Statistical theory of multiphoton excitation of polyatomic molecules based on the Wigner function

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This paper is aimed at establishing a statistical theory of rotational and vibrational excitation of polyatomic molecules by an intense IR laser. Starting from the Wigner function of quantum statistical mechanics, we treat the rotational motion in the classical approximation; the vibrational modes are classified into active ones which are coupled directly with the laser and the background modes which are not coupled with the laser. The reduced Wigner function, i.e., the Wigner function integrated over all background coordinates should satisfy an integro-differential equation. We introduce the idea of "viscous damping" to handle the interaction between the active modes and the background. The damping coefficient can be calculated with the aid of the well-known Schwartz–Slawsky–Herzfeld theory. The resulting equation is solved by the method of moment equations. There is only one adjustable parameter in our scheme; it is introduced due to the lack of precise knowledge about the molecular potential. The theory developed in this paper explains satisfactorily the recent absorption experiments of SF_6 irradiated by a short pulse CO_2 laser, which are in sharp contradiction with the prevailing quasi-continuum theory. We also refined the density of energy levels which is responsible for the muliphoton excitation of polyatomic molecules.

I. INTRODUCTION

Using lasers to excite and dissociate molecules selectively is one of the most important topics in laser chemistry. A large amount of experimental data has already been accumulated. Theoretical approaches also have made great advances.[1–4] However, the generally accepted quasi-continuum theory, though quite successful in interpreting the main features of the physical process, is still schematic and not an *ab initio* theory, and the basic idea of quasi-continuum, i.e., the density of energy states relevant to the multiphoton absorption is still of some controversy.[5] As far as the present authors are aware, only few attempts were made to develop a systematic theory. In the work of GYFH,[6] the authors started from the Schrödinger equation of molecular vibration and applied the idea of intramolecular energy exchange through Fermi resonance to calculate the process of excitation and dissociation of SF_6; the rotational motion was considered in an *ad hoc* way in connection with the idea of rotational compensation. The approach adopted by Ho and Chu[4] is difficult to extend to polyatomic molecules due to the computational complexity. Recently Kwok, Yablonovitch, and Bloembergen[7] made a series of elaborate experiments on SF_6 and discovered a remarkable deviation from the predictions of the prevailing quasi-continuum theory. Due to the progress in short pulse techniques, the study of the physical phenomena pertaining to the molecular excitation is expected to be even more active, and it is worthwhile to attempt a systematic theory of coherent excitation, including both rotational and vibrational motions, from first principles. We shall show in the following our plan to achieve this goal.

II. THE WIGNER FUNCTION AND ITS SIMPLIFICATION

Compared with the usual presentation of quantum statistical mechanics with a density matrix, the function named after Wigner and originated by him in the early period of quantum mechanics apparently has not been widely used. Except for being able to take negative values, the Wigner function shares many properties of a probability distribution function.[8] For a system of weakly anharmonic oscillators, we can make use of the classical concept and the mathematical method thereof, since for a system of harmonic oscillators, the Wigner function reduces simply to the classical distribution function.

We assume the molecule is comprised of N atoms (the motion of the electrons is neglected by adiabatic approximation) with the Cartesian coordinates $\mathbf{Q}_k$, momenta $\mathbf{P}_k$, and masses M_k, then the corresponding Wigner function $f(\mathbf{Q}, \mathbf{P}, t)$ satisfies[8]

$$\frac{\partial f}{\partial t} + \sum_{k=1}^{N} \frac{\mathbf{P}_k}{M_k} \nabla_{\mathbf{Q}_k} f - \frac{2}{\hbar} \sin \times \left[\frac{\hbar}{2} \nabla_{\mathbf{Q}} \nabla_{\mathbf{P}} \right] \mathbf{U}(\mathbf{Q},t) f(\mathbf{Q},\mathbf{P},t) = 0, \tag{1}$$

where $\mathbf{Q}$, $\mathbf{P}$ are the sets of $\mathbf{Q}_k$ and $\mathbf{P}_k$, $\mathbf{U}$ consists of the molecular potential and the potential due to external field (in dipole approximation). $\nabla_{\mathbf{Q}}$ operates only on $\mathbf{U}(\mathbf{Q})$. We can also write

$$\frac{\partial f}{\partial t} + \frac{2}{\hbar} \sin \left\{ \frac{\hbar}{2} \left(\frac{\partial}{\partial \mathbf{P}}, \frac{\partial}{\partial \mathbf{Q}} \right) \right\} H f = 0, \tag{2}$$

where

$$\left(\frac{\partial}{\partial \mathbf{P}},\frac{\partial}{\partial \mathbf{Q}}\right)Hf=\left\{\frac{\partial}{\partial \mathbf{P}_1}\cdot\frac{\partial}{\partial \mathbf{Q}_2}\longrightarrow\frac{\partial}{\partial \mathbf{Q}_1}\cdot\frac{\partial}{\partial \mathbf{P}_2}\right\}$$
$$\times H(\mathbf{P}_1,\mathbf{Q}_1,t)f(\mathbf{P}_2,\mathbf{Q}_2,t)\big|_{\substack{\mathbf{P}_1=\mathbf{P}_2=\mathbf{P}\\ \mathbf{Q}_1=\mathbf{Q}_2=\mathbf{Q},}} \quad (3)$$

$$H=\sum_k \mathbf{P}_k^2/2M_k+\mathrm{U}(\mathbf{Q},t), \quad (4)$$

are classical Poisson bracket and Hamiltonian, respectively. If $\hbar \to 0$ Eq. (1) or Eq. (2) reduces to Liouville's theorem. It is noteworthy that although the Poisson bracket is invariant with respect to canonical transformations,[9] Eq. (2) is valid only for rectangular coordinates and not valid for arbitrary canonical coordinates.[10] Introducing the new coordinates: mass center **R** (neglected in subsequent discussion), the Eulerian angles for rotation (θ,ϕ,χ) and the coordinates of principal vibrational mode q_i $(i=1,2,\ldots,3N\text{–}6)$ and their conjugate momenta $(p_\theta,p_\phi,p_\chi),p_i$, we can write Eq. (1) as

$$\frac{\partial f}{\partial t}+\{H,f\}_{\theta,p_\theta}-\left\{\frac{2}{\hbar}\sin\left[\frac{\hbar}{2}\nabla_{\mathbf{Q}}\cdot\nabla_{\mathbf{P}}\right]-\nabla_{\mathbf{Q}}\cdot\nabla_{\mathbf{P}}\right\}$$
$$\times\mathrm{U}(\mathbf{Q},t)f=0, \quad (5)$$

where

$$\{H,f\}_{\theta,p_\theta}=\frac{\partial H}{\partial p_\theta}\frac{\partial f}{\partial \theta}+\frac{\partial H}{\partial p_\phi}\frac{\partial f}{\partial \phi}+\frac{\partial H}{\partial p_\chi}\frac{\partial f}{\partial \chi}$$
$$+\sum_i\frac{\partial H}{\partial p_i}\frac{\partial f}{\partial q_i}-\frac{\partial H}{\partial \theta}\frac{\partial f}{\partial p_\theta}-\frac{\partial H}{\partial \phi}\frac{\partial f}{\partial p_\phi}$$
$$-\frac{\partial H}{\partial \chi}\frac{\partial f}{\partial p_\chi}-\sum_i\frac{\partial H}{\partial q_i}\frac{\partial f}{\partial p_i}. \quad (6)$$

The third term in Eq. (5) represents the quantum effect and is very complex if written out in the new coordinates. However, due to the smallness of the rotational energy spacing in comparison with the laser frequency in experiments, we can treat the rotation classically and this is already included in the second term of Eq. (5), while in the third term we can take all the rotational coordinates as frozen, only appearing as parameters in U(**Q**), and in the operators we only need to consider the role of q_i and p_i. Since the principal mode coordinates q_i, p_i can be taken as rectangular, the quantum effect in it is obviously $\{(2/\hbar)\sin[(\hbar/2)\nabla_{\mathbf{q}}\cdot\nabla_{\mathbf{p}}]-\nabla_{\mathbf{q}}\cdot\nabla_{\mathbf{p}}\}\mathrm{U}f$ (**q**, **p**, stand for the sets of q_i and p_i). Therefore Eq. (5) can be simplified to

$$\frac{\partial f}{\partial t}+\{H,f\}_{\theta,p_\theta}-\left\{\frac{2}{\hbar}\sin\left(\frac{\hbar}{2}\nabla_{\mathbf{q}}\cdot\nabla_{p}\right)-\nabla_{\mathbf{q}}\cdot\nabla_{\mathbf{p}}\right\}\mathrm{U}f=0, \quad (7)$$

$$H=T_r+T_v+U_{\mathrm{int}}+U_{\mathrm{ext}}, \quad (8)$$

where T_r, T_v, U_{int}, U_{ext} are the molecular rotational and vibrational energies, molecular potential and potential energy due to external field, respectively. If the principal moments of inertia of the molecule are A, B, C, then

$$T_r=\{p_\theta\sin\chi-(p_\phi-p_\chi\cos\theta)(\sin\theta)^{-1}\cos\chi\}^2/2A$$
$$+\{p_\theta\cos\chi+(p_\phi-p_\chi\cos\theta)(\sin\theta)^{-1}\sin\chi\}^2/$$
$$2B+p_\chi^2/2C. \quad (9)$$

(The following discussions are referred to SF_6, so $A=B=C$.) We take the vibrational modes coupled directly with the laser as active (such as ν_3 of SF_6), with coordinates (q,p), and take all the remaining modes not coupled directly or coupled weakly with the laser as background with coordinates (q_j,p_j), the corresponding reduced masses being m and m_j, then

$$T_v=p^2/2m+\sum_j p_j^2/2m_j. \quad (10)$$

In regard to U_{int}, the harmonic part is easy to write, but for most molecules, the anharmonic part is not known precisely. By spectroscopic data of the active mode, it is usually possible to describe its anharmonic effect by $(-\epsilon q^4)$ (see Sec. V), hence we write

$$U_{\mathrm{int}}=m\omega^2q^2/2-\epsilon q^4+\sum_j m_j\omega_j^2q_j^2/2+U'(q,q_j), \quad (11)$$

where $U'(q,q_j)$ stands for all other anharmonic terms. In dipole approximation

$$U_{\mathrm{ext}}=-E(t)\mu q\cos\theta, \quad (12)$$

where $E(t)$ is the laser electric field (linearly polarized), μ the dipole moment. For the sake of simplicity, we only write one term for the active mode in Eqs. (10)–(12), but the ν_3 mode of SF_6 has degeneracy 3, it suffices to multiply the final relevant results by the factor 3.

We integrate Eq. (7) with respect to $\prod_j dq_j\,dp_j$. Define

$$\int f\prod_j dp_j dq_j \equiv F(\theta,\phi,\chi,p_\theta,p_\phi,p_\chi,q,p,t)$$

and with the help of the natural boundary condition

$$f|_{q_j\to\infty}=f|_{p_j\to\infty}=0,$$

we get

$$\frac{\partial F}{\partial t}+\frac{\partial H'}{\partial p_\theta}\frac{\partial F}{\partial \theta}+\frac{\partial H'}{\partial p_\phi}\frac{\partial F}{\partial \phi}$$
$$+\frac{\partial H'}{\partial p_\chi}\frac{\partial F}{\partial \chi}+\frac{p}{m}\frac{\partial F}{\partial q}-\frac{\partial H'}{\partial \theta}\frac{\partial F}{\partial p_\theta}$$
$$-(m\omega^2q-4\epsilon q^3-\mu E\cos\theta)\frac{\partial F}{\partial p}-\hbar^2\epsilon q\frac{\partial^3F}{\partial p^3}$$
$$-\frac{2}{\hbar}\sin\left(\frac{\hbar}{2}\frac{\partial}{\partial q}\frac{\partial}{\partial p}\right)\int U'f\prod_j dq_j dp_j=0, \quad (13)$$

where

$$H'=p^2/2m+T_r+(m\omega^2q^2/2-\epsilon q^4)-\mu E(t)q\cos\theta. \quad (14)$$

In the last term of Eq. (13), due to the action of the operator

$$\sin\left(\frac{\hbar}{2}\frac{\partial}{\partial q}\frac{\partial}{\partial p}\right),$$

all terms in $U'(q, q_j)$ that contain merely the background coordinates disappear, only the terms containing the product of q and q_j, i.e., representing the interaction between the active mode and the background will be reserved. Equation (13) contains the integral of the unknown function f, so it is difficult to handle. But it is remarkable that for a system of harmonic oscillators with linear interactions, Ford *et al.*[11] had proved rigorously that when the number of oscillators is large, the interaction between the active oscillator and others can be characterized simply by viscous force. We borrow this idea to simplify the last term in Eq. (13), and rewrite it as

$$\frac{\partial F}{\partial t}+\frac{\partial H'}{\partial p_\theta}\frac{\partial F}{\partial \theta}+\frac{\partial H'}{\partial p_\phi}\frac{\partial F}{\partial \phi}+\frac{\partial H'}{\partial p_\chi}\frac{\partial F}{\partial \chi}+\frac{p}{m}\frac{\partial f}{\partial q}$$
$$-\frac{\partial H'}{\partial \theta}\frac{\partial F}{\partial p_\theta}-(m\omega^2 q-4\epsilon q^3-\mu E\cos\theta)\frac{\partial F}{\partial p}-\hbar^2\epsilon q\frac{\partial^3 F}{\partial p^3}$$
$$-\left(\frac{\nu p}{m}\frac{\partial F}{\partial p}+\frac{\nu}{m}F\right)=0. \tag{15}$$

It can be shown readily by the method of classical statistical mechanics,[12] when $\hbar\to 0$, Eq. (15) is the equation of continuity in phase space of a system of oscillators with viscous damping, while the equation of motion of each oscillator is $m\ddot{q}+\nu\dot{q}+(m\omega^2 q-4\epsilon q^3)=E(t)\cdot\mu$ (Here and afterwards, the dot means differentiation with respect to t.) We shall clarify how to determine the coefficient of viscosity ν later on.

III. THE MOMENT EQUATIONS

Since the coefficient of viscosity ν can not be a constant (see Sec. IV), we shall use the approximate method of moment equations to treat Eq. (15). We define the rotational energy

$$E_r=\{p_\theta^2+(p_\phi-p_\chi\cos\theta)^2(\sin\theta)^{-2}+p_\chi^2\}/2A,$$

the vibrational energy

$$E_v=m\omega^2q^2/2-\epsilon q^4+p^2/2m,$$

and use the symbol " ∧ " to represent the ensemble average in terms of Wigner's function, e.g., $\hat{E}_r=\int E_rFd\Omega$, $(d\Omega=d\theta d\phi d\chi dp_\theta dp_\phi dp_\chi dqdp)$ then from Eq. (15) we can get

$$\frac{d\hat{E}_r}{dt}=-\frac{\mu E}{A}(\widehat{p_\theta q\sin\theta}), \tag{16}$$

$$\frac{d\hat{E}_v}{dt}=\frac{\mu E}{m}(\widehat{p\cos\theta})-\frac{\nu}{m^2}\widehat{p^2}, \tag{17}$$

$$\frac{d}{dt}(\widehat{q\cos\theta})=\frac{1}{m}(\widehat{p\cos\theta})-\frac{1}{A}(\widehat{p_\theta q\sin\theta}), \tag{18}$$

$$\frac{d}{dt}\widehat{q^2}=\frac{2}{m}(\widehat{pq}), \tag{19}$$

$$\frac{d}{dt}\widehat{p^2}=2\mu E(\widehat{p\cos\theta})+8\epsilon(\widehat{pq^3})-2m\omega^2(\widehat{pq})-\frac{2\nu}{m}\widehat{p^2}, \tag{20}$$

$$\frac{d}{dt}(\widehat{pq})=\frac{1}{m}\widehat{p^2}-m\omega^2\widehat{q^2}+4\epsilon\widehat{q^4}+\mu E(\widehat{q\cos\theta})-\frac{\nu}{m}(\widehat{pq}), \tag{21}$$

$$\frac{d}{dt}(\widehat{p\cos\theta})=\mu E\,\widehat{\cos^2\theta}-\frac{\nu}{m}(\widehat{p\cos\theta})-\frac{1}{A}(\widehat{p_\theta p\sin\theta})-m\omega^2(\widehat{q\cos\theta})+4\epsilon(\widehat{q^3\cos\theta}). \tag{22}$$

In deriving Eqs. (16)–(22), use was made of the boundary conditions $F|_{\theta=0}=F|_{\theta=\pi}=0$ which are valid for the classical distribution function and assumed to hold here too. These moment equations cannot be closed without further physical assumptions. For polyatomic molecules at room temperature (much less under low temperature) the rotational frequency is much lower than the vibrational one (the ratio is about 1/100 for SF_6), while the laser frequency is close to the latter, hence viewed from the rotational motion, laser is of high frequency, the rotational energy cannot change appreciably even in multiphoton process.[13] For the term $(\widehat{p_\theta q\sin\theta})$, q is a high frequency part while p_θ is a low frequency part hence $(\widehat{p_\theta q\cos\theta})\approx\hat{p}_\theta(\widehat{q\cos\theta})\cong 0(\hat{p}_\theta\approx 0)$, $(\widehat{p_\theta q\sin\theta})\approx 0$. Obviously we can take $\widehat{\cos^2\theta}=1/3$. Finally we assume $(\widehat{q^3\cos\theta})\cong(\widehat{q^2})(\widehat{q\cos\theta})$, $\widehat{q^4}=(\widehat{q^2})^2$, the physical significance of these is that for an anharmonic oscillator with potential

$$\frac{m}{2}(\omega^2-\frac{2\epsilon}{m}q^2)q^2,$$

we take it to be a harmonic oscillator with an equivalent frequency $\omega_{\rm eq}$, while $\omega_{\rm eq}$ is calculated by the Wigner ensemble average, i.e., $\omega_{\rm eq}^2=\omega^2-2\widehat{\epsilon q^2(t)}/m$. With all these in mind and writing $q_c=q\cos\theta$, $p_c=p\cos\theta$, $u=(\widehat{q^2})$, $v=(\widehat{pq})$, $w=(\widehat{p^2})$, we get from Eqs. (16) – (22),

$$\dot{q}_c=p_c/m, \tag{23}$$

$$\dot{p}_c+\nu p_c/m+m\omega^2q_c=\mu E/3+4\epsilon uq_c, \tag{24}$$

$$\dot{u}=2v/m, \tag{25}$$

$$\dot{v}+\nu v/m-w/m+m\omega^2u=\mu Eq_c+3\epsilon u^2, \tag{26}$$

$$\dot{w}+2\nu w/m-2m\omega^2v=2\mu Ep_c+8\epsilon uv, \tag{27}$$

$$\frac{d\hat{E}_v}{dt}=\frac{\mu}{m}Ep_c-\frac{\nu}{m^2}w, \tag{28}$$

and $E_r\cong$const. Equations (23)–(27) form a closed system. It can be seen that they are not completely equivalent to the equation of motion of a classical anharmonic oscillator with damping. The quantum effect ($\hbar$) does not appear explicitly and this is a simplification brought forth by our assumption ($-\epsilon q^4$) about the anharmonic potential. However, $\hbar$ will enter eventually through the coefficient of viscosity ν.

IV. INTRAMOLECULAR ENERGY EXCHANGE BETWEEN VIBRATIONAL MODES AND COEFFICENT ν

Now we turn to the problem as how to determine ν,ν characterizes the energy exchange between the active mode and the background. The most important process regulating the energy exchange between various vibrational modes is Fermi resonance. Two conditions must be met for such process to occur. First, the resonance condition must be satisfied, at least nearly, i.e., the energy defect of the corresponding process is small (say, less than 30–50 cm^{-1}) and second, the anharmonic term of the potential that causes such modal transition should be consistent with the symmetry of the molecule. Since the more the vibrational modes involved, the smaller the corresponding probability, it generally suffices to consider the lowest order processes. For the molecules SF_6, the Fermi resonances and the anharmonic terms causing the corresponding transitions are the following[6]:

$$\begin{aligned} &\nu_3+\nu_6=\nu_1+\nu_5+16\ \mathrm{cm}^{-1}\ (q_1q_3q_5q_6),\\ &\nu_3+\nu_4=2\nu_1+16\ \mathrm{cm}^{-1}\ (q_1^2q_3q_4),\\ &\nu_3+\nu_6=2\nu_2+28\ \mathrm{cm}^{-1}\ (q_2^2q_3q_6),\\ &\nu_3+\nu_6=\nu_2+\nu_4+55\ \mathrm{cm}^{-1}\ (q_2q_3q_4q_6). \end{aligned} \tag{29}$$

We apply the well-known SSH theory[14] to treat these random processes. The SSH theory, though simple enough, has yielded quite good results in treating the intermolecular process of vibrational energy exchange.[15] Neglecting all deductions (see the Appendix), for the processes (29), we get

$$\begin{aligned} \frac{d\lambda_3}{dt}&=R\,(1{,}5\to3{,}6)+R\,(2{,}4\to3{,}6)\\ &\quad+R\,(1{,}1\to3{,}4)+R\,(2{,}2\to3{,}6), \end{aligned} \tag{30}$$

where

$$\begin{aligned} R\,(k,l\to i,j)&=P_{\binom{i,j}{k,l}}\{(1+\lambda_i)(1+\lambda_j)\lambda_k\lambda_l\\ &\quad-\lambda_i\lambda_j(1+\lambda_k)(1+\lambda_l)\}, \end{aligned} \tag{31}$$

and $R\,(k,l\to i,j)=-R\,(i,j\to k,l)$, $\lambda_i=E_i/\hbar\omega_i$ is the number of quanta of mode i (E_i the vibrational energy, ω_i the frequency). When $i=j$ (or $k=l$), we take them to be belonging to different degenerate energy levels. $P_{\binom{i,j}{k,l}}=P_{\binom{k,l}{i\,j}}$ is the transition probability of the process $(\nu_i+\nu_j=\nu_k+\nu_l)$ such that the quanta of i,j change from 1 to 0 (or 0→1) and the quanta of k,l from 0 to 1 (or 1→0). It is noteworthy that if the relevant modes of some process are in thermal equilibrium and can be characterized by temperature T, then $\lambda_i=\lambda_i^{(0)}\equiv\{\exp(\hbar\omega_i/kT)-1\}^{-1}$ and $R=0$ (the energy defect of the process being neglected), i.e. there is no energy exchange among them in average. For a polyatomic molecule, the number of background modes is numerous, and because they are not coupled with the laser, we can use the idea of "heat bath" and characterize their states by temperature T. For the active modes, naturally its energy cannot be described by temperature T. Specifically for SF_6 we put $\lambda_i=\lambda_i^{(0)}(T)$ $(i\neq3)$, $\lambda_3=\lambda_3^{(0)}+\lambda_3'$. From Eq. (30) we get

$$\frac{d\lambda_3}{dt}\cong-f^*(T)[\lambda_3-\lambda_3^{(0)}(T)], \tag{32}$$

where

$$\begin{aligned} &f^*(T)\\ &\quad=\left(\frac{1}{\lambda_3^{(0)}}-\frac{1}{1+\lambda_3^{(0)}}\right)\Big\{P_{\binom{1,5}{3,6}}(1+\lambda_6^{(0)})(1+\lambda_3^{(0)})\lambda_1^{(0)}\lambda_5^{(0)}\\ &\qquad+P_{\binom{3,4}{1,1}}(1+\lambda_1^{(0)})^2\lambda_3^{(0)}\lambda_4^{(0)}+P_{\binom{3,6}{2,2}}(1+\lambda_2^{(0)})^2\lambda_3^{(0)}\lambda_6^{(0)}\\ &\qquad+P_{\binom{3,6}{2,4}}(1+\lambda_2^{(0)})(1+\lambda_4^{(0)})\lambda_3^{(0)}\lambda_6^{(0)}\Big\}. \end{aligned} \tag{33}$$

Obviously the change of the background temperature T is much slower than the change of λ_3, we can take T as quasistationary. Equation (32) can be written as

$$\frac{d}{dt}[\lambda_3-\lambda_3^{(0)}(T)]=-f^*(T)[\lambda_3-\lambda_3^{(0)}(T)]. \tag{34}$$

On the other hand, for a harmonic oscillator with damping $m\ddot{x}+\nu\dot{x}+m\omega^2x=0$, the energy dissipation rate is $-\nu\dot{x}^2$. If we count the energy from its equilibrium value in Eq. (34), then Eq. (34) is also the dissipation equation, therefore $\nu\dot{x}^2=f^*(T)[\lambda_3-\lambda_3^{(0)}(T)]\hbar\omega$. Moreover, $\widehat{m\dot{x}^2/2}\cong\hbar\omega\lambda_3/2$ thus we get

$$\begin{aligned} \nu&=mf^*(T)[1-\lambda_3^{(0)}/\lambda_3]\\ &=mf^*(T)[1-E_v^{(0)}(T)/\hat{E}_v], \end{aligned} \tag{35}$$

where $E_v^{(0)}(T)=\hbar\omega\lambda_3^{(0)}(T)$, $\hat{E}_v$ is the energy of the active mode. Equation (35) makes the bridge connecting the viscosity ν and the probability P. The background temperature T is determined by the total energy $\hat{E}_t$. We use the convention that when $\hat{E}_t$ is distributed over all modes to reach an equilibrium state, the corresponding temperature T is called the background temperature. SF_6 has 15 modes, so the temperature T is defined by

$$\hat{E}_t=\sum_{i=1}^{15}\hbar\omega_i\{\exp(\hbar\omega_i/kT)-1\}^{-1}. \tag{36}$$

If the energy of the active mode is also characterized by T, then $\nu=0$ from Eq. (35). From Eq. (28) we see equation governing $\hat{E}_t$ should be (ν_3 has degeneracy 3)

$$\frac{d\hat{E}_t}{dt}=3\left(\frac{dE_v}{dt}+\frac{\nu}{m^2}w\right)=\frac{3\mu}{m}E(t)p_c. \tag{37}$$

Now the only problem unresolved is the transition probability P.

V. THE TRANSITION PROBABILITY P

Neglecting the rotational band temporarily, the energy levels of a specific vibrational mode can be approximately represented by $E_n=\hbar\omega[(n+1/2)-x_e(n+1/2)^2]$. It can be proved readily by perturbation theory[16] that an oscillator with the potential $(m\omega^2q^2/2-\epsilon q^4)$ possesses this energy structure, where $\epsilon=2x_em^2\omega^3/3\hbar$. From the spectroscopic data of SF_6,[17] for mode ν_3 we have $x_e=0.0013$. It is legitimate to assume the anharmonic part of the potential being derived from the expression, such as

$$\mathrm{U}_{AH} = -\frac{2}{3}x_e\left(\sum_{i=1}^{6} q_i'\right)^4, \tag{38}$$

where $q_i' = m_i^{1/2}\omega_i^{3/4}q_i/\hbar^{1/4}$, because this reduces to $(-\epsilon q^4)$ if all q_i vanish except $i = 3$. Expanding Eq. (38), we get the terms such as $q_1' q_3' q_5' q_6'$, which induces the transition $(1,5 \rightleftarrows 3,6)$ etc., therefore, we take the interaction potential among various modes as $-\frac{2}{3}x_e C q_1' q_3' q_5' q_6'$, etc., where C is a constant of order 1–10. From the conventional perturbation theory we get

$$P_{\binom{1,5}{3,6}} = \frac{\pi C^2}{18} x_e^2 \hbar (\omega_1\omega_5\omega_3\omega_6)^{1/2}\rho(E), \tag{39}$$

etc. In regard to the density of energy levels, if we follow the current quasi-continuum concept and consider the inevitable rotational energy change accompanying the vibrational energy transfer caused by Coriolis effect, we should seem to take the density of rotational energy levels. For the spherical top SF_6, its rotational energy $E_J = \hbar^2 J(J+1)/2A$ with degeneracy $(2J+1)^2$, thus $\rho(E) = dN/dE \cong 4AJ/\hbar^2$. The typical value of J at room temperature is 50. The result of numerical computation with this data put in shows that the energy exchange is too fast and the energy absorption can not match with the experiments. Recently, Abram *et al.*[5] also cast doubt on the quasi-continuum hypothesis. We are inclined to consider the correct physical picture as following. The Coriolis effect induces the degenerate vibrational levels to split and induces the scrambling of vibrational modes (this effect is particularly remarkable for spherical top[16]). In the intermodal energy exchange, not all $(2J+1)^2$ rotational levels play the same role, the density responsible for this energy exchange should be $dN/dE \cong (\Delta \mathrm{E})_c^{-1}$ where $(\Delta E)_c$ is the order of Coriolis splitting of degenerate vibrational levels, i.e.,[18] $(\Delta E)_c = \zeta J\hbar^2/A$, the constant ζ has order 1. This can also be interpreted as one kind of rotational compensation. For SF_6, $(\Delta E)_c$ is about 10 cm^{-1}, thus $\rho(E) \cong A/\hbar^2 J$. Put $J = 50$ into Eq. (39), we get

$$P_{\binom{1,5}{3,6}} = \frac{\pi C^2}{50\times 18\hbar} x_e^2 (\omega_1\omega_5\omega_3\omega_6)^{1/2} A. \tag{40}$$

The other probabilities can be calculated in a similar way. Thus far, we have completed our theoretical scheme. Except one adjustable parameter C, all is derived from the basic principles of physics.

VI. COMPUTATIONAL RESULTS AND DISCUSSION

The system of equations to be solved are Eqs. (23)–(27), or after eliminating p_c and v, are the following three equations involving q_c, u and w:

$$m\ddot{q}_c + v\dot{q}_c + m\omega^2 q_c = \frac{\mu}{3}E_0 \cos\omega_e t + 4\epsilon u q_c, \tag{41}$$

$$m\ddot{u} + v\dot{u} + 2m\omega^2 u - 2w/m - 8\epsilon u^2 = 2\mu E_0 \cos\omega_e t \cdot q_c, \tag{42}$$

$$m\dot{w} + 2vw + m^3\omega\dot{u} - 4\epsilon m^2 u\dot{u} = 2\mu m^2 E_0 \cos\omega_e t \cdot \dot{q}_c \times [E(t) = E_0\cos\omega_e t]. \tag{43}$$

$\hat{E}_v$ and $\hat{E}_t$ can be determined from Eqs. (28) and (37). We use the usual method of "slowly varying amplitude"[19] to solve Eqs. (41)–(43). Put

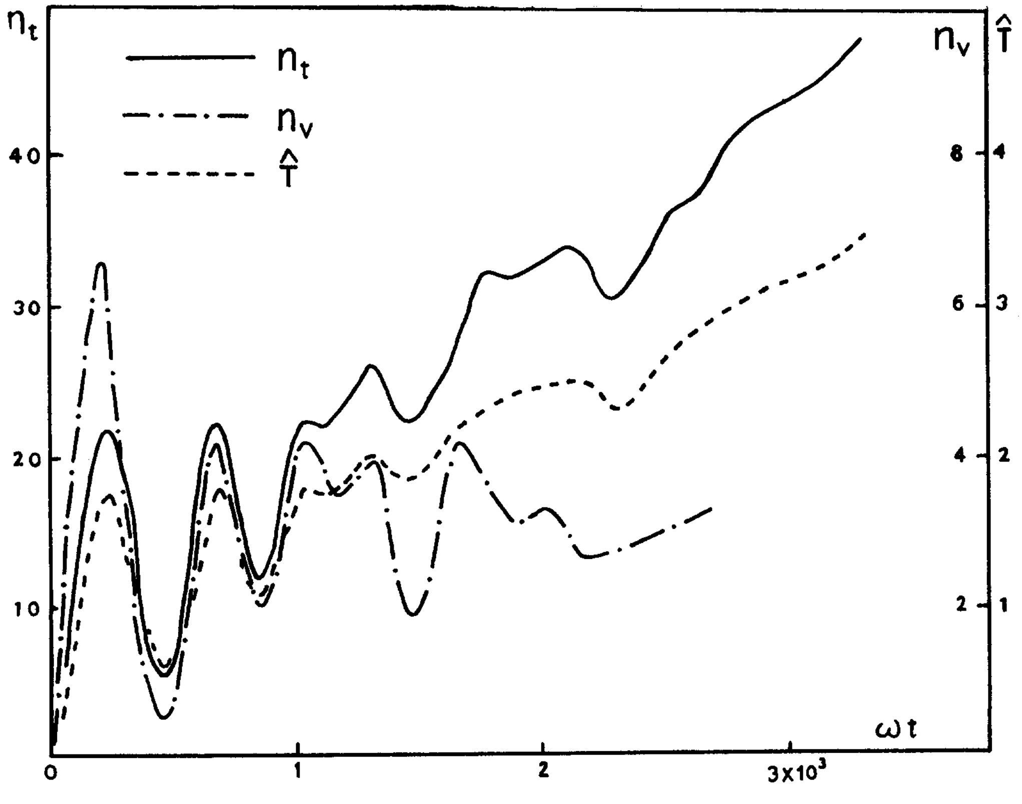

FIG. 1. Unimolecular energy absorption of SF_6. Intensity of laser $I = 10^{10}$ W/cm^2. Laser frequency $\omega_e = CO_2\,P(20) = 0.996\omega$, ω the frequency of ν_3 mode. n_t = number of photons absorbed by one molecule. n_v = number of photons absorbed by each ν_3 mode. $T = kT/\hbar\omega$. T the equivalent vibrational temperature.

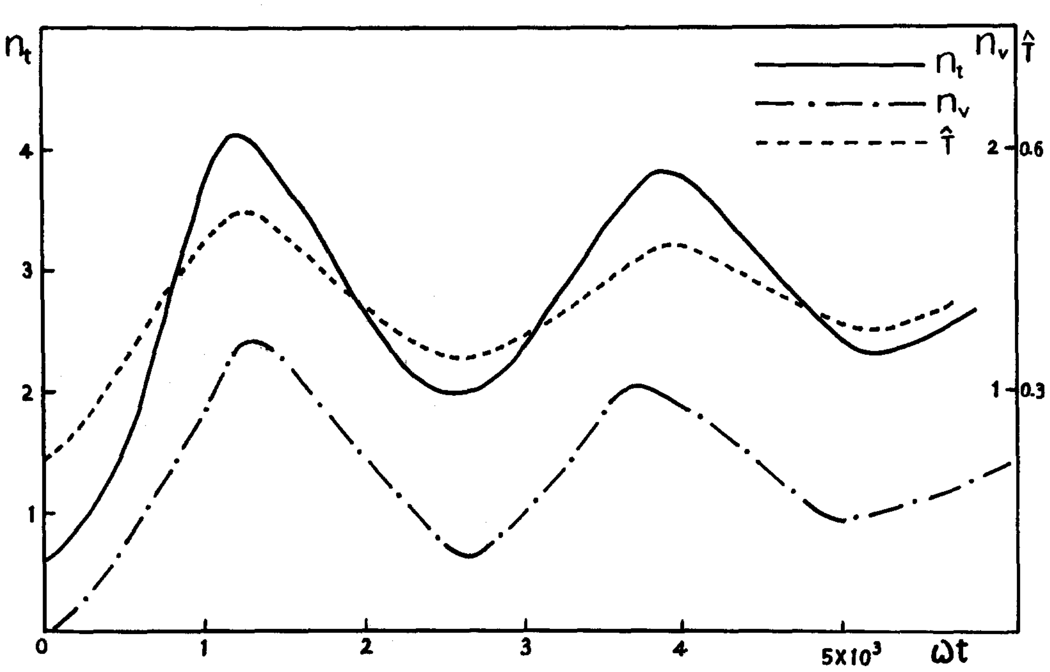

FIG. 2. Unimolecular energy absorption of SF_6. $I = 10^8$ W/cm^2. $\omega_e = 0.999\omega$. Other symbols have the same meanings as in Fig. 1.

$$
\begin{aligned}
q_c &= Q_1(t)\cos\omega_e t + Q_2(t)\sin\omega_e t,\\
u &= U_0(t) + U_1(t)\cos 2\omega_e t + U_2(t)\sin 2\omega_e t, \qquad (44)\\
w &= W_0(t) + W_1(t)\cos 2\omega_e t + W_2(t)\sin 2\omega_e t,
\end{aligned}
$$

where all Q, U, W are assumed to be slowly varying (compared with ω_e) functions of t. Substituting Eq. (44) into Eq. (41)–(43), neglecting $\ddot{Q}$, $\ddot{U}$, $\ddot{W}$ and all terms of frequencies higher than ω_e or $2\omega_e$, we obtain a system of equations involving $\dot{Q}, \dot{U}$, $\dot{W}$, and then solve them numerically. In the course of computation, v is determined from Eq. (35), T from Eq. (36), $P_{\left(\substack{1,5\\3,6}\right)}$ from Eq. (40), etc. After trial computations, we decided to take $C = 1$. If C varies in a certain range (e.g., $0.8 < C < 3$), only the numerical value of energy absorption changes, the physical picture remains the same. The other data needed in such computations are: The frequencies of various modes of SF_6, $\omega_1 = 773.6$, $\omega_2 = 642$, $\omega_3 = 948$, $\omega_4 = 615$, $\omega_5 = 523$, $\omega_6 = 364$ cm^{-1}, the dipole moment of each ν_3 mode taken from the average value given by Bloembergen[20] but divided by $\sqrt{3}$. As for the initial conditions, we should take into account the zero point oscillation,[22] so $m\omega^2\widehat{q^2_{(0)}} = \widehat{p^2_{(0)}}/2m = \hbar\omega/4$ (the effect of room temperature is neglected due to its smallness). Since $\widehat{\cos^2\theta} \cong 1/2$, we take $q_c(0) = \sqrt{\widehat{q_c^2(0)}} = \frac{1}{2\sqrt{2}}\sqrt{\hbar/(m\omega)}$. Besides, we put $U(0) = \hbar(2m\omega)^{-1}$, $W(0) = m\omega\hbar/2$, $U_1(0) = U_2(0) = W_1(0) = W_2(0) = 0$, $T(0) = 300°$ K. Figures 1 and 2 depict the typical results. At low laser intensity, the bottle neck effect due to anharmonicity is not overcome yet, the average absorption shows nearly periodic structure with average value slowly increasing with time. At high laser intensity, due to the strong intermodal interaction and the scrambling of energy levels, the energy absorption is significantly enhanced. If the pulse duration is fixed, the energy absorptions increase with the fluence (Fig. 3), i.e., with the intensity. The increase of absorption with laser intensity is much faster than the increase with time at fixed intensity. At high intensities, particularly, the absorption strongly depends on laser intensity (Fig. 4). This demonstrates clearly the difference between the present theory and the quasi-continuum (QC) theory. In the latter case, one replaces the Schrödinger equation by appropriate rate equations, and in doing so, the phase relation between the excitation force and the molecular vibration is completely neglected. This approximation is valid only when the intramolecular dephasing time T_2 is much shorter than the characteristic transition time ω_R^{-1}, or[7]

$$\omega_R < T_2^{-1}, \qquad (45)$$

where $\omega_r = \hbar^{-1}\mu E_0$ is the Rabi frequency. But for the picosecond pulses with high intensity, as pointed out in Ref. 7, the inequality (45) is not obeyed and hence the QC theory is

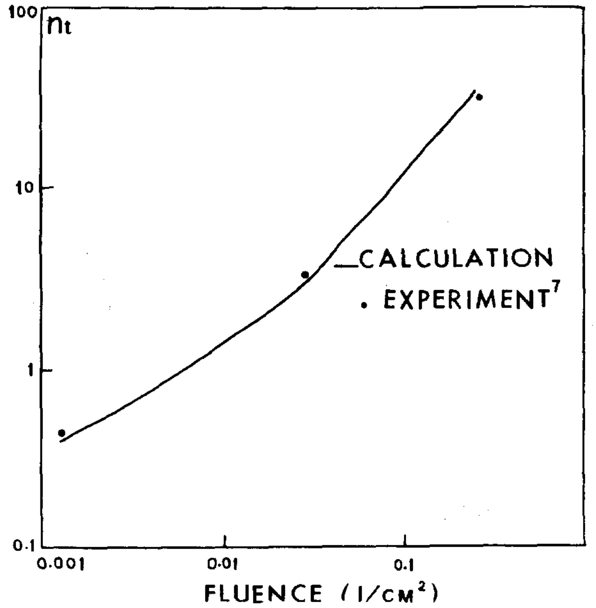

FIG. 3. Relationship between energy absorption of SF_6 and fluence. $\omega_e = P(20)CO_2$. Pulse duration 30 ps.

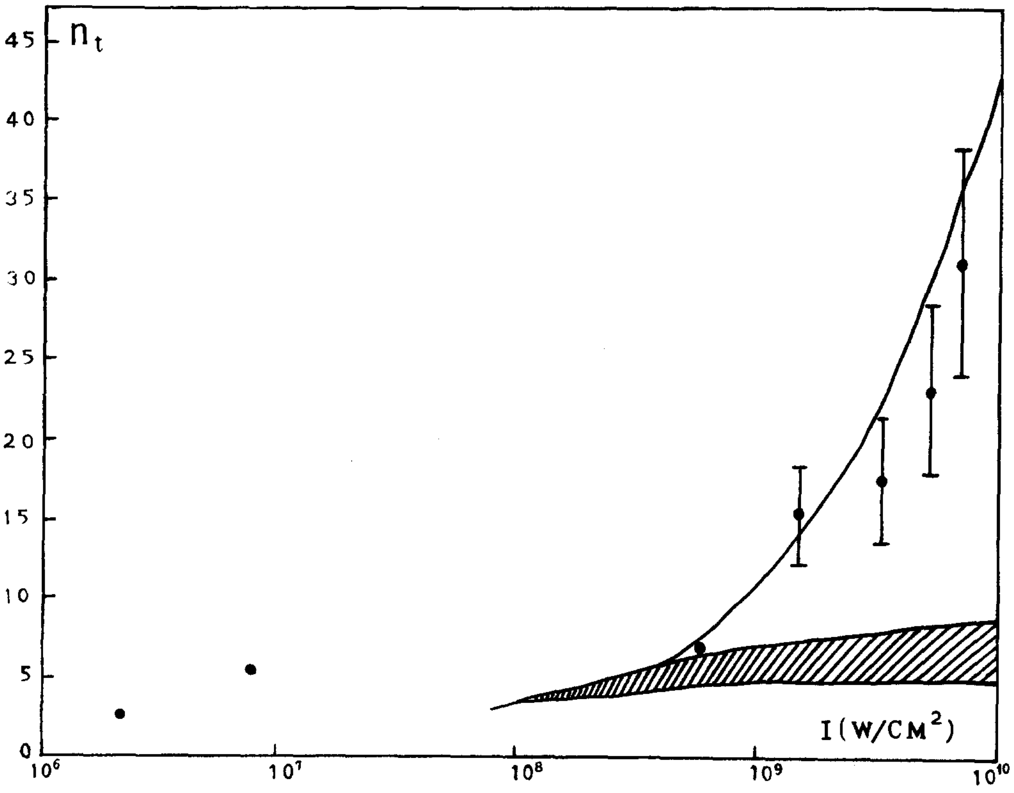

FIG. 4. Relationship of energy absorption of SF_6 with laser intensity. Fluence = 0.2 J/cm^2. ● experimental results (Ref. 7),— present theory. The shade area represents the asymptotic behavior based on quasicontinuum theory (Ref. 7). The vertical lines are the error bars in the experiments.

invalid. While in this paper, we observe the phase relation between the excitation and the active mode from the beginning and therefore the effect of coherent excitation is included, though approximately. But due to the introduction of viscosity ν, the dephasing time T_2 can not be predicted accurately. The familiar results of red shift in absorption for SF_6 is also revealed in our computation. For instance, when $I = 10^{10}$ W/cm^2, the peak of absorption is at $\omega_e = 0.996\omega$, while when $I = 10^8$ W/cm, it is at $\omega_e = 0.999\omega$. Figure 5 shows the change of $E_v^{(0)}/\hat{E}_v$ with time, this ratio embodies the extent of approaching equilibrium among various modes. When the intensity is low, although the absorption is

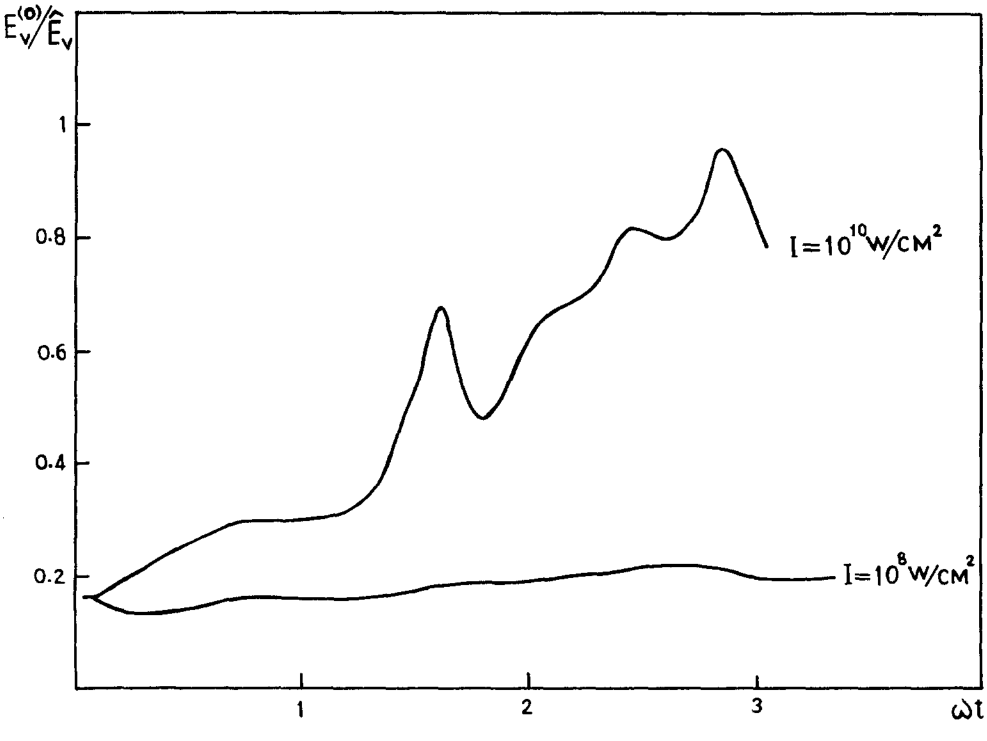

FIG. 5. $\hat{E}_v$, the vibrational energy of ν_3 mode. $E_v^{(0)}$, the vibrational energy of ν_3 mode at "equilibrium" temperature.

weak, the imbalance of the energy between the active mode and the background persists and does not decay to thermal equilibrium. But when the intensity is high, the energy distribution approaches thermal equilibrium more readily. We can also see from these results that just as in previous investigations,[21] the isotope selectivity is determined essentially by the match of laser frequency with the frequency of the active mode. This match or mismatch controls the excitation of molecular vibration. Due to intermodal interaction, say when $I = 10^{10}$ W/cm^2, after the duration of several hundreds of vibrational periods, the energy absorbed is basically distributed evenly over different modes, and the excitation cannot be bond- selective, neither can the dissociation channel be controlled. Also no wonder that the experiments carried out several years ago with a ns pulse could be explained very well by the statistical RRKM theory.[21] If we want to achieve mode-selective excitation, it seems we should further compress the pulse duration and experiment on the molecules with less symmetry and less degeneracy.

ACKNOWLEDGMENTS

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APPENDIX: THE PROBABILITY DESCRIPTION OF THE INTRAMOLECULAR VIBRATIONAL ENERGY EXCHANGE

The process of vibrational energy exchange in SF$_6$ molecule through Fermi resonance, e.g.,

$$\nu_3 + \nu_6 = \nu_1 + \nu_5 + 16\ \mathrm{cm}^{-1}$$

is governed by the anharmonic term $q_1 q_3 q_5 q_6$ of the potential. We abbreviate this process as $(a + b \rightleftarrows c + d)$. For this monomolecular reaction of a system of molecules, suppose that the probability of the vibrational quanta number being (l, k, i, j) is (here and afterwards, we use the approximation of harmonic oscillators)

$$C_{l,k,i,j} = C_l^{(a)} C_k^{(b)} C_i^{(c)} C_j^{(d)}, \tag{A1}$$

where $C_l^{(a)}$ is the probability such that the quanta number of vibrational mode a is l. Let $P\begin{pmatrix} l\to l+1, i\to i-1 \\ k\to k+1, j\to j-1 \end{pmatrix}$ be the transition rate of the corresponding process, then we have

$$\begin{aligned}\frac{dP_l^{(a)}}{dt} = &-\sum_{\substack{k=0\\ i=j=l}} C_{l;k,i,j} P\begin{pmatrix} l\to l+1, i\to i-1 \\ k\to k+1, j\to j-1 \end{pmatrix} \\ &-\sum_{\substack{k=1\\ i=j=0}} C_{l,k;i,j} P\begin{pmatrix} l\to l-1, i\to i+1 \\ k\to k-1, j\to j+1 \end{pmatrix} \\ &+\sum_{\substack{k=1\\ i=j=0}} C_{l+1,k;i,j} P\begin{pmatrix} l+1\to l, i\to i+1 \\ k\to k-1, j\to j+1 \end{pmatrix} \\ &+\sum_{\substack{l=0\\ i=j=1}} C_{l-1,k;i,j} P\begin{pmatrix} l-1\to l, i\to i-1 \\ k\to k+1, j\to j-1 \end{pmatrix}.\end{aligned} \tag{A2}$$

Also we have

$$P\begin{pmatrix} a,b,0\to 1 \\ c,d,1\to 0 \end{pmatrix} = P\begin{pmatrix} a,b,1\to 0 \\ c,d,0\to 1 \end{pmatrix} \equiv P \tag{A3}$$

and

$$P^{(a)}_{l\to l+1} = (l+1) P^{(a)}_{0\to 1}, \tag{A4}$$

then multiplying Eq. (A2) by l, summing over l, and noticing that

$$\begin{aligned} &P\begin{pmatrix} l\to l+1, i\to i-1 \\ k\to k+1, j\to j-1 \end{pmatrix} \\ &= P^{(a)}_{l\to l+1} P^{(b)}_{k\to k+1} P^{(c)}_{i\to i-1} P^{(d)}_{j\to j-1}, \end{aligned} \tag{A5}$$

$$\sum_{l=0}^{\infty} P_l^{(a)} = 1, \tag{A6}$$

$$\sum_{l=0}^{\infty} l P_l^{(a)} = \frac{E^{(a)}}{\hbar \omega_a} = \lambda_a, \tag{A7}$$

etc., where $E^{(a)}$ is the energy of mode a, we finally get

$$\begin{aligned}\frac{1}{P}\frac{d\lambda_a}{dt} = &(\lambda_a + 1)(\lambda_b + 1)\lambda_c \lambda_d \\ &- \lambda_a \lambda_b (\lambda_c + 1)(\lambda_d + 1).\end{aligned} \tag{A8}$$

Considering all the relevant processes, we get Eq. (30) in the text.

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