the number of atoms increased in the molecules they studied.

In this paper we describe in detail our earlier MPE model, and report results of extended computations on the model and modifications thereof. We show that the role of chaos in these classical models is to give rise to "incoherence" in the sense of fluence-dependent excitation. Although these classical models provide a rather attractive interpretation of fluence-dependent MPE in large polyatomic molecules, the question, of course, arises as to their range of validity. Bloembergen[8] and Lamb[9] have advocated classical approaches to certain important aspects of MPE, but we feel that the question of the validity of the classical theory in this context is still not entirely resolved. We discuss this point in the final section of this paper.

II. THE QUASICONTINUUM MODEL

We assume that only one vibrational mode of a molecule interacts strongly with an applied laser field, and neglect interactions of any other "background" modes with the field. The background modes, which can exchange energy with the laser-pumped mode, are furthermore assumed to be harmonic. In the specific case of the SF_6 molecule, for instance, there are two infrared-active normal modes (ν_3 and ν_4) with a rather large frequency separation (about 300 cm^{-1}), so that a laser can interact selectively with one of the modes. In particular, the $\nu_3(\nu_2+\nu_6)$ mode lies near 10 μm and has been studied extensively with CO_2-laser radiation.[10] The nearest background mode to ν_3 has a small anharmonicity compared with that of ν_3, thus providing some justification for the treatment of the background modes as harmonic oscillators. Our idealized model for the MPE dynamics is then based on the following Hamiltonian:

$$\hat{H}=\Delta\hat{a}^{\dagger}\hat{a}-\chi(\hat{a}^{\dagger}\hat{a})^2+\Omega(\hat{a}+\hat{a}^{\dagger})+\sum_m(\Delta+\varepsilon_m)\hat{b}^{\dagger}_m\hat{b}_m + \sum_m\beta_m(\hat{a}^{\dagger}\hat{b}_m+\hat{b}^{\dagger}_m\hat{a}) , \tag{2.1}$$

in units in which $\hbar=1$. Here $\hat{a}$ and $\hat{b}_m$ are, respectively, the annihilation operators for the pumped mode and the mth background mode. Δ is the detuning of the laser from the pumped mode, and ε_m is the frequency of background mode m as measured from the pumped mode. χ is the anharmonicity of the pumped mode, corresponding to about 2 cm^{-1} in SF_6. Ω is the Rabi frequency associat-

ed with the applied field, which is treated as a prescribed, classical monochromatic field. The last term in the Hamiltonian (2.1) describes one-quantum vibrational energy exchanges between the pumped and background modes. For simplicity we ignore interactions among the background modes.

The Heisenberg equations of motion following from the Hamiltonian (2.1) are

$$\dot{\hat{a}} = -i(\Delta - \chi)\hat{a} + 2i\chi \hat{a}^\dagger \hat{a}\,\hat{a} - i\Omega - i\sum_m \beta_m \hat{b}_m \ , \quad (2.2)$$

$$\dot{\hat{b}}_m = -i(\Delta + \varepsilon_m)\hat{b}_m - i\beta \hat{a} \ . \quad (2.3)$$

The rate at which the molecule absorbs energy from the field is determined by the rate of change of $\hat{a}^\dagger \hat{a}$ associated with the third term on the right-hand side of (2.2)

$$\frac{d}{dt}(\hat{a}^\dagger \hat{a})_\Omega = i\Omega(\hat{a} - \hat{a}^\dagger) \ . \quad (2.4)$$

Thus we define the expectation value

$$n(t) = -2\Omega \mathrm{Im}\left[\int_0^t dt' \langle \hat{a}(t') \rangle\right] \quad (2.5)$$

as the number of photons absorbed by the molecule. This number is determined explicitly only by the pumped-mode amplitude, because by assumption the background modes do not couple directly to the field. Of course, they do couple indirectly to the field via their coupling to the pumped mode.

In our classical model we replace all operators in Eqs. (2.2) and (2.3) by their expectation values:

$$\dot{a} = -i(\Delta - \chi)a + 2i\chi |a|^2 a - i\Omega - i\sum_m \beta_m b_m \ , \quad (2.6)$$

$$\dot{b}_m = -i(\Delta + \varepsilon_m)b_m - i\beta_m a \ , \quad (2.7)$$

where $a \equiv \langle \hat{a} \rangle$ and $b_m \equiv \langle \hat{b}_m \rangle$. In particular, we ignore the quantum-mechanical difference $\langle \hat{a}^\dagger \hat{a}\,\hat{a} \rangle - |a|^2 a$ in the anharmonic contribution to (2.6). Thus our classical model is defined by the ordinary c-number equations (2.6) and (2.7) together with the equation

$$n(t) = -2\Omega \mathrm{Im}\left[\int_0^t dt' a(t')\right] \quad (2.8)$$

for the number of absorbed photons.

There is a further approximation that is useful in either the classical or quantum-mechanical model, namely the so-called quasicontinuum approximation. In this approximation we assume there are an infinite number of background modes above and below the pumped mode in frequency, and furthermore that these background-mode frequencies are evenly spaced by some amount ρ^{-1}, with ρ representing the density of background modes. We also assume the background modes have equal couplings β_m to the pumped mode. Thus we take

$$\varepsilon_m = \Delta_0 + m\rho^{-1}, \quad m = -\infty, \ldots, \infty \quad (2.9a)$$

$$\beta_m = \beta \ \text{ for all } m \ , \quad (2.9b)$$

where Δ_0 is the frequency spacing between the pumped mode and the nearest background mode.

The utility of the quasicontinuum approximation is easily realized by using the formal solution of (2.7) in the last term in (2.6):

$$\sum_m \beta_m b_m(t) = -i\beta^2 \sum_m \int_0^t dt'\, a(t') e^{i(\Delta + \Delta_0 + m\rho^{-1})(t' - t)}$$
$$= -i\beta^2 \int_0^t dt'\, e^{i(\Delta + \Delta_0)(t' - t)} a(t') \times \sum_{m=-\infty}^{\infty} e^{im\rho^{-1}(t' - t)} \ . \quad (2.10)$$

According to the Poisson summation formula[11] we have

$$\sum_{m=-\infty}^{\infty} e^{im\rho^{-1}(t' - t)} = 2\pi\rho \sum_{m=-\infty}^{\infty} \delta(t' - t - 2\pi m\rho) \ , \quad (2.11)$$

so that

$$\sum_{m=-\infty}^{\infty} \beta_m b_m(t) = -2\pi i\beta^2 \rho \int_0^t dt'\, e^{i(\Delta + \Delta_0)(t' - t)} a(t') \times \sum_{m=-\infty}^{\infty} \delta(t' - t + 2\pi m\rho) \ . \quad (2.12)$$

Defining

$$\gamma \equiv 2\pi\beta^2\rho \ , \quad (2.13a)$$

$$\tau_R \equiv 2\pi\rho \ , \quad (2.13b)$$

$$\varphi \equiv (\Delta + \Delta_0)\tau_R \ , \quad (2.13c)$$

and using (2.12) in (2.6), the classical model in the quasicontinuum approximation reduces to the equation

$$\dot{a}(t) = -i(\Delta - \chi)a(t) + 2i\chi |a(t)|^2 a(t) - i\Omega - \frac{\gamma}{2} a(t) - \gamma \sum_{m=1}^{\infty} e^{-im\varphi} a(t - m\tau_R)\Theta(t - m\tau_R) \ , \quad (2.14)$$

for the pumped-mode amplitude, together with Eq. (2.8) determining the number of absorbed quanta. In (2.14) $\Theta(x)$ is the unit step function.

The quasicontinuum model for the coupling of some system or quantum state to some background was used by Bixon and Jortner[12] in radiationless transition theory, and by Stey and Gibberd[13] and Lefebvre and Savolainen[14] in somewhat different contexts. Recently it has been used and studied further by Eberly *et al.*,[15] Kyröla *et al.*,[16] and Burkey and Cantrell.[17] We have also noted certain conservation laws and discussed the notion of quantum-mechanical spreading within the framework of the quasicontinuum model.[18] To our knowledge, however, the present model[5] is the first to employ the quasicontinuum model in a nonlinear setting.

Before exploring the consequences of the present model, it is worth connecting it with earlier classical models for MPE. In particular, suppose we proceed to the limit of a very large density of background modes, so that $\tau_R \to \infty$. In this case (2.14) is replaced by

$$\dot{a} = -i(\Delta - \chi)a + 2i\chi |a|^2 a - i\Omega - \frac{\gamma}{2} a \ . \quad (2.15)$$

Note that the effect of the background modes in this limit is to introduce an irreversible decay of pumped-mode en-

ergy at the rate γ given by the Fermi "golden rule." Moreover, Eq. (2.15) may be regarded as an approximation to the Duffing equation

$$\ddot{x}+\gamma\dot{x}+\omega_0^2 x-\tfrac{4}{3}\omega\chi x^3=-4\omega\Omega\cos(\omega t)\ . \tag{2.16}$$

To see this, let

$$x(t)=a(t)e^{-i\omega t}+a^*(t)e^{i\omega t}\ , \tag{2.17}$$

and assume that $\gamma\ll\omega$, $|\omega_0-\omega|=|\Delta|\ll\omega$, and $|\ddot{a}|\ll\omega^2|a|$. Then we have the Duffing (or van der Pol, or first Bogoliubov-Mitropolsky) approximation to (2.16):

$$\dot{a}=-i\Delta a+2i\chi|a|^2a-i\Omega-\frac{\gamma}{2}a\ , \tag{2.18}$$

which is just (2.15) with a trivial redefinition of the detuning Δ. In quantum optics, of course, the approximation leading from (2.16) to (2.18) is called the *rotating-wave approximation* (RWA). Thus we can say that our model leading to (2.14) reduces to the RWA Duffing equation in the limit of a very dense distribution of background modes.[19]

The Duffing oscillator has been considered previously by Bloembergen[8] and Lamb[9] as a model of a driven molecular vibrator. It is worth noting that, although the Duffing oscillator can exhibit chaotic behavior,[20] the RWA Duffing oscillator cannot.[21] However, the RWA Duffing system does share the properties of bistability and hysteresis in common with the full Duffing equation.[21] Our model amounts to the RWA Duffing oscillator coupled to a background of non-pumped background modes, and in this sense is an extension of the earlier classical models of Bloembergen and Lamb.

At the other extreme for the background modes is the limit $\tau_R\to 0$, corresponding to a sparse distribution. In this case the sum in (2.14) may be replaced by an integral. Equivalently, it is clear that the limit $\tau_R\to 0$, or $\rho\to 0$, means that all background modes except that separated by Δ_0 from the pumped mode are so far off resonance from the pumped mode that they may be ignored. Then we may replace (2.6) and (2.7) by the equations

$$\dot{a}=-i(\Delta-\chi)a+2i\chi|a|^2a-i\Omega-i\beta b\ , \tag{2.19a}$$

$$\dot{b}=-i(\Delta+\Delta_0)b-i\beta a\ , \tag{2.19b}$$

which describe a driven anharmonic oscillator coupled to a single harmonic oscillator.

Neither of these two limits for the background mode distribution are of particular interest to us here. We now turn our attention to the predictions of the quasicontinuum model for finite values of the background mode density ρ.

III. RESULTS FOR THE QUASICONTINUUM MODEL

For numerical computations it is convenient to cast (2.14) in the form

$$\dot{a}(t)=-i(\Delta-\chi)a(t)+2i\chi|a(t)^2|a(t)-i\Omega-\frac{\gamma}{2}a(t)-\gamma s(t)\ , \tag{3.1a}$$

where $s(t)$ satisfies the recurrence equation

$$s(t)=e^{-i\varphi}[s(t-\tau_R)+a(t-\tau_R)]\ . \tag{3.1b}$$

In terms of the new independent variable $T=\gamma t$, and the scaled variables

$$A=\frac{\gamma}{\Omega}a,\quad S=\frac{\gamma}{\Omega}s\ ,$$
$$\tilde{\Delta}=\frac{\Delta}{\gamma},\quad \tilde{\chi}=\frac{\chi}{\gamma}\ , \tag{3.2}$$
$$T_R=\gamma\tau_R,\quad \alpha=\chi\Omega^2/\gamma^3\ ,$$

we have

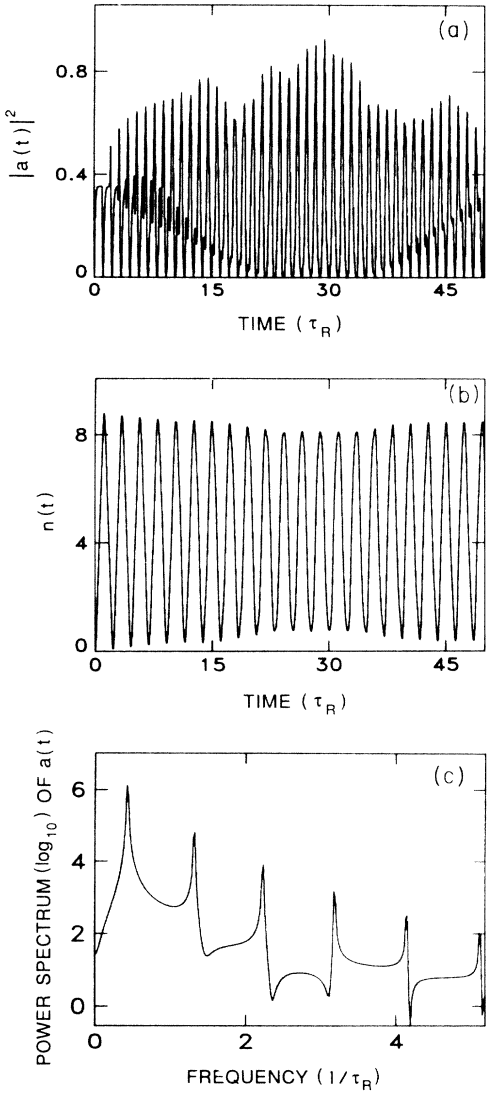


FIG. 1. (a) Number of photons absorbed by the pumped mode for the case $\Omega=0.3$ cm^{-1}, $\beta=0.2$ cm^{-1}, $\rho=4$ cm, $\Delta-\chi=\Delta_0=0$, and the anharmonicity $\alpha=0$. The time is given in units of the quasicontinuum recurrence time τ_R. (b) Total number of photons absorbed by the molecule. (c) Power spectrum of the function $a(T)$, obtained by applying a fast Fourier transform to the time series $a(T)$.

$$\dot{A}(T)=-i(\tilde{\Delta}-\tilde{\chi})A(T)+2i\alpha\,|A(T)|^2A(T)-i$$
$$-\tfrac{1}{2}A(T)-S(T) \tag{3.3a}$$
$$S(T)=e^{-i\varphi}[S(T-T_R)+A(T-T_R)]\,, \tag{3.3b}$$

and (2.8) becomes

$$n(T)=-2\left[\frac{\Omega}{\gamma}\right]^2\mathrm{Im}\left[\int_0^T dT'A(T')\right]. \tag{3.4}$$

The simplest case of the system (3.3), of course, is the harmonic case $\alpha=0$. In this case it is not difficult to obtain a closed-form solution for $A(T)$.[22] Figure 1(a) is a plot of the number of photons absorbed by the pumped mode $[=\Omega^2|A(T)|^2/\gamma^2]$ in this case, assuming $\Delta-\chi=\Delta_0=0$, and in Fig. 1(b) we show the total number of photons $n(T)$ absorbed by all the modes. The absorbed energy is oscillatory, which is the kind of behavior usually expected of a system of coupled harmonic oscillators. (It is possible to have energy growth proportional to T^2 for the special case $\varphi=\pi$, but this case is nongeneric.) In Fig. 1(c) we show the power spectrum of the time series $A(T)$. The regularity of the spectrum is, of course, a reflection of the linearity of the system, for in computing the spectrum we are essentially looking at the frequency spectrum of a system of coupled harmonic oscillators.

The situation of real interest, of course, is when the pumped mode is anharmonic, so that $\alpha\neq0$. In Figs. 2(a)–2(c) we show how the results of Fig. 1 are modified when there is an anharmonicity $\chi=2$ cm^{-1}, corresponding to $\alpha=0.18$ in the scaled system (3.3). After a few intervals of time T_R both the number of photons absorbed by the pumped mode and the total number of photons absorbed become quite erratic functions of time, and the power spectrum [Fig. 2(c)] is considerably richer than in the harmonic case [Fig. 1(c)]. In Fig. 3 we extend the results shown in Figs. 2(a) and 2(b) out to 500 intervals. We find that a saturation regime is reached in which the number of photons absorbed by the molecule oscillates about a constant value [approximately 4.5 photons of energy in Fig. 3(b)].

This saturation behavior, however, is unusual in that it depends on our choice of φ, which enters the model through the parameter $e^{-i\phi}$. In Figs. 1–3 we chose $\varphi=0$, the case in which one of the background modes is exactly resonant with the pumped mode. In Figs. 4–7 we show the results for the total number of photons absorbed when

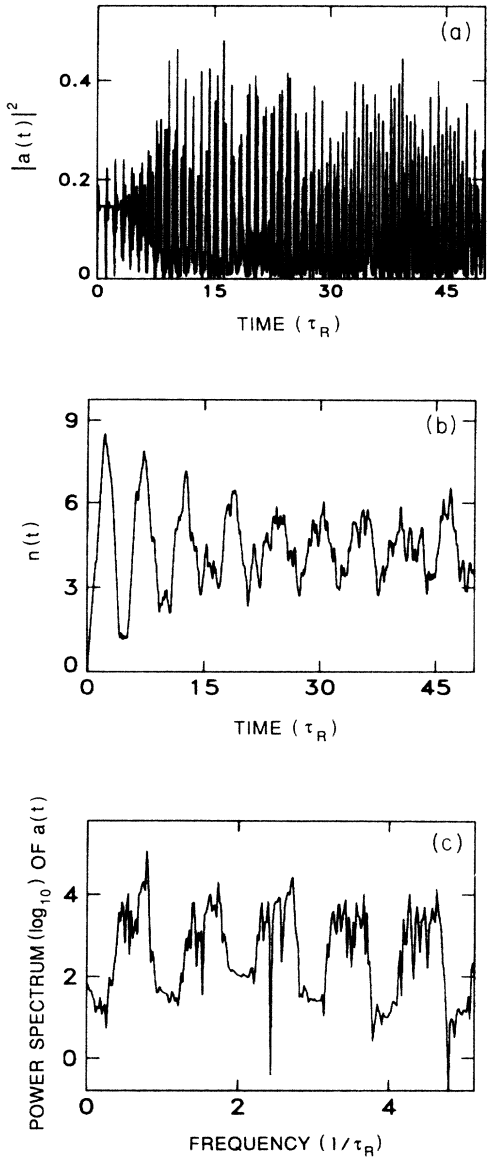


FIG. 2. Same as Fig. 1, except the anharmonicity $\alpha=0.18$.

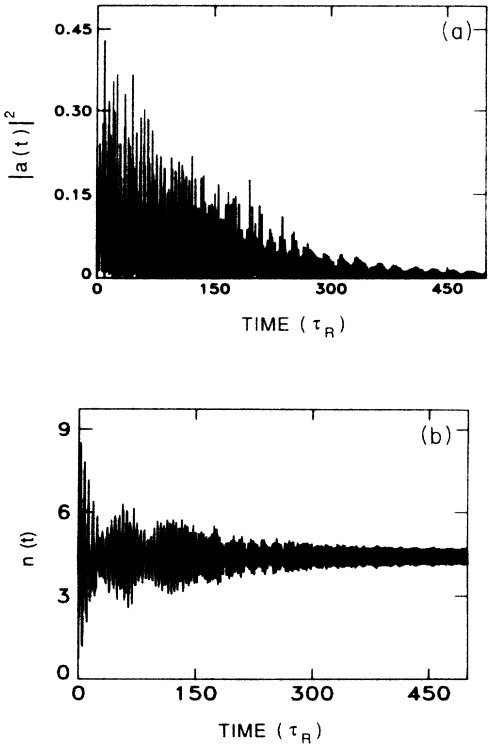


FIG. 3. Total number of photons absorbed for the case of Fig. 2, extended out to 500 intervals.

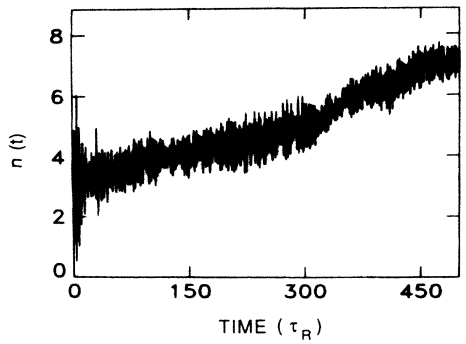


FIG. 4. Same as Fig. 3, except $\varphi=\pi/8$.

$\varphi=\pi/8$, $\pi/4$, $\pi/2$, and π, respectively. For the $\pi/2$ case we also show the number of photons absorbed by the pumped mode and the low-frequency power spectrum of $A(T)$. From these and similar computations we draw the following conclusions. First, the total energy (number of photons) absorbed by the molecule increases with time, on average, when $\varphi\neq 0$. This growth is approximately linear, with a slope that increases as φ is varied away from zero. That is, the number of photons absorbed by the molecule is proportional to the intensity multiplied by the time, or the fluence of the laser pulse, which is assumed to be long in duration compared with τ_R. (500 intervals in the figures shown, for instance, correspond to a time duration of 500×133 psec$=67$ nsec.) The energy absorbed by the molecule goes predominantly into the background modes, with the pumped mode acting only as an intermediary channel through which the laser can dump energy into the background modes. The possible relevance of these results to actual MPE experiments is discussed in Sec. V; for the present we continue to focus our attention on the properties of our model dynamical system.

Consider the following expression for the total number of quanta in the background modes:

$$\sum_m |b_m(t)|^2=\gamma\int_0^t dt'\,|a(t')|^2 + 2\gamma\,\mathrm{Re}\sum_{m=1}^{\infty}\beta^m\Theta(t-m\tau_R)\times\int_{m\tau_R}^{t} dt' a^*(t'-m\tau_R)a(t')\ . \tag{3.5}$$

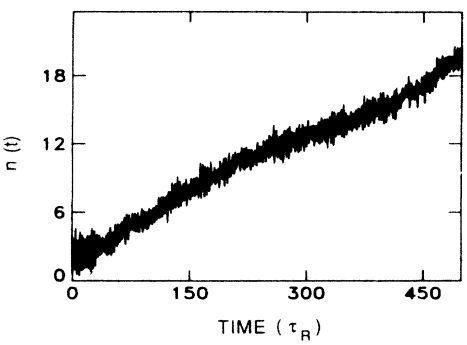
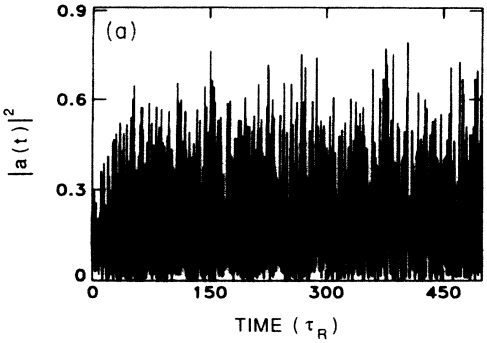
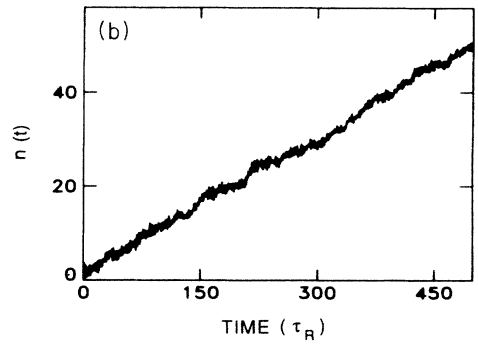


FIG. 5. Same as Fig. 3, except $\varphi=\pi/4$.





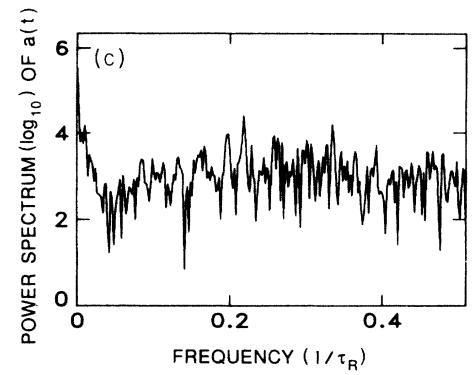


FIG. 6. Same as Fig. 2, except $\varphi=\pi/2$ and $\alpha=0.18$.

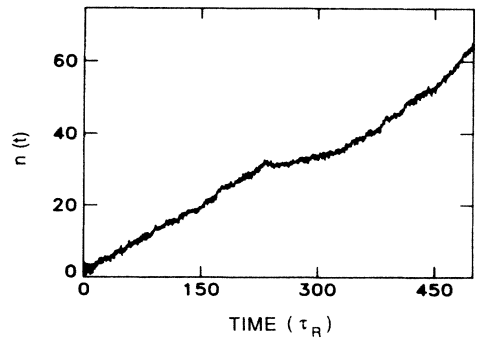


FIG. 7. Same as Fig. 3, except $\varphi=\pi$.

Except for the small quantity $|a(t)|^2$, representing the number of quanta in the pumped mode, this expression gives the total number of photons absorbed by the molecule. The two terms on the right-hand side of (3.5) are compared in Fig. 8 for the case of Fig. 6. It is seen that both terms vary approximately linearly in time (measured in the figures in units of τ_R). Figure 6(b) gives just the algebraic sum of the two terms in (3.5), except again for the small contribution $|a(t)|^2$. The result, as shown in Fig. 6(b), is just an approximately linear growth of the absorbed energy with time, with a slope much smaller than either of the lines found in Fig. 8.

In the limit $\tau_R \to \infty$ of a continuum of background modes, the second term in (3.5) would be absent. In this case the number of photons absorbed in the background modes grows at a rate γ given by the golden rule:

$$\frac{d}{dt}\sum_m |b_m(t)|^2=\gamma|a(t)|^2 . \tag{3.6}$$

Our model then reduces to the RWA Duffing system (2.15). We show in Fig. 9 the number of absorbed photons (2.5) computed using the RWA Duffing equation for $a(t)$. As in the preceding figures we have taken $\Delta-\chi=0$, $\chi=2\ \mathrm{cm}^{-1}$, $\Omega=3\ \mathrm{cm}^{-1}$, and $\gamma=1.01\ \mathrm{cm}^{-1}$. Not surprisingly, the result agrees very well with the first term in (3.5) for the full quasicontinuum model.

The most interesting feature of the results shown in Figs. 4–7 is that the absorbed energy grows, approximately linearly, with time (fluence-dependent absorption), even though the density of background modes chosen is too small to make the golden rule applicable. That is, we have not constructed a model in which fluence dependence is expected *a priori* due to an incoherent, irreversible decay of the pumped mode into a bath of background modes. Even without such an *a priori* assumption, however, the model does predict, to a good approximation, a fluence-dependent absorption of energy. In other words, the absorbed energy is proportional to the time and the intensity of the applied field, *as if* a simple rate-equation description were applicable.

To better understand these results, let us write (3.5) in the form

$$\sum_m |b_m(t)|^2=\gamma t\langle|a(t)|^2\rangle_0 + 2\gamma t\,\mathrm{Re}\sum_{m=1}^{\infty}\beta^m[X_m(t)\langle|a(t)|^2\rangle_m + |\langle a(t)\rangle_m|^2] , \tag{3.7}$$

where we introduce a "correlation function"

$$X_m(t)=\frac{\langle a^*(t-m\tau_R)a(t)\rangle_m-|\langle a(t)\rangle_m|^2}{\langle|a(t)|^2\rangle_m} , \tag{3.8}$$

and define an "average" $\langle\ \rangle_m$ by

$$\langle f(t)\rangle_m=(1/t)\Theta(t-m\tau_R)\int_{m\tau_R}^{t}dt'f(t') . \tag{3.9}$$

The approximately linear growth with time of the absorbed energy is a consequence of the fact that both terms multiplying t in equation (3.7) are approximately constant after many intervals, as is clear from Fig. 8. In Fig. 10 we show computed values of $X_1(t)$ and $X_{25}(t)$ for the case of Fig. 6, and in Figs. 11 and 12 are shown corresponding results for $\langle|a(t)|^2\rangle_m$ and $|\langle a(t)\rangle_m|^2$. The results shown for the correlation function $[X_m(t)]$ are especially interesting, because they indicate the role played by chaos in establishing the linear growth with time, and therefore the fluence dependence, of the absorbed energy. Whereas (quasi-) periodic motion gives rise to oscillatory correlations, it is typical of chaotic motion that correlations are

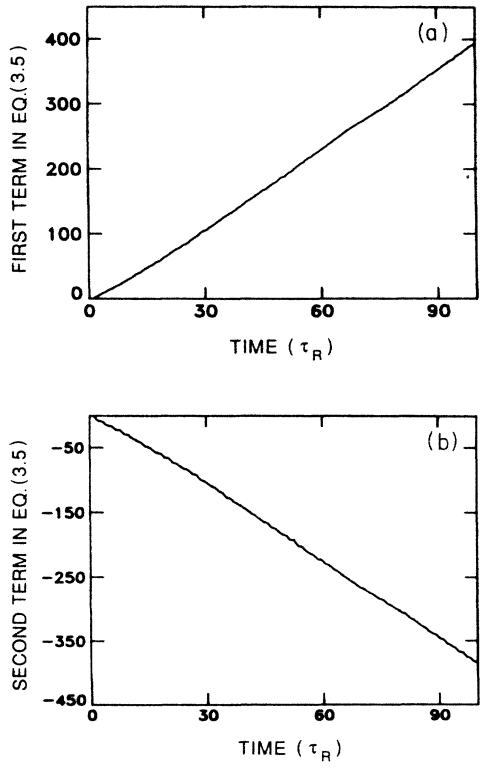


FIG. 8. (a) First and (b) second terms of Eq. (3.5) for the case of Fig. 6.

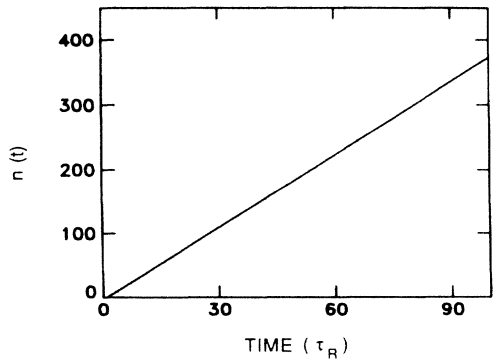


FIG. 9. Number of absorbed photons computed using the RWA Duffing equation (2.15) for $a(t)$ (see text).

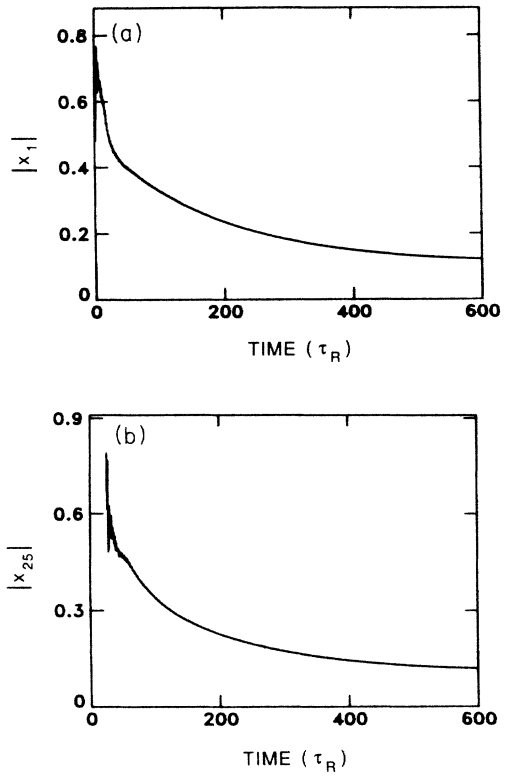


FIG. 10. Correlation function $X_m(t)$ for the case of Fig. 6, for (a) $m=1$ and (b) $m=25$.

decaying functions of the time difference. In particular, the fact that all the $X_m(t)$ damp to constant values gives rise to the linear dependence of the absorbed energy with time, as is obvious from Eq. (3.7). [We note again that in our model the absorbed energy goes predominantly into the background modes, with total excitation given by (3.7).]

It is important to note, because the correlations decay to constant values, the linear dependence of the absorbed energy with time will persist for all times. That is, the energy-versus-time curves shown in Fig. 6(b), for instance, will not saturate. Also, in such figures we are certainly not observing an early portion of some oscillatory energy-versus-time curve.

Although power spectra and correlation functions can provide strong evidence for chaotic behavior, the sure test is to compute the Lyapunov exponents: if one of these is positive, the system is chaotic. We have computed for our model the maximal Lyapunov exponent, using the technique described by Benettin and co-workers.[23] Figure 13 shows the result of the computation for the case of Fig. 6. The computation extends over a period of 10 000 intervals of time τ_R, and it appears that the maximal Lyapunov exponent is converging to a positive value. Thus we have the property of "very sensitive dependence on initial conditions," the hallmark of chaotic behavior. In the linear (nonchaotic) case $\alpha=0$, on the other hand, the computation gives zero for the Lyapunov exponent, which is the signature of regular behavior.

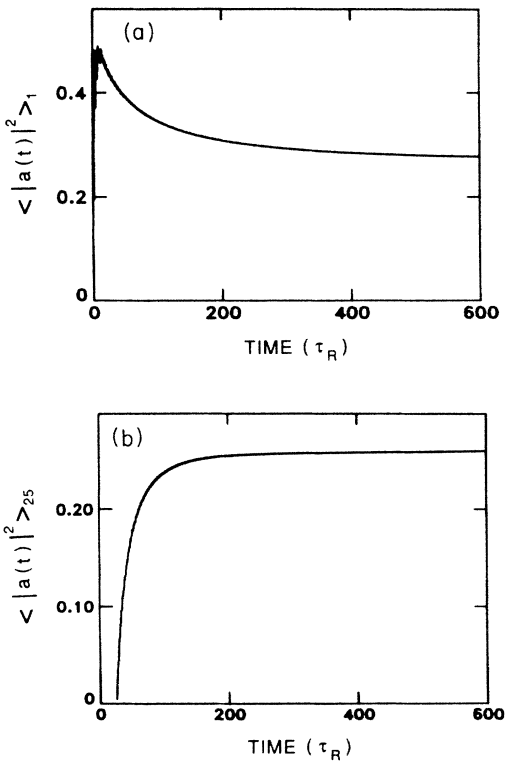


FIG. 11. Average $\langle |a(t)|^2\rangle_m$ for the case of Fig. 6, for (a) $m=1$ and (b) $m=25$.

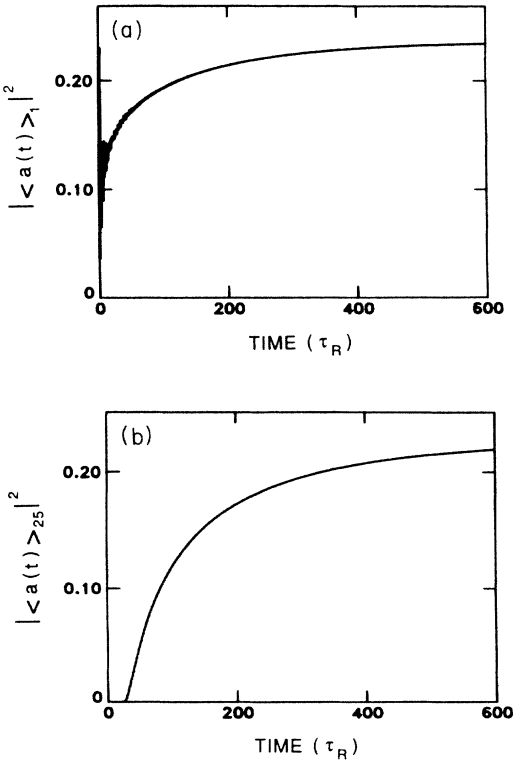


FIG. 12. Function $|\langle a(t)\rangle_m|^2$ for the case of Fig. 6, for (a) $m=1$ and (b) $m=25$.

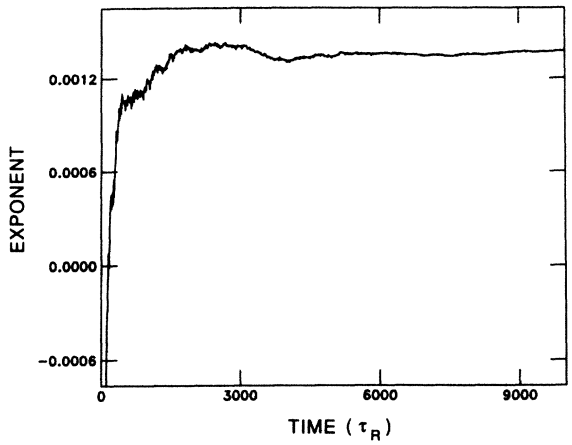


FIG. 13. Results of the computation of the maximal Lyapunov exponent for the case of Fig. 6.

IV. MODEL WITH A FINITE NUMBER OF BACKGROUND MODES

The quasicontinuum assumption of an evenly spaced, infinite ladder of background modes may seem highly artificial, but in fact it is not very crucial for our results about the nature of energy deposition. In this section we assume a finite number of background modes, which need not be evenly spaced, and obtain results in good agreement with the basic predictions of the quasicontinuum model.

The equations of motion are (2.6) and (2.7). Consider first an example in which there are ten background modes with energies

$$\varepsilon_m = -(\Delta-\chi)+(m-6)\rho^{-1}, \quad m=2,3,\ldots,11 \quad (4.1)$$

and $\rho=4$ cm, $\beta=0.2$ cm^1, $\chi=2$ cm^{-1}, and $\Delta-\chi=0$ as in all the examples considered with the quasicontinuum model. Note that in this case one of the background modes ($m=6$) is exactly resonant with the pumped mode, and so we can compare with the results shown in Fig. 3 for the quasicontinuum model for the case $\varphi=0$. We show the results obtained with (2.6), (2.7), and (4.1) in Fig. 14. The time axis in Fig. 14 corresponds to about 150 intervals τ_R for the quasicontinuum limit. Although the predictions shown in Fig. 14 differ in detail from those of Fig. 3, it is clear that the total number of absorbed photons is again predicted to show a saturation behavior rather than to grow approximately linearly with time.

Suppose, however, that the background mode closest to the pumped mode is displaced in frequency from the pumped mode. In Fig. 15 we show the results of the model with ten background modes, when the background mode is displaced from the pumped mode by an amount that corresponds to $\varphi=\pi/2$ in the notation used for the quasicontinuum model [Eq. (2.13c)]. Now we observe an approximately linear growth with time of the absorbed energy, which is consistent with the prediction of the quasicontinuum model (Fig. 6).

These results can be made to look more similar to the quasicontinuum results by increasing the number of background modes. In Fig. 16 we show the results for the

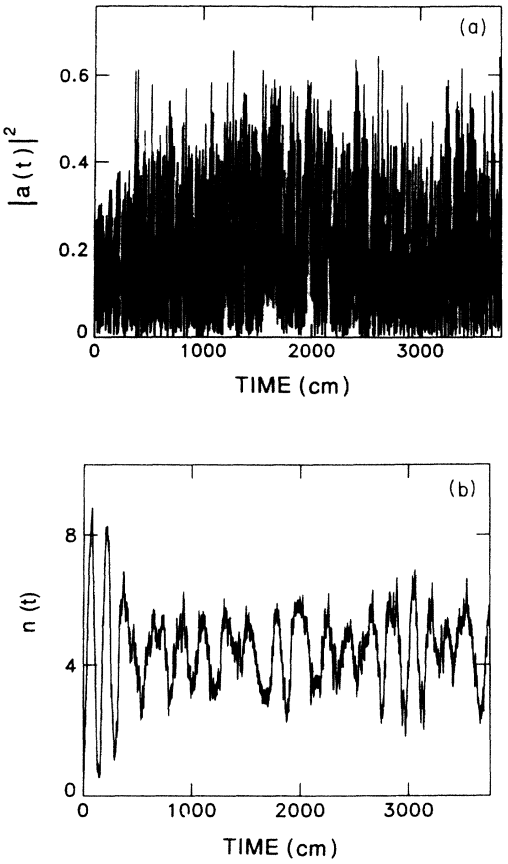


FIG. 14. Number of photons absorbed by (a) pumped mode and (b) all modes for a model with ten evenly spaced background modes, one of which is resonant with the pumped mode (see text).

number of absorbed photons when the preceding example is extended to include 20 background modes. The time axis corresponds to a total of about 250 quasicontinuum intervals τ_R, and there is good agreement with the corresponding prediction of the quasicontinuum model [Fig. 6(b)].

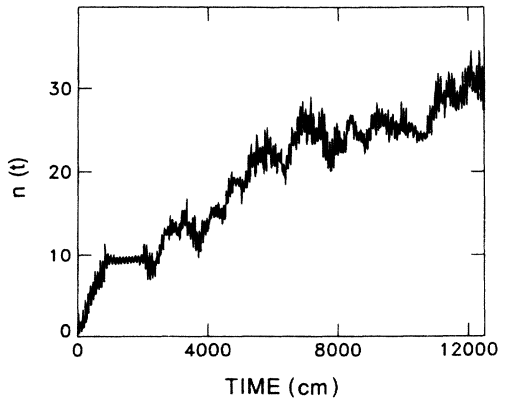


FIG. 15. Number of photons absorbed by the molecule for the case of Fig. 14, but without resonance between the pumped mode and any of the background modes (see text).

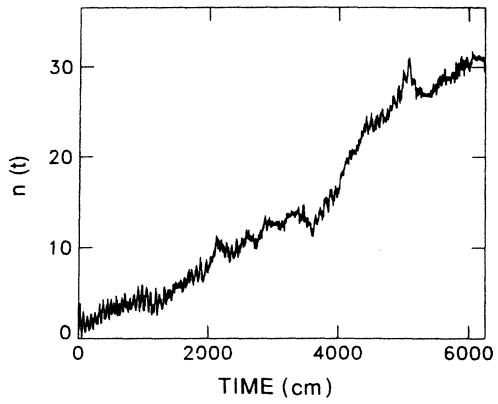


FIG. 16. Number of photons absorbed by the molecule when the number of background modes is increased to 20.

It is not surprising that the quasicontinuum limit is approached with only a relatively small number of background modes.[12,18] The quasicontinuum model is very useful because it greatly expedites the computations, and we have seen that it also aids in the understanding of the role played by chaos in the predicted fluence dependence.

However, we find that fluence-dependent behavior is not predicted when the number of background modes is as small as two or three. We have already considered the limit (2.19) in which there is just one background mode; in this limit the absorbed energy is oscillatory rather than linear with time. Thus a certain number of background modes must be reached before fluence-dependent behavior sets in, but beyond this number the results are roughly independent of how many background modes are present.

The most important predictions of the quasicontinuum model, for our purposes, are also preserved when the background-mode frequencies are not evenly spaced. In Fig. 17 we show the number of absorbed photons obtained with a model of ten background modes with "randomly" chosen ε_m values of -0.98, -0.62, -0.23, 0.054, 0.17, 0.20, 0.31, 0.67, 1.06, and 1.46 cm^{-1}. In general the growth of energy with time in cases with unevenly spaced background modes seems to be less accurately linear than with even spacings. The result shown in Fig. 17 is fairly typical of such cases. We can also lift the restriction of equal coupling constants (β_m) without significantly affecting the results.

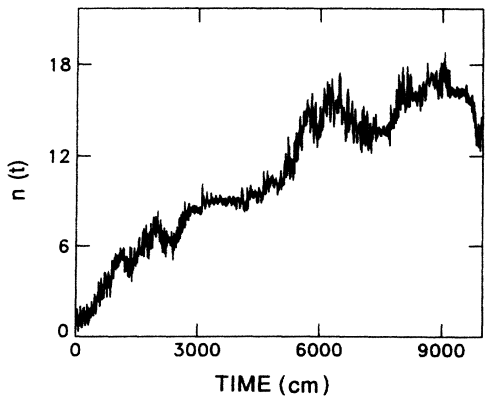


FIG. 17. Number of photons absorbed by the molecule for a case with ten unevenly spaced background modes (see text).

V. DISCUSSION

We have considered a classical model for multiple-photon excitation of molecular vibrations by infrared-laser fields. The model consists of an anharmonic pumped mode coupled to a background of harmonic, infrared-inactive modes, and driven by a monochromatic applied field. For reasonable values of molecular parameters the model typically predicts approximate fluence-dependent behavior, more or less independently of the detailed assumptions made for the background modes. Although we have focused our attention here on the case of a quartic (Duffing) nonlinearity, we feel that the basic model is fairly generic, but this remains a point for more careful investigation.

To the extent that the classical model is a reasonable one for a molecular vibrator in a laser field, we can understand the kind of behavior observed experimentally for some time in MPE experiments.[6,7,10] Perhaps the most significant experimental result is that a polyatomic molecule can be highly excited (and dissociated) by absorption of tens of photons in infrared laser pulses of fluence ≈ 1 J/cm^2 and intensities ≈ 10 MW/cm^2 or less. In our model such behavior is predicted for realistic values of the molecular parameters. Another important feature of the experiments is that the MPE process in all but the smallest polyatomics[7] depends on the laser fluence. This behavior is also predicted by our model, as is reflected in the (approximately) linear growth with time of the absorbed energy in a field of constant intensity.

Fluence-dependent excitation is naturally predicted by rate-equation models of multiphoton excitation, where the vibrational populations are assumed to change at rates proportional to the laser intensity.[10] Such behavior is not necessarily predicted by the density-matrix (or multilevel Bloch) equations, except of course when the rate-equation description is a valid approximation. In particular, the density of background modes may be insufficient to justify a golden-rule, rate-equation theory. In fact, there is evidence that an *a priori* assumption of the validity of rate equations may be unjustified in a molecule like SF_6.[24] In our model, fluence dependence is predicted without any rate-equation or statistical assumptions about background modes. We have explained this fluence dependence in terms of decaying correlations associated with the chaotic time evolution of the pumped-mode amplitude.

The currently accepted description of MPE in polyatomic molecules may be briefly summarized as follows. For the lower vibrational levels of a pumped mode, energy is absorbed by resonant, stepwise excitation, with the anharmonic energy defects being compensated for by the rotational energy levels.[25,26] Due to the large number of vibrational-rotational modes, the density of states in a polyatomic molecule increases rapidly with increasing excitation, so that after sufficient excitation a quasicontinuum regime is reached. The large number of levels in this quasicontinuum regime allows resonant stepwise excita-

tion to proceed without bottlenecking. This sort of behavior provided motivation for the present classical model, which predicts that most of the absorbed energy is soaked up by the background modes, with very little going into the pumped mode.

The complexity of the problem has made it difficult to develop the accepted theory of MPE in a detailed, quantitative way. For this reason there has been frequent resort to classical models.[8,9] The work reported in this paper extends these earlier models, and shows that *fully classical models can account for the most significant features of MPE.* Furthermore, as noted in the Introduction, our model is of some interest in connection with the nature of energy deposition in chaotic systems with external driving forces.

Although our model system is interesting in the context of dynamical systems theory, and as a classical model of MPE, it cannot really be regarded as a realistic alternative to the standard picture of MPE. For one thing, we have not accounted here for molecular rotations, which *cannot* be treated additively as a kind of inhomogeneous broadening.[24] We have previously considered the case of a pumped, triply degenerate harmonic vibrational mode and an uncoupled rigid rotator.[27] In this case the field introduces a vibration-rotation nonlinearity that breaks the conservation of molecular angular momentum, which can lead to chaotic behavior when the vibrational angular momentum exceeds the purely rotational angular momentum.

A more fundamental limitation on our model, of course, is that it is completely classical. One might expect reasonably good agreement between the classical and quantum-mechanical predictions when the molecule is already highly pumped up the vibrational ladder, but our computations show that the pumped mode does not get very highly excited. Support for classical MPE theories is sometimes sought in the numerical results of Walker and Preston,[28] who compared the classical and quantum results for the energy absorbed by a driven anharmonic oscillator.[29] However, these computations did not extend very far out in time, as was possible in our computations because of our use of the rotating-wave approximation to eliminate rapidly oscillating terms. In fact, it is precisely for such long times that one expects the largest differences between the classical and quantum predictions. Furthermore, we have strong evidence for chaotic behavior in our classical model, and it is not yet clear to what extent our predictions would survive a fully quantum treatment.[29] We hope to be able to address these questions in the near future.

ACKNOWLEDGMENTS

We wish to thank Dr. H. W. Galbraith for collaboration during the early stages of this work, and Dr. Mei-Li Shih for useful discussions. We have also benefitted in this work from conversations over the past few years with many other colleagues, especially F. T. Arecchi, C. M. Bowden, J. H. Eberly, and F. A. Hopf. One of us (P.W.M.) acknowledges the support of the National Science Foundation through grants No. PHY-83-08048 and No. PHY-84-18070 at the University of Arkansas.

[1]G. Casati, B. V. Chirikov, F. M. Izrailev, and J. Ford, *Stochastic Behavior in Classical and Quantum Hamiltonian Systems,* Vol. 93 of *Lecture Notes in Physics,* edited by G. Casati and J. Ford (Springer, Berlin, 1979).

[2]J. G. Leopold and I. C. Percival, Phys. Rev. Lett. **41**, 944 (1978).

[3]K. A. H. van Leeuwen, G. v. Oppen, S. Renwick, J. B. Bowlin, P. M. Koch, R. V. Jensen, O. Rath, D. Richards, and J. G. Leopold, Phys. Rev. Lett. **55**, 2231 (1985).

[4]J. E. Bayfield and L. A. Pinnaduwage, Phys. Rev. Lett. **54**, 313 (1985), and references therein.

[5]J. R. Ackerhalt, H. W. Galbraith, and P. W. Milonni, Phys. Rev. Lett. **51**, 1259 (1983).

[6]N. R. Isenor and M. C. Richardson, Appl. Phys. Lett. **18**, 224 (1971); Opt. Commun. **3**, 360 (1971).

[7]T. B. Simpson, J. G. Black, I. Burak, E. Yablonovich, and N. Bloembergen, J. Chem. Phys. **83**, 628 (1985).

[8]N. Bloembergen, Opt. Commun. **15**, 416 (1975).

[9]See, for instance, W. E. Lamb, Jr., *Laser Spectroscopy III,* edited by J. L. Hall and J. L. Carlsten (Springer-Verlag, New York, 1977); *Laser Spectroscopy IV,* edited by H. Walther and K. Rothe (Springer-Verlag, New York, 1979).

[10]See, for instance, J. L. Lyman, G. P. Quigley, and O. P. Judd, *Multiple-Photon Excitation and Dissociation of Polyatomic Molecules,* edited by C. D. Cantrell (Springer-Verlag, New York, to be published); O. P. Judd, J. Chem. Phys. **71**, 4515 (1979).

[11]See, for instance, M. J. Lighthill, *Introduction to Fourier Analysis and Generalized Functions* (Cambridge University Press, Cambridge, 1970), p. 67.

[12]M. Bixon and J. Jortner, J. Chem. Phys. **48**, 715 (1968).

[13]G. C. Stey and R. W. Gibberd, Physica (Utrecht) **6**, 7 (1972).

[14]R. Lefebvre and J. Savolainen, J. Chem. Phys. **60**, 2509 (1974).

[15]J. H. Eberly, J. J. Yeh, and C. M. Bowden, Chem. Phys. Lett. **86**, 76 (1982); J. J. Yeh, C. M. Bowden, and J. H. Eberly, J. Chem. Phys. **76**, 5936 (1982).

[16]E. Kyröla and J. H. Eberly, J. Chem. Phys. **82**, 1841 (1985); E. Kyröla, Ph.D. thesis, University of Rochester, 1984 (unpublished); J. Javanainen and E. Kyröla, Opt. Commun. **56**, 17 (1985).

[17]R. S. Burkey and C. D. Cantrell, J. Opt. Soc. Am. B **1**, 169 (1984).

[18]P. W. Milonni, J. R. Ackerhalt, H. W. Galbraith, and M.-L. Shih, Phys. Rev. A **28**, 32 (1983).

[19]Details of the transition to the continuum limit have recently been investigated by J. Javanainen and E. Kyröla, Opt. Commun. **56**, 17 (1985).

[20]B. A. Huberman and J. P. Crutchfield, Phys. Rev. Lett. **43**, 1743 (1979).

[21]J. R. Ackerhalt, H. W. Galbraith, and P. W. Milonni, *Coherence and Quantum Optics,* edited by L. Mandel and E. Wolf (Plenum, New York, 1984).

[22]M.-L. Shih, Ph.D. thesis, University of Arkansas, 1985 (unpublished).

[23]G. Benettin, L. Galgani, and J.-M. Strelcyn, Phys. Rev. A **14**, 2338 (1976); G. Benettin, L. Galgani, A. Giorgilli, and J.-M. Strelcyn, Meccanica **15**, 9 (1980); **15**, 27 (1980).

[24]H. W. Galbraith and J. H. Ackerhalt, in *Laser-Induced Chem-*

ical Processes, edited by J. I. Steinfeld (Plenum, New York, 1981).

[25]R. V. Ambartzumian, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, and A. A. Puetskii, Pis'ma Zh. Eksp. Teor. Fiz. **23**, 26 (1976) [Sov. Phys.—JETP Lett. **23**, 22 (1976)].

[26]D. M. Larsen and N. Bloembergen, Opt. Commun. **17**, 254 (1976); D. M. Larsen, *ibid.* **17**, 250 (1976).

[27]H. W. Galbraith, J. R. Ackerhalt, and P. W. Milonni, J. Chem. Phys. **79**, 5345 (1983).

[28]R. B. Walker and R. K. Preston, J. Chem. Phys. **67**, 2017 (1977).

[29]Fully quantum-mechanical computations with finite numbers of basis states have been begun by R. E. Wyatt (private communication). Quantum-mechanical approaches to anharmonic oscillators have also been described by G. P. Berman and G. M. Zaslavsky, Physica **91A**, 450 (1978) and S. Abe and S. Mukamel, J. Chem. Phys. **79**, 5457 (1983).

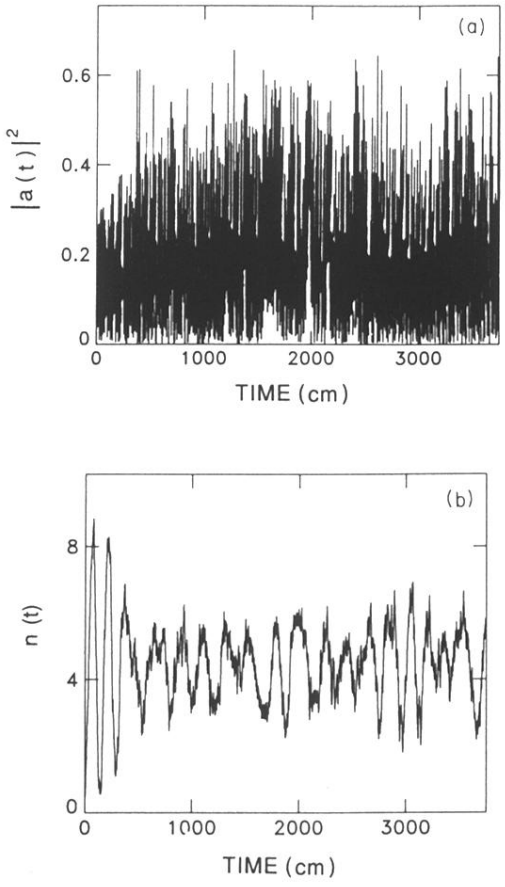


FIG. 14. Number of photons absorbed by (a) pumped mode and (b) all modes for a model with ten evenly spaced background modes, one of which is resonant with the pumped mode (see text).

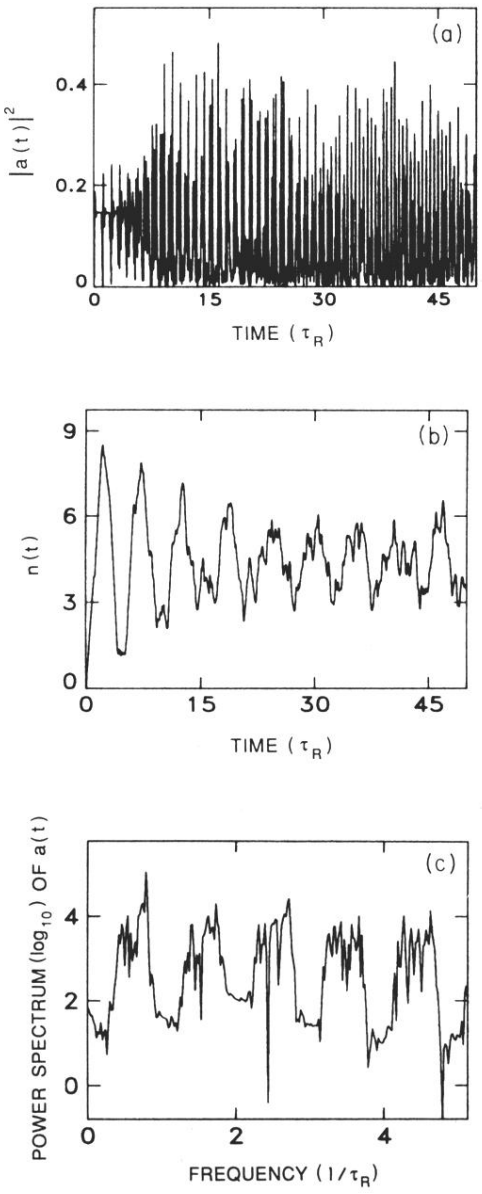


FIG. 2. Same as Fig. 1, except the anharmonicity $\alpha=0.18$.

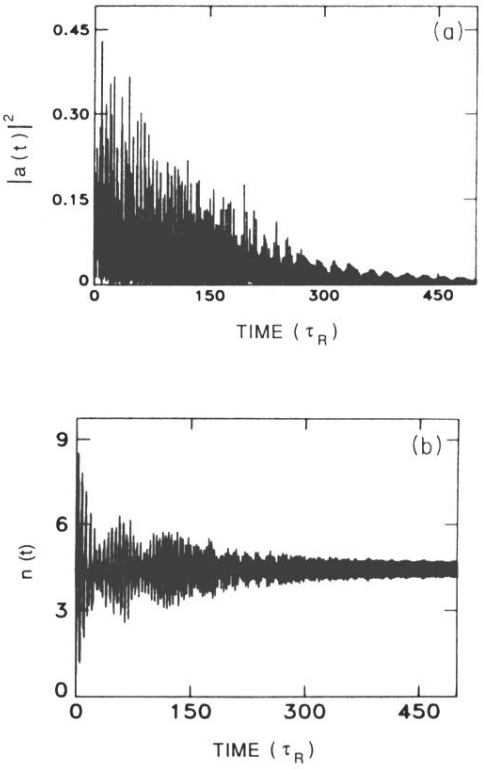


FIG. 3. Total number of photons absorbed for the case of Fig. 2, extended out to 500 intervals.

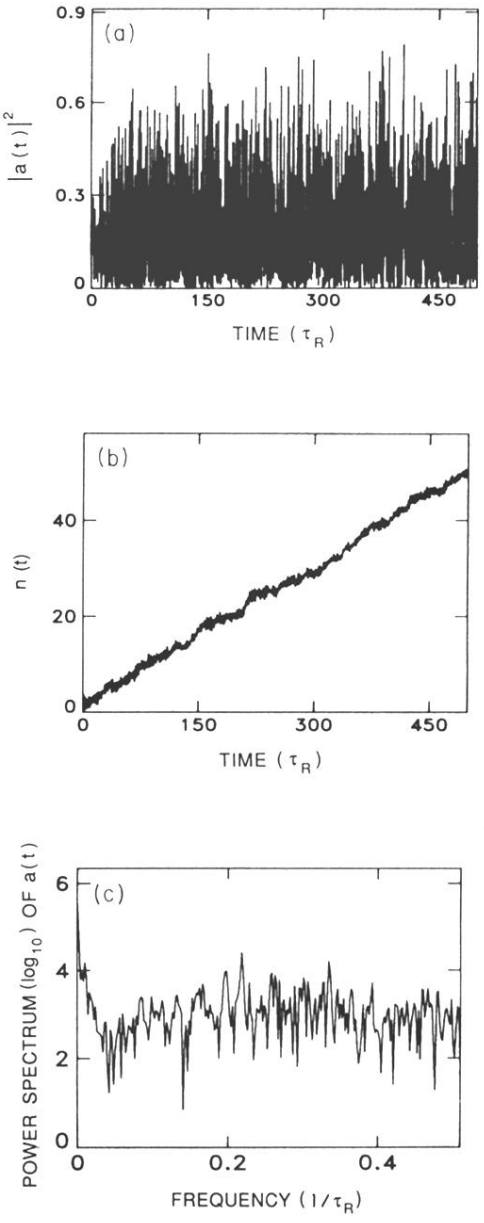


FIG. 6. Same as Fig. 2, except $\varphi=\pi/2$ and $\alpha=0.18$.