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Resonant photon-catalyzed predissociation and autoionization: Fragment yield, rate constant, and rotational line strengths

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General theory and analytic results are given for calculating the fragment yield and the rate constant of bound-to-continuum decompositions of atoms or molecules induced by a multiphoton effect called the resonant photon-as-catalyst effect (PCE). In this effect the rate constant of the reaction is increased due to the presence of the photons while the total number N of photons in a given mode of the electromagnetic field is conserved. The decomposition processes include (1) photon-catalyzed (PC) predissociation from excited states of molecules in general, as well as from ground states in some cases of polyatomic molecules: $AB+N\hbar\omega\rightarrow A+B+N\hbar\omega$; and (2) PC autoionization of atoms or molecules: $A+N\hbar\omega\rightarrow A^{+}+e^{-}+N\hbar\omega$. Both pulsed and continuous-wave laser irradiation are studied. Optimization of the yield and the rate constant by the lifetimes of the molecular states are studied for the first time. Resonant enhancement [Lau, Phys. Rev. Lett. <u>43</u>, 1009 (1979)] and coherent saturation [Lau, Phys. Rev. A <u>22</u>, 614 (1980)] in this effect are further elaborated. Laser-stimulated decays and optical Stark shifts due to the continua and other nonresonant discrete states are included in the theory. The rotational line strengths for symmetric top molecules predissociated by resonant PCE using linear-polarized laser radiation are also given.

I. INTRODUCTION

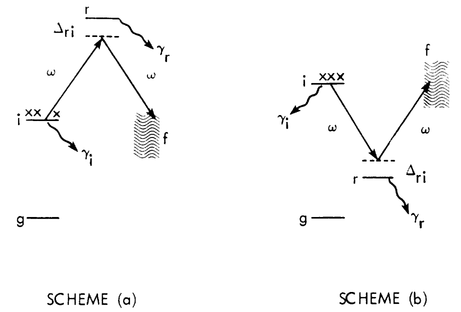
This paper gives the general theory and analytic results for the calculation of the fragment yield and the rate constant (i.e., the probability rate per unit time per molecule) of atomic or molecular decompositions involving bound-to-free transitions induced by the photon-as-catalyst effect (PCE). Specifically, these processes include: (1) photon-catalyzed (PC) predissociation of molecules AB,

$$AB+N\hbar\omega\rightarrow A+B+N\hbar\omega\ , \tag{1.1}$$

and (2) PC autoionization of atoms and molecules A,

$$A+N\hbar\omega\rightarrow A^{+}+e^{-}+N\hbar\omega\ , \tag{1.2}$$

where the reaction conserves the total number N of photons in a given mode of the electromagnetic field (EMF), such as that provided by a single-mode laser. As illustrated in Fig. 1, the PCE consists of a parent atom or molecule initially in a bound state $|i\rangle$ being induced to make transition via the intermediate states $|r\rangle$ to an "equal-energy" continuum $|f\rangle$ leading to the fragments by the virtual or real absorption of one (or more) photons of a given EMF mode and the stimulated emission of an equal number of laser photons of the same mode (i.e., the same frequency ω, polarization $\hat{e}$, and propagation vector $\hat{k}$). Since the rate constants of these unimolecular reactions are increased while the number of photons N is conserved, the photons are acting as catalysts.



SCHEME (a) SCHEME (b)

FIG. 1. Photon-as-catalyst effect in laser-induced decomposition of atoms or molecules consists of the population in initial bound states $|i\rangle$ making transition to the continuum $|f\rangle$ via intermediate states $|r\rangle$ by the absorption of one (or more) laser photons and the stimulated emission of an equal number of laser photons. The decay rates of the states are represented by γ's.

The PCE was first introduced by Lau and Rhodes[1,2] and was novel to laser-induced molecular processes and photochemistry, where the molecular processes are usually initiated by the actual absorption or emission of photons.[3] In principle, the effect consumes zero photon per product molecule in the PC reaction itself. It is therefore a *highly nonstoichiometric* use of laser photons to do photochemistry. From the viewpoint of practical applications, this is a desirable feature, according to the recommendations of two recent surveys of laser photochemistry.[4,5] There are, of course, other processes causing the loss of laser photons, such as Raleigh and Raman light scattering, and perhaps single-photon or multiphoton absorption. Depending on the particular molecule under consideration, some of these undesirable losses may be minimized or avoided. Through the laser-intensity dependence in its rate constant, the PCE may become dominant over other processes by increasing the laser intensity.

For PC bound-to-free processes, the works of Lau and Rhodes and some later works[6,7] have studied the common cases in which the laser frequency ω is nonresonant with the molecular transitions between the initial and the intermediate states. However, two earlier papers[8,9] have analyzed the (near) resonant cases. Generally speaking, the bound-free PCE, for example, in its lowest order of absorption of one photon and stimulated emission of another photon of the same mode, is at least as likely to occur as the known two-photon dissociation or ionization process starting from the same initial states and for comparable magnitudes of transition moments. The resonant (denotes hereafter both near-resonant and on-resonant) cases have several advantages. First, the signal is greatly enhanced compared to that of nonresonant cases, thus reducing the required laser power for a given signal.[8] Secondly, the resonant bound-bound transition can readily be coherently saturated. Then the rate constant or cross section for PCE becomes as large as a single-photon bound-free process.[9] This has the important consequence that the PCE can compete with and may, in some cases, dominate over the single-photon processes. The simple theoretical expressions of the probability rate given without derivation in these earlier papers[8,9] were adequate to discuss these physical points. However, for obtaining a probability of fragment yield over a given interaction time, these probability rates are sufficient only when the interaction time is short compared to the lifetimes of the molecular states.

Continuing the study of the resonant PCE, the present paper gives considerably more general and more detailed results, together with their theoretical justifications. With the new results here, it is now possible to calculate the probability of fragment yield for laser pulses whose durations are comparable to or longer than the molecular lifetimes, as well as for those that are short. In the present treatment, the effective lifetimes of the initial and intermediate states are allowed to be unequal. This is, of course, more realistic. The probability rate given here becomes identical to that in earlier works[8,9] when the two lifetimes are equal.

While the initial bound states in PC predissociation are in many cases electronically excited states of diatomic or polyatomic molecules, or excited rotational-vibrational states in the ground electronic states of polyatomic molecules, the PCE can be applied to some polyatomic molecules in the thermally populated *ground* states if their energies lie higher than the sum of the internal energies of the two fragments. The molecule is initially stable in this case due to the high activation energy barrier, as shown in Fig. 2. The resonant PCE can induce transition from these ground states to the dissociative continuum (corresponding to the two fragments) via intermediate states lying above or below the peak of the energy barrier. For the theoretical results in this paper to be directly applicable, the same intermediate state must have vibrational overlaps with both the bound and the continuum states. In general, however, the PCE transitions may involve absorption into a bound intermediate state which rapidly decays intramolecularly into another intermediate state. From the latter, stimulated em-

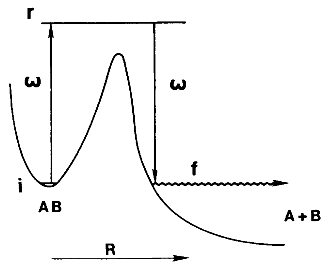


FIG. 2. Photon-catalyzed predissociation (or dissociation) of polyatomic molecules in thermally populated ground states, whose energies lie higher than the sum of internal energies of the fragments A and B. As the plot of potential surface along the dissociation coordinate shows, the initial states are stable due to the high activation energy barrier.

ission to the final continuum completes the PCE transitions. In any case, if the high activation energy barrier forbids any tunneling, the PCE in effect opens up a new dissociation channel by circumventing the potential barrier. This is in addition to the possibility of new channels due to new selection rules[2,6,7] Having the molecules in the thermally populated ground states as initial states for PCE is advantageous because no additional energy of any form is needed to prepare the initial-state population and because the PCE can act over the long lifetimes of the ground states. This would likely reduce the required laser power (see below). Although one may call the situations described in this paragraph photon-catalyzed dissociation, we shall include it under PC predissociation. The reason is that the term predissociation further conveys the notion that the dissociation does not require the net absorption of an amount of external energy in order to overcome the dissociation barrier.

Although all published works on PC bound-free transitions so far were presented in the context of PC predissociation of molecules, where the bound-free transition involves vibrational motion, it is clear[10,11] that the same idea, formal theory, and analytic results also apply to autoionization,[12] where the bound-free transition is electronic. Since the PC fragments in this case are charged particles, which can be detected more readily by such techniques as ejected-electron spectroscopy,[13] autoionizing states, especially the metastable ones, are good candidates for experimental demonstration of PCE. The peak(s) in the electron spectrum due to PCE should be narrow, equal in energy to the initial states, and possess laser-parameter dependence described in this and earlier papers.[1,2,6–9] As examples, the long-lived quartet states in the alkali atoms[14,15] can be PC autoionized via the metastable doubly excited even-parity ^2P states.[15,16] An example for Li,

$$\mathrm{Li}(1s\,2s\,2p\,^4P^o)+N\hbar\omega\rightarrow\mathrm{Li}^+(1s^2\,^1S)+e^-+N\hbar\omega\ , \tag{1.3}$$

is given in Fig. 3. The initial-state population can be prepared by electron or ionic bombardment of the neutral atoms in the ground state.[13,14] Recently, these quartet and discrete doublet states are the proposed storage states and upper lasing states, respectively, for XUV lasers.[17,18] Since the intermediate-to-continuum transition in process (1.3) is electric-dipole allowed, process (1.3) and two-photon ionization via the $(1s\,2p^2\,^2P)$ level may perhaps become significant processes when the proposed high-power transfer laser irradiates on the quartet-state populations.

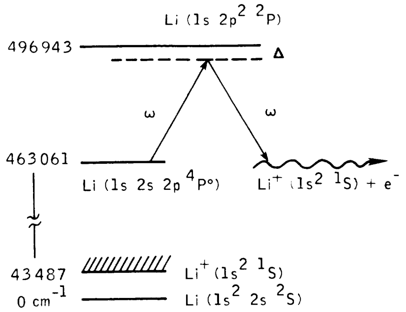


FIG. 3. Proposed photon-catalyzed autoionization of Li in the metastable quartet state $|\,1s\,2s\,2p\,^4P^o\rangle$ to yield Li^+ ions and electrons.

The bound-to-free transitions in PC predissociation and PC autoionization are induced directly by the radiation. Similarly, laser-induced predissociation from predissociative states by actual absorption or stimulated emission of photons has also been studied[7] and it was shown that the PCE may be considered as a new type of photon-number-conserving multiphoton processes. Recently, laser-induced autoionization by actual single-photon or two-photon absorption from autoionizing states was also analyzed.[19] In the more familiar photo-predissociation[20] and photo-autoionization[12,21] processes, although the population in the bound states are prepared by single-photon or multiphoton absorption, the predissociative or autoionizing transitions are not radiatively stimulated. Although the idea of PCE and the theoretical formulation given in Lau and Rhodes were shown to be applicable also to free-free transitions such as dissociations and collisions,[1,2] the theory and results in this paper cannot be applied directly to such cases. Recently, Weiner applied the theory of Lau and Rhodes to analyze PCE-modified dissociation in alkali halides.[22] In this PC free-free transition, the molecule is already in the dissociative continuum when the PCE causes transition to another equal-energy continuum belonging to a different channel, thus changing the branching ratio of ion versus neutral production. Generally speaking, the PC free-free transition requires higher laser power to induce the same probability than the PC bound-free transition, because in the latter case, the PCE can act over the considerably longer lifetime of the bound state.

The rest of the paper is organized as follows.

Section II contains the main body of the theory and results for resonant PC decompositions represented in Figs. 1 and 2. Section II A presents the treatment on single-mode laser pulses of smooth but arbitrary shape in time. Section II B gives the analytic results for pulsed or continuous-wave irradiation at constant laser intensity. In Secs. II C and II D, the effect of lifetimes on the coherent saturation and the resonance enhancement, respectively, are studied. From the results in Sec. II, we deduce a set of optimization criteria for selecting atomic or molecular candidates for PCE. This is given in Sec. III. In Appendix A, it is shown that when the optical Stark shifts of molecular energy levels or the laser-stimulated decays are important, they can be incorporated into the results in Sec. II by a straightforward substitution of parameters. In Appendix B, the rotational transition strengths for the resonant PC predissociation of symmetric-top molecules (including the diatoms) interacting with linear-polarized laser radiation are given. Previously, only those for the nonresonant PC predissociation were given.[6]

II. CALCULATION OF YIELD AND PROBABILITY RATE

A. Smooth time-varying laser pulses

For the reactions (1.1) and (1.2), the total yield Y of one of the photon-catalyzed fragments is given by $Y=N_m P$, where N_m is the total number of irradiated atoms or molecules in all the initial bound states $|i\rangle$ and where P is the average probability of photon-catalyzed decomposition (predissociation or autoionization) from the initial states $|i\rangle$,

$$P=\sum_i g_i P_i \ , \tag{2.1}$$

and g_i are the probability distribution of population in $|i\rangle$ such that $\sum_i g_i=1$, and P_i is the probability of photon-catalyzed decomposition from the state $|i\rangle$. This section gives the theory for the calculation of P_i.

The total Hamiltonian H for the present problem consists of the Hamiltonian for the molecule H_m; the Hamiltonian for the electromagnetic field H_r; and the interaction Hamiltonian H'. The eigenvalues and eigenstates of H_m and H_r are defined by the following relations:

$$H_m\,|m\rangle=E_m\,|m\rangle\equiv\hbar\omega_m\,|m\rangle \ , \tag{2.2}$$

and

$$H_r\,|n\rangle=\hbar\omega a^{\dagger}a\,|n\rangle=n\hbar\omega\,|n\rangle \ . \tag{2.3}$$

Although higher multipole moments may be readily included, it is sufficient for most purposes to consider the electric-dipole interaction only. In this case, the interaction Hamiltonian H' is given by

$$H'=-\sum_l q_l\vec{r}_l\cdot\vec{\mathrm{E}} \ , \tag{2.4}$$

where the electric field operator $\vec{\mathrm{E}}$ is given by[23]

$$E=i\left[\frac{2\pi\omega\hbar}{V}\right]^{1/2}(a-a^{+})\hat{\epsilon} \ , \tag{2.5}$$

for one electromagnetic field mode having angular frequency ω, linear polarization $\hat{\epsilon}$, and propagation vector $\hat{k}$. (V is the quantization volume.) Expanding the total wave function ψ in terms of the basis states $|m'n'\rangle\equiv|m'\rangle|n'\rangle$ of the noninteracting molecule-field composite system,

$$\psi(t)=\sum_{m'n'} b_{m'n'}(t)e^{-i\omega_{m'n'}t}\,|m'n'\rangle \ , \tag{2.6}$$

and substituting into the Schrödinger equation, one obtains

$$i\hbar\frac{db_{mn}(t)}{dt}=\sum_{m'n'}H'_{mnm'n'}e^{-i\Delta_{m'n'mn}t}b_{m'n'}(t) \ . \tag{2.7}$$

Note that the molecular states $|m\rangle$ and $|m'\rangle$ refer to continua as well as to discrete states. The interaction matrix element $H'_{mnm'n'}$ will be expressed in terms of the electric-dipole transition moment $D_{mm'}\equiv\langle m\,|\sum_l q_l\vec{r}_l\,|m'\rangle\cdot\hat{\epsilon}$ or the Rabi flopping frequency $\chi_{mm'}$ by the following relations[24]:

$$\begin{aligned}H'_{mnm'n'}&=\pm i\left[\frac{2\pi}{c}I\right]^{1/2}D_{mm'}\delta_{n,n'\pm1}\\&=\pm i\tfrac{1}{2}\hbar\chi_{mm'}\delta_{n,n'\pm1} \ ,\end{aligned} \tag{2.8}$$

where the spectrally integrated laser intensity I is related to the mean number N (a very large number compared to unity) of photons in the EMF mode by the relation

$$I=c\hbar\omega N/V\cong c\hbar\omega(N\pm1)/V \ . \tag{2.9}$$

The frequency difference $\Delta_{m'n'mn}$ used in Eq. (2.7) is defined by

$$\Delta_{m'n'mn}\equiv\omega_{m'}-\omega_m+(n'-n)\omega \ . \tag{2.10}$$

With reference to Fig. 1, the photon-as-catalyst effect consists of transitions from $|iN\rangle$ to $|fN\rangle$ via $|rN-1\rangle$ in scheme (a) or via $|rN+1\rangle$ in scheme (b). For a given initial state $|i\rangle$, it is assumed that $|r\rangle$ is the only state that is near resonant with the laser frequency, i.e., when the frequency detuning,

$$\Delta_{ri} \equiv \omega_r - \omega_i \mp \omega \ , \tag{2.11}$$

is not much larger than $i \leftrightarrow r$ transition linewidth nor the laser linewidth. The probability amplitudes $b_i \equiv b_{iN}$ and $b_r \equiv b_{rN\mp 1}$ of the two discrete composite states are coupled by the differential equations obtained from Eq. (2.7),

$$\frac{d}{dt} b_i = -\frac{\gamma_i}{2} b_i \pm \frac{\chi_{ir}}{2} b_r e^{-i\Delta_{ri} t} \ , \tag{2.12}$$

and

$$\frac{d}{dt} b_r = -\frac{\gamma'_r}{2} b_r \mp \frac{\chi_{ri}}{2} b_i e^{+i\Delta_{ri} t} \ . \tag{2.13}$$

In Eqs. (2.11)–(2.13) the upper and lower signs correspond to the schemes (a) and (b), respectively. The total decay rate γ'_r for the intermediate state is a sum of its natural decay rate γ_r and the laser-stimulated $|r\rangle \rightarrow |f\rangle$ transition rate, γ_{fr}, which is necessarily present in PCE:

$$\gamma'_r \equiv \gamma_r + \gamma_{fr} \ , \tag{2.14}$$

and

$$\gamma_{fr} = \frac{4\pi^2}{\hbar c} I \sum_f{}' \, |D_{fr}|^2 \rho_f(E_i) \ , \tag{2.15}$$

where $\rho_f(E_f)$ is the density of the vibrational continuum of the final states defined in the normalization of the continuum, $\langle E_f | E'_f \rangle = \rho_f^{-1} \delta(E_f - E'_f)$; and the summation $\sum'_f$ is carried over other discrete quantum numbers of the final states. For simplicity here, we shall use just the natural decay rate γ_i for the state $|i\rangle$. If any laser-stimulated decays of $|i\rangle$ are important, they can be readily incorporated into the results as shown in the Appendix A. The natural rates γ_i and γ_r may include spontaneous radiative decay, nonradiative relaxation, and collisional quenching. In Eqs. (2.12) and (2.13), treating the original interaction term of $|r\rangle$ with the $|f\rangle$ state as a decay term (see Appendix A) means that the continuum states are acting as a sink of molecular population from $|r\rangle$. It neglects any coherent Rabi population oscillation from the continuum $|f\rangle$ back to the bound state $|r\rangle$. This assumption is intuitively very reasonable, since the fragments once in the region of small separation of the continuum state will fly apart rapidly into the large-distance region where there is negligible transition to the bound wave functions.[25]

Eqs. (2.12) and (2.13) are to be solved with the initial conditions,

$$b_i(0) = 1, \quad b_r(0) = 0 \ , \tag{2.16}$$

at the time $t=0$ when the interaction is switched on. For the general case of a time-varying laser pulse, the intensity $I(t)$ and hence χ_{ri} and γ'_r are time dependent. Then the above equations can be solved numerically for $b_r(t)$. But in Sec. II B below, an analytic solution is given for a field amplitude constant over a time interval whose value may range from short to long compared to the lifetimes of the states.

The Schrödinger equation for the probability amplitude $b_f(t) \equiv b_{fN}(t)$ is

$$\frac{d}{dt} b_f = \pm \frac{1}{\hbar} \left[\frac{2\pi}{c} I \right]^{1/2} D_{fr} b_r e^{-i\Delta_{rf} t} \ , \tag{2.17}$$

where

$$\Delta_{rf} \equiv \omega_r - \omega_f \mp \omega \ , \tag{2.18}$$

and $b_f(0) = 0$. In general, it can be integrated immediately to obtain the desired probability amplitude,

$$b_f(t) = \pm \frac{1}{\hbar} \int_0^t dt' \left[\frac{2\pi}{c} I \right]^{1/2} D_{fr} b_r e^{-i\Delta_{rf} t'} \ , \tag{2.19}$$

with b_r obtained from the solution of Eqs. (2.12) and (2.13). Alternatively, a result can be obtained as follows. The factor Δ_{rf} in Eq. (2.19) may be rewritten as $\Delta_{ri} - \Delta_{fi}$, where $\Delta_{fi} = \omega_f - \omega_i$. Then, consider a time interval δt such that it is small compared to the duration τ_p of the slow time-varying laser pulse, to the Rabi flopping period χ_{ri}^{-1}, to the inverse of the frequency detuning, $1/\Delta_{ri}$ and to the lifetimes $1/\gamma'_r$ and $1/\gamma_i$, i.e.,

$$\delta t << \tau_p \ , \tag{2.20a}$$

$$\delta t << \chi_{ri}^{-1}, \quad 1/\Delta_{ri} \ , \tag{2.20b}$$

and

$$\delta t << 1/\gamma'_r, \quad 1/\gamma_i \ . \tag{2.20c}$$

Then over the short-time domain, $\omega_i^{-1}, \omega_f^{-1} << t < \delta t$, the quantities $I(t)$ and $b_r(t) e^{-i\Delta_{ri} t}$ may be assumed to be essentially constant and may be taken out of the time-integral in integrating Eq. (2.19) over this time domain. The result after taking absolute square is

$$|b_f(t)|^2=\frac{4\pi^2}{\hbar^2 c}I\,|D_{fr}|^2|b_r|^2 t\delta(\Delta_{fi})\ , \tag{2.21}$$

where the identity[23] for $t >> \omega_f^{-1}$, and ω_i^{-1},

$$\frac{1-\cos\Delta_{fi}t}{\Delta_{fi}^2}=\pi t\delta(\Delta_{fi})\ , \tag{2.22}$$

has been used. Summing the contribution to all the final continuum states, one obtains the total probability at time t,

$$\sum_f{}' \int dE_f\rho_f\,|b_f(t)|^2=\frac{4\pi^2}{\hbar c}I\sum_f{}'\,|D_{fr}|^2\rho_f\,|b_r|^2 t\ . \tag{2.23}$$

From Eq. (2.23), an "instantaneous" (but on coarse-grained time $t\sim\delta t$) probability rate $\tilde{\gamma}_i(t)$ for a given initial state $|\,i\,\rangle$ can be defined,

$$\tilde{\gamma}_i(t)=\gamma_{fr}(t)\,|b_r(t)|^2\ , \tag{2.24}$$

where $\gamma_{fr}(t)$, given in Eq. (2.15), is the instantaneous probability rate of transition from $|\,r\,\rangle$ to $|\,f\,\rangle$. Equation (2.24) says that for near-resonant transition from $|\,i\,\rangle$ to $|\,r\,\rangle$, the instantaneous photon-catalyzed probability rate is given by the probability $|b_r(t)|^2$ of finding the molecular system in the state $|\,r\,\rangle$ multiplied by the probability rate of transition from $|\,r\,\rangle$ to $|\,f\,\rangle$. In an experiment where the fragment yield is measured, the probability of PC decompositions in Eq. (2.1) is

$$P_i(\tau)=\int_0^\tau dt\,\gamma_{fr}(t)\,|b_r(t)|^2\ , \tag{2.25}$$

obtained by integrating the instantaneous probability rate over the time from $t=0$ when the laser interaction is switched on to the time τ, which is the shorter of the interaction time or collection time.

For a smooth laser pulse of arbitrary shape in time, the integral in Eq. (2.25) can be readily evaluated numerically with $b_r(t)$ solved from Eqs. (2.12) and (2.13). However, for some special pulse shapes, analytic results for Eqs. (2.12), (2.13), and (2.25) may be obtained. One such case is given in Sec. II B.

B. Solutions for constant laser intensity: Pulsed or continuous wave

In this section, the situations considered are those in which the laser intensity is constant over a time interval τ, whose value may range from short to very long compared to the lifetimes $1/\gamma_i$ and $1/\gamma_r'$. During this time τ, χ_{ir} in Eqs. (2.12) and (2.13) can be treated as constant. Exact analytic solutions for b_i and b_r can be obtained as follows.[24] From Eq. (2.12), b_r is expressed in terms of b_i and db_i/dt and is used to eliminate b_r and db_r/dt in Eq. (2.13), yielding a second-order differential equation of b_i with constant coefficients. Substituting $b_i(t)=e^{i\lambda t}$ in this differential equation and solving for the roots of the resulting auxiliary equation gives

$$\lambda_\pm=-\tfrac{1}{2}\left[\Delta_{ri}-i\frac{\gamma_i+\gamma_r'}{2}\right]\pm\tfrac{1}{2}\Omega\ , \tag{2.26}$$

where

$$\Omega\equiv\{[\Delta_{ri}+i\tfrac{1}{2}(\gamma_i-\gamma_r')]^2+|\chi_{ir}|^2\}^{1/2}\ . \tag{2.27}$$

Now letting $b_i(t)=A_+e^{i\lambda_+t}+A_-e^{i\lambda_-t}$, and requiring $b_i(t)$ and the corresponding expression of $b_r(t)$ to satisfy the initial conditions (2.16) give

$$b_i(t)=\left[\cos\tfrac{1}{2}\Omega t+i\frac{\Delta_{ri}+i\frac{1}{2}(\gamma_i-\gamma_r')}{\Omega}\sin\tfrac{1}{2}\Omega t\right]\times\exp\left[-i\tfrac{1}{2}\left[\Delta_{ri}-i\frac{\gamma_i+\gamma_r'}{2}\right]t\right] \tag{2.28}$$

and

$$b_r(t)=\mp\frac{\chi_{ri}}{\Omega}\sin\tfrac{1}{2}\Omega t\times\exp[i\tfrac{1}{2}\Delta_{ri}t-\tfrac{1}{4}(\gamma_i+\gamma_r')t]\ , \tag{2.29}$$

where the upper and lower signs correspond to the schemes (a) and (b), respectively.

Substituting the solutions in Eqs. (2.29) and (2.15) into Eq. (2.25) and performing the time integration, one obtains without further approximation the probability at time τ of PC decomposition,

$$P_i(\tau)=A_i+B_i(\tau)\ , \tag{2.30}$$

where A_i is a time-independent term,

$$A_i=\frac{\gamma_{fr}\,|\chi_{ri}|^2\gamma_{ri}}{4\gamma_i\gamma_r'\Delta_{ri}^2+\gamma_{ri}^2\,|\chi_{ri}|^2+\gamma_i\gamma_r'\gamma_{ri}^2}\ , \tag{2.31}$$

and $B_i(\tau)$ is a time-dependent term,

$$B_i(\tau)=-\frac{\gamma_{fr}\,|\chi_{ri}|^2}{|\Omega|^2}e^{-(1/2)\gamma_{ri}\tau}\times\left[\frac{2\Omega_i\sinh\Omega_i\tau+\gamma_{ri}\cosh\Omega_i\tau}{\gamma_{ri}^2-4\Omega_i^2}+\frac{2\Omega_r\sin\Omega_r\tau-\gamma_{ri}\cos\Omega_r\tau}{\gamma_{ri}^2+4\Omega_r^2}\right], \tag{2.32}$$

with the definitions: (a) γ_{ri} is the total decay rate of the $|i\rangle \leftrightarrow |r\rangle$ transition due to all the incoherent broadening processes,

$$\gamma_{ri} = \gamma_r' + \gamma_i \ , \tag{2.33}$$

and (b) Ω_r and Ω_i are, respectively, the real and imaginary parts of Ω defined in Eq. (2.27),

$$\Omega_r = \left(\tfrac{1}{2}[\Delta_{ri}^2 + |\chi_{ri}|^2 - \tfrac{1}{4}(\gamma_r' - \gamma_i)^2] + \tfrac{1}{2}\{[\Delta_{ri}^2 + |\chi_{ri}|^2 - \tfrac{1}{4}(\gamma_r' - \gamma_i)^2]^2 + (\gamma_r' - \gamma_i)^2 \Delta_{ri}^2\}^{1/2}\right)^{1/2} , \tag{2.34}$$

and

$$\Omega_i = \frac{-(\gamma_r' - \gamma_i)\Delta_{ri}}{2\Omega_r} \ . \tag{2.35}$$

From its definition Eq. (2.25), we see that $P_i(\tau) \geq 0$ and $P_i(\tau \neq \infty) \leq P_i(\tau = \infty)$. We can show using the result $P_i(\infty) = A_i$ from Eq. (2.30) that $P_i(\infty) \leq 1$ even under very strong coherent-saturated pumping [see Eq. (2.54) below]. To summarize the conditions of validity of the result (2.30), it is derived by assuming (a) that there is only one discrete state $|r\rangle$ near resonant with the initial state $|i\rangle$; and (b) that the interaction strength (i.e., laser intensity) is constant during the interaction time or the observation time τ.

Two separate limits of Eqs. (2.30)–(2.32) are of particular interest. In one case, when the lifetime of the initial state is infinite (i.e., $\gamma_i = 0$) such as the case of PC predissociation from the ground states shown in Fig. 2,

$$P_i(\tau) = \frac{\gamma_{fr}}{\gamma_r'} + B_i(\tau) \ , \tag{2.36}$$

where $B_i(\tau)$ is formally the same as Eq. (2.32) but with γ_i set equal to zero. In connection to studying the second case, the long-time limit, we note first that the magnitude of $B_i(\tau)$ is almost equal to A_i for very small τ, i.e., $|B_i(\tau)| \to A_i$ as $\tau \to 0$. The term $B_i(\tau)$ consists of summands, each of which contains an exponential time-decay factor. In the limit of long interaction time (due to a long pulse or continuous wave) and long collection time, i.e., when

$$\tau >> \frac{2}{\gamma_r'(1 - |\Delta_{ri}/\Omega_r|)} \ , \tag{2.37a}$$

or when

$$\tau >> \frac{2}{\gamma_i(1 - |\Delta_{ri}/\Omega_r|)} , \text{ if } \gamma_i \neq 0 \ , \tag{2.37b}$$

it can be proved by using the property $|\Delta_{ri}/\Omega_r| < 1$ for $|\chi_{ri}| \neq 0$ that $B_i(\tau)$ becomes negligible compared to A_i. In the case $\gamma_i = 0$, only condition (2.37a) is needed to determine the $B_i(\tau) \approx 0$ result. Then P_i of Eq. (2.30) becomes

$$P_i = \begin{cases} \dfrac{\gamma_{fr}\beta_{ri}|\chi_{ri}|^2\tau_{ri}}{\Delta_{ri}^2 + \beta_{ri}|\chi_{ri}|^2 + \frac{1}{4}\gamma_{ri}^2} \quad \text{if } \gamma_i, \gamma_r' \neq 0 \ , & (2.38) \\[2ex] \dfrac{\gamma_{fr}}{\gamma_r'} \quad \text{if } \gamma_i = 0 \ , & (2.39) \end{cases}$$

where the dimensionless saturation enhancement factor,

$$\beta_{ri} \equiv (\gamma_i + \gamma_r')^2/(4\gamma_i\gamma_r') \ , \tag{2.40}$$

and the lifetime,

$$\tau_{ri} \equiv \gamma_{ri}^{-1} \ . \tag{2.41}$$

The right-hand side of Eq. (2.38) is essentially the A_i term with the numerator and denominator divided by $4\gamma_i\gamma_r'$. According to the result Eq. (2.39), the probability of PC decomposition for the case $\gamma_i = 0$ in the long-time limit is simply the branching ratio of stimulated $|r\rangle \to |f\rangle$ transition rate to the total decay rate from $|r\rangle$, as it should.

A time-averaged probability rate per unit time, Γ_i, for a molecule in a given initial state $|i\rangle$ to be decomposed, can be extracted from Eq. (2.38) by noting that $P_i = 2\Gamma_i\tau_{ri}$, where

$$\Gamma_i \equiv \frac{1}{2}\gamma_{fr}\frac{\beta_{ri}|\chi_{ri}|^2}{\Delta_{ri}^2 + \beta_{ri}|\chi_{ri}|^2 + \frac{1}{4}\gamma_{ri}^2} \ . \tag{2.42}$$

With the restriction of time t short compared to all τ_{ri}, an overall probability rate γ may be defined by

$$\gamma = \sum_i g_i \Gamma_i \ , \tag{2.43}$$

which can be useful in rate equations and in considerations of competition with other processes. Note that without such restriction, an overall probability rate γ for all initial states cannot be defined from Eq. (2.38) in conjunction with Eq. (2.1) because the τ_{ri}'s for different initial state $|i\rangle$ could be quite different in magnitude. When $\beta_{ri} = 1$ (i.e., $\gamma_i = \gamma_r'$), Eqs. (2.42) and (2.43) are the results used in earlier analyses.[8,9] The results given here are therefore more general. The probability rate Eq. (2.42) can be interpreted quite physically as the probability rate γ_{fr} of stimulated transition from the intermediate state to the continuum multiplied by the time-averaged probability of finding the molecule in the intermediate state.

While there are useful applications and other simplifications of the results Eqs. (2.30)–(2.36) under various conditions, we shall defer their discussion to future publications on specific systems. In the rest of the paper, we shall concentrate our study on the long-time limit Eq. (2.38).

C. Optimizing coherent saturation and yield by choosing lifetimes

It has been shown that the bound-bound $|i\rangle \rightarrow |r\rangle$ transition can saturate quite readily under resonance condition.[9] After saturation, the probability rate for this effect becomes in magnitude that of a single-photon dissociation process.[9] An aspect of coherent saturation new in this effect as indicated by the more general result Eq. (2.38) [or Eq. (2.42)] is that in the coherent saturation condition,

$$\beta_{ri}\,|X_{ri}|^2 >> \Delta_{ri}^2 + \tfrac{1}{4}\gamma_{ri}^2 \ , \qquad (2.44)$$

the square of the Rabi flopping frequency, is modified by the factor β_{ri}. This factor can be rewritten as

$$\beta_{ri} = \tfrac{1}{4}(2+R+R^{-1}) \ , \qquad (2.45)$$

where

$$R \equiv \gamma_i/\gamma_r' \ \text{or}\ \gamma_r'/\gamma_i \ . \qquad (2.46)$$

It has a minimum value $\beta_{ri}=1$ at $R=1$ (i.e., $\gamma_i=\gamma_r'$). For any $R \neq 1$, $\beta_{ri}>1$, which means that by having $\gamma_i \neq \gamma_r'$, coherent saturation occurs at lower laser intensity than that would be expected by just examining the Rabi flopping frequency X_{ri}. This enhancement is larger when this ratio R (or R^{-1}) becomes larger, since

$$\beta_{ri} \approx \begin{cases} \tfrac{1}{4}R \ \text{for}\ R >> 1 \ , & (2.47) \\ \tfrac{1}{4}R^{-1} \ \text{for}\ R << 1 \ . & (2.48) \end{cases}$$

A plot of β_{ri} as a function of R is given in Fig. 4.

Before coherent saturation, i.e., when

$$\beta_{ri}\,|X_{ri}|^2 << \Delta_{ri}^2 + \tfrac{1}{4}\gamma_{ri}^2 \ , \qquad (2.49)$$

Eq. (2.38) for P_i in the long-time case becomes

$$P_i = \frac{\tfrac{1}{4}\gamma_{fr}\,|X_{ri}|^2}{\Delta_{ri}^2+\tfrac{1}{4}\gamma_{ri}^2}\left[\frac{1}{\gamma_r'}+\frac{1}{\gamma_i}\right] , \qquad (2.50)$$

which has several interesting limits:

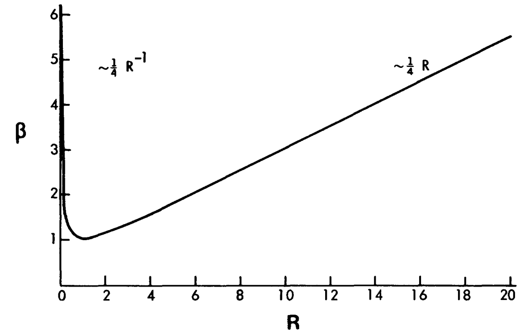


FIG. 4. Plot of the saturation enhancement factor β (Eq. 2.45) as a function of the ratio R of the effective lifetimes of the initial and intermediate states.

(a) If $\gamma_i=\gamma_r' \equiv \tau^{-1}$,

$$P_i = \left[\frac{\tfrac{1}{2}\gamma_{fr}\,|X_{ri}|^2}{\Delta_{ri}^2+\tfrac{1}{4}\gamma_{ri}^2}\right]\tau \ , \qquad (2.51)$$

(b) If $\gamma_r' >> \gamma_i \equiv \tau_i^{-1}$,

$$P_i = \left[\frac{\tfrac{1}{4}\gamma_{fr}\,|X_{ri}|^2}{\Delta_{ri}^2+\tfrac{1}{4}\gamma_r'^2}\right]\tau_i \ , \qquad (2.52)$$

(c) If $\gamma_i >> \gamma_r' \equiv \tau_r^{-1}$,

$$P_i = \left[\frac{\tfrac{1}{4}\gamma_{fr}\,|X_{ri}|^2}{\Delta_{ri}^2+\tfrac{1}{4}\gamma_i^2}\right]\tau_r \ , \qquad (2.53)$$

so that in each case, it is a product of a probability rate, the quantity in parenthesis, and a lifetime. In each of the cases (b) and (c), the lifetime involved is the *longer* of the two lifetimes. This seems reasonable if, in case (b), P_i is considered as the probability rate of a second-order process multiplying the effective lifetime of the initial state; whereas in case (c), since the initial population decays away rapidly, the final probability P_i of going into the continuum $|f\rangle$ consists of the probability, $\frac{1}{4}|X_{ri}|^2/(\Delta_{ri}^2+\frac{1}{4}\gamma_i^2)$, of the molecule being in the state $|r\rangle$, multiplied by the probability of stimulated transition at a rate γ_{fr} from $|r\rangle$ to $|f\rangle$ acting over the effective lifetime τ_r.

It is seen from Eq. (2.50) [and also Eqs. (2.52) and (2.53)] that without coherent saturation, a choice of γ_r' *or* γ_i being very small would enhance the yield of this effect.

However, when the condition (2.44) is satisfied, Eq. (2.38) for P_i in the long-time case gives

$$P_i = \gamma_{fr}/(\gamma_i+\gamma_r') = \gamma_{fr}\tau_{ri} \ , \qquad (2.54)$$

which becomes:

$$\text{(a) for } \gamma'_r=\gamma_i=\tau^{-1},\quad P_i=\tfrac{1}{2}\gamma_{fr}\tau\ , \tag{2.55}$$

$$\text{(b) for } \gamma_i<<\gamma'_r=\tau_r^{-1},\quad P_i=\gamma_{fr}\tau_r\ , \tag{2.56}$$

and

$$\text{(c) for } \gamma'_r<<\gamma_i=\tau_i^{-1},\quad P_i=\gamma_{fr}\tau_i\ . \tag{2.57}$$

These results state that after coherent saturation of the $|i\rangle\rightarrow|r\rangle$ transition, the probability P_i is reduced simply to the probability rate γ_{fr} of stimulated transition from the intermediate state $|r\rangle$ to the final continuum $|f\rangle$ times the effective lifetime. In each of the cases (b) and (c), the effective lifetime is the *shorter* of the two. This can be understood since after coherent saturation, the rapid Rabi cycling of population among the two bound states makes the faster decay of the short-lived state as the dominant loss of total population. From Eq. (2.54) [and also Eqs. (2.56) and (2.57)], it is seen that after coherent saturation, *both* γ_i *and* γ'_r have to be small in order to have an enhancement of yield. Since γ'_r includes γ_{fr}, the probability $P_i\leq 1$, as it should.

D. Enhancement of yield by resonance

It has been shown that the probability rate for the photon-as-catalyst effect can be increased by orders of magnitude due to resonance.[8] The same holds true for the probability P_i and hence the yield. For nonresonant situations, i.e.,

$$\Delta_{ri}^2>>\beta_{ri}\,|\chi_{ri}\,|^2+\tfrac{1}{4}\gamma_{ri}^2\ , \tag{2.58}$$

the probability P_{iN} is given by a typical term as[7]

$$P_{iN}\sim\frac{\gamma_{fr}\,|\chi_{ri}\,|^2\tau_i}{4\Delta_{ri}^2}\ , \tag{2.59}$$

whereas for resonance,

$$\Delta_{ri}^2<<\beta_{ri}\,|\chi_{ri}\,|^2+\tfrac{1}{4}\gamma_{ri}^2\ , \tag{2.60}$$

it is given by Eq. (2.38),

$$P_{iR}=\frac{\gamma_{fr}\beta_{ri}\,|\chi_{ri}\,|^2\tau_{ri}}{\beta_{ri}\,|\chi_{ri}\,|^2+\tfrac{1}{4}\gamma_{ri}^2}\ . \tag{2.61}$$

The enhancement ratio for the same laser intensity in both cases is given by

$$\frac{P_{iR}}{P_{iN}}\sim\frac{\Delta_{ri}^2}{\beta_{ri}\,|\chi_{ri}\,|^2+\tfrac{1}{4}\gamma_{ri}^2}\left[1+\frac{\gamma_i}{\gamma'_r}\right]\ , \tag{2.62}$$

which is the square of the ratio of the detuning Δ_{ri} to the power-broadened half width at half maximum, $(\beta_{ri}\,|\chi_{ri}\,|^2+\frac{1}{4}\gamma_{ri}^2)^{1/2}$, and is modified by the factor $(1+\gamma_i/\gamma'_r)$. This ratio becomes: (a) before coherent saturation (i.e., $\frac{1}{4}\gamma_{ri}^2>>\beta_{ri}\,|\chi_{ri}\,|^2$),

$$\frac{P_{iR}}{P_{iN}}\sim\frac{4\Delta_{ri}^2}{\gamma_{ri}\gamma'_r}\ , \tag{2.63}$$

and (b) after coherent saturation (i.e., $\beta\,|\chi_{ri}\,|^2>>\frac{1}{4}\gamma_{ri}^2$),

$$\frac{P_{iR}}{P_{iN}}=\frac{4\Delta_{ri}^2\gamma_i}{|\chi_{ri}\,|^2(\gamma_i+\gamma'_r)}\ . \tag{2.64}$$

It is seen from Eq. (2.62) that coherent saturation (i.e., power broadening) reduces the resonance enhancement from what it could be without power broadening.[9] The factor β_{ri}, while enhancing coherent saturation to achieve a probability of a first-order process, reduces the resonance enhancement. These points may be illustrated with the PC predissociation of molecular iodine by scheme (a) proposed in Ref. 9. The initial, intermediate, and final states are $|i\rangle=|B0_u^+vJM\rangle$, $|r\rangle=|E0_g^+v'J'M\rangle$ and $|f\rangle=|1uE_fJ''M\rangle$, respectively. For the $|i\rangle\rightarrow|r\rangle$ transition, we may take typical values of the Franck-Condon factors to be 0.001, of the rotational factor for large J values to be $\frac{1}{2}$ for most M states (see Appendix B), and the electronic transition moment to be about 2.7 D.[26,27] The Rabi flopping frequency χ_{ri} in cm^{-1} is $2\times10^{-5}I^{1/2}$, where the laser intensity I is in W/cm^2. The typical natural decay rate of $|i\rangle$ is around 10^6/sec (Ref. 28). The corresponding decay rate for an E state was measured to be about 3.7×10^7/sec (Ref. 26). For the $|r\rangle\rightarrow|f\rangle$ transition, we may take as typical values of the Franck-Condon density to be $10^{-4}/\text{cm}^{-1}$, of the sum of the squares of the rotational factors for $J''=J'\pm1$, J' to be $\frac{1}{8}$ for large J', and as a guess (based on a similar transition[29]) of the square of the electronic transition moment to be 0.1 D^2. Then $\gamma_{fr}=0.16I$/sec where I is in W/cm^2. For $I=10^8$ W/cm^2, $\gamma'_r=\gamma_r+\gamma_{fr}\approx5.3\times10^7\ \text{sec}^{-1}$. It follows that $\gamma_{ri}\approx0.18\times10^{-2}\ \text{cm}^{-1}$ and $\beta_{ri}\approx13$. Since χ_{ri} at $I=10^8\ \text{W/cm}^2$ is 0.19 cm^{-1}, we see that β_{ri} enhances the power broadening. Since $\beta_{ri}\,|\chi_{ri}\,|^2\approx0.5\ \text{cm}^{-2}$ is much larger than $\frac{1}{4}\gamma_{ri}^2\approx8\times10^{-7}\ \text{cm}^{-2}$, the power-broadened width, $2\beta_{ri}^{1/2}\chi_{ri}$, becomes the dominant term in the denominator of Eq. (2.62) and reduces the resonance enhancement. The ratio $P_{ir}/P_{iN}\sim\Delta_{ri}^2/0.5$, where Δ_{ri} is in cm^{-1}. In this example, Δ_{ri} can vary from 10 cm^{-1} for nonresonant situations to $2\times10^4\ \text{cm}^{-1}$ for far off-resonant situations, depending on the laser frequency used. Therefore in spite of power broadening, the general statement that resonance can enhance the PCE signal, or equivalently reduce the required laser powers, by orders of magnitude holds true quite generally.[8]

III. DISCUSSIONS

In the theory and results presented in Sec. II, only the interactions among the principal states, their natural decays, and laser-stimulated decay γ_{fr} from the intermediate state $|r\rangle$ to the final continuum $|f\rangle$ are included. They have neglected any laser-stimulated decays of these principal states to other continua and optical Stark shifts[30] due to their interaction with other nonresonant molecular states. The former could be important if there exist continua coupling in the initial or the intermediate states. Such decays lead to competing losses of molecular population and they broaden the molecular levels further. The optical Stark shifts could be important for near-resonant transitions, such as the cases of their being shifted into resonance.[31] When these shifts and decays are important, they can be readily incorporated into the theory and results of Sec. II. It is shown in Appendix A that, in all the results of Sec. II one needs only to replace the quantities in the left column by the corresponding quantities in the right column:

$$\begin{aligned}&\omega_i \to \omega_i + \delta_i \ ,\\ &\omega_r \to \omega_r + \delta_r \ ,\\ &\gamma_i \to \gamma_i + \sum_c \gamma_{ci} \ ,\\ &\gamma'_r \to \gamma'_r + \sum_c \gamma_{cr} \ ,\end{aligned} \tag{3.1}$$

where the δ's are the optical Stark shifts and γ_{cj} are the laser-stimulated transition rate from the discrete state $|j\rangle$ to the continuum state $|c\rangle$.

For the quantitative calculation of PC decomposition using the results in Sec. II, the transition matrix elements D_{jk} (consisting of electronic, vibrational, and rotational factors) and the summation over the initial states in Eq. (2.1) need to be evaluated. Unlike the electronic transition moments and the Franck-Condon factors, which in almost all cases must be calculated numerically for each individual molecule of interest, the rotational transition strengths can be given in analytic forms for symmetric-top molecules, which include the diatomic molecules as a subclass. These are given in Appendix B here for linear-polarized laser radiation, which is the most commonly encountered case. Application of these results to specific states in a molecule requires only simple substitution of the appropriate rotational quantum numbers. The analytic results for left- and right-circularly polarized radiation have also been derived and will be published elsewhere.

The theoretical results presented in this paper enable us to calculate the fragment yield for (near) resonant PC decomposition. For this purpose, the key results are Eq. (2.25) for smooth time-varying laser pulse, and Eqs. (2.30)–(2.32) and (2.36)–(2.39) for laser pulses with constant intensity. An effective rate constant is given by Eq. (2.42). These results are also useful to other formally similar bound-free processes, e.g., two-photon dissociation or ionization from the ground or excited states.

From our discussions of various features (resonance enhancement, coherent saturation, lifetime dependence, etc.), a set of criteria for optimizing the photon-catalyzed decomposition process become clear. They are useful in selecting the most favorable set of molecular states for calculation or observation. These criteria are:

(1) The initial states are preferred to be long lived for population storage and enhancement of yield, as discussed in Sec. II C. For polyatomic molecules, the states that are thermally populated or in the ground states as illustrated in Fig. 2 are most desirable. For a given laser frequency range, it is preferred that single-photon dissociation from such initial states are forbidden either by symmetry or by energetics. For a large signal-to-noise ratio, it is desirable not to have a natural transition from the initial state to the same final state as the PC transitions.

(2) For the choice of the intermediate discrete states, the most important criterion is to be as much resonant with the laser frequency as possible (Sec. II D). This can be achieved either by having a laser tunable over the molecular transitions or by choosing the right combination of initial-intermediate states if the laser frequency is fixed. The next most important criterion for the intermediate states is that its transition moment to the final continuum states is as large as possible. It is also desirable to have large transition moment between the initial and intermediate states for the coherently unsaturated case. But once coherent saturation is achieved for the given laser intensity, its magnitude does not enhance the overall process anymore. Whether the lifetime of the intermediate

state enhances the yield or not depends on various cases. For nonresonant situation [see Eq. (2.59)] or if the laser-stimulated decay from it is larger than its natural decay rate, then its natural lifetime is unimportant at all. If both of the above cases are not true, then for near-resonant situation, a *longer* lifetime enhances the yield: (a) for the coherently unsaturated case if the lifetime is longer than the lifetime of the initial state; and (b) for the coherently saturated case if the lifetime is shorter than the lifetime of the initial state (see Sec. II C).

(3) For the choice of the final states, it has been mentioned in item (1) above that it is desirable to have a zero or very small intramolecular coupling with the initial states. Another desirable feature is for its decomposed fragments to be readily detected, such as excited fragments giving fluorescence, or charged fragments such as those in PC autoionization.

Further works on photon-catalyzed predissociation and autoionization are in progress. These include both developments of theory and calculations on specific systems. The results will be reported in the future.

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APPENDIX A: LASER-STIMULATED DECAYS AND OPTICAL STARK SHIFTS

We show here that when laser-stimulated decays or optical Stark shifts are important, the theory and results in Sec. II can be generalized to include these effects in a straightforward way prescribed by Eq. (3.1). This is accomplished by starting with the Schrödinger equations including the interactions between the principal states and other states in the molecule and then reducing these equations to the same forms as Eqs. (2.12), (2.13), and (2.17) but with the parameters changed according to Eq. (3.1).

According to Eq. (2.7), the probability amplitudes b_{iN} and $b_{rN'}$ for the principal states $|iN\rangle$ and $|rN'\rangle$ [where $N'=N\mp 1$ for schemes (a) and (b) respectively], and b_{mn} of the other states $|mn\rangle$ are coupled as follows:

$$\frac{db_{iN}}{dt}=\frac{-\gamma_i}{2}b_{iN}-\frac{i}{\hbar}H'_{iNrN'}b_{rN'}e^{-i\Delta_{ri}t}-\frac{i}{\hbar}\sum_{mn}H_{iNmn}b_{mn}e^{-i\Delta_{mniN}t}\,, \tag{A.1}$$

$$\frac{db_{rN'}}{dt}=-\frac{\gamma_r}{2}b_{rN'}-\frac{i}{\hbar}H'_{rN'iN}b_{iN}e^{i\Delta_{ri}t}-\frac{i}{\hbar}\sum_{mn}{}'H'_{rN'mn}b_{mn}e^{-i\Delta_{mnrN'}t}\,, \tag{A2}$$

where the natural decay rates γ_i and γ_r of levels i and r have been inserted as in Eqs. (2.12) and (2.13). The summations in Eqs. (A1) and (A2) exclude the $|iN\rangle$ and $|rN'\rangle$ states; and the states $|m\rangle$ include both discrete and continuum states. Similarly for b_{mn},

$$\frac{db_{mn}}{dt}=-\frac{\gamma_m}{2}b_{mn}-\frac{i}{\hbar}\sum_{m'n'}H_{mnm'n'}b_{m'n'}e^{-i\Delta_{m'n'mn}t}\,, \tag{A3}$$

where the γ_m are needed only for formal mathematical manipulation and will not appear in the final results. Equation (A3) can be integrated formally to give

$$b_{mn}(t)=\sum_{mn}\frac{H'_{mnm'n'}b_{m'n'}e^{-i\Delta_{m'n'mn}t}}{\hbar(\Delta_{m'n'mn}+i\gamma_m/2)}\,, \tag{A4}$$

where it has been assumed that $H'_{mnm'n'}$ and $b_{m'n'}$ are slowly time varying, i.e.,

$$\frac{dH'_{mnm'n'}b_{m'n'}}{dt}<<H'_{mnm'n'}b_{m'n'}\Delta_{m'n'mn}\,. \tag{A5}$$

Substituting Eq. (A4), into Eq. (A1), one obtains for b_{iN}

$$\frac{db_{iN}}{dt}=-\frac{\gamma_i}{2}b_{iN}-\frac{i}{\hbar}H'_{iNrN'}b_{rN'}e^{-i\Delta_{ri}t}-\frac{i}{\hbar^2}\sum_{mn}{}'\sum_{m'n'}\frac{H'_{iNmn}H'_{mnm'n'}}{\Delta_{m'n'mn}+i\frac{1}{2}\gamma_m}b_{m'n'}e^{-i\Delta_{m'n'iN}t}\,. \tag{A6}$$

Now keeping only the terms with $m'n'=iN$ and neglecting all other terms which correspond to higher-order interaction, one obtains

$$\frac{db_{iN}}{dt}=-\frac{\gamma'_i}{2}b_{iN}-i\delta_i b_{iN}-\frac{i}{\hbar}H'_{iNrN'}b_{rN'}e^{-i\Delta_{ri}t}\,, \tag{A7}$$

where the identity[23]

$$\lim_{\gamma\to 0}\frac{1}{\chi+i\gamma}=P\frac{1}{\chi}-i\pi\delta(\chi)\ , \tag{A8}$$

has been used. The decay rate γ_i' includes the laser-stimulated decay rates, γ_{ci}, to all single-photon resonant continuum states $|c\rangle$,

$$\gamma_i'=\gamma_i+\sum_c \gamma_{ci}\ , \tag{A9a}$$

where

$$\gamma_{ci}=\frac{4\pi^2}{\hbar c}I{\sum}'\,|D_{ci}|^2\rho_c(E_i\pm\hbar\omega)\ , \tag{A9b}$$

where $\rho_c(E)$ is the density of states for the continuum and $\sum'$ refers to the summation over the discrete quantum numbers of the particular continuum c. Note that transitions to the final continuum f, if allowed, are included in the above as γ_{fi}. In Eq. (A7), $\hbar\delta_i$ is the optical Stark energy shift,

$$\begin{aligned}\delta_i=&\frac{4\pi}{\hbar c}I\sum_{d\neq i,r}\frac{(E_i-E_d)|D_{id}|^2}{(E_i-E_d)^2-(\hbar\omega)^2}\\&+\frac{2\pi}{\hbar c}I\sum_c\left[P\int dE_c\,\rho_c\frac{|D_{ci}|^2}{E_i-E_c-\hbar\omega}\right.\\&\left.+P\int dE_c\,\rho_c\frac{|D_{ci}|^2}{E_i-E_c+\hbar\omega}\right]\ ,\end{aligned} \tag{A10}$$

where d stands for discrete states, c stands for all the continua, and P stands for the principal value of the integration. Equation (A10) is valid if

$$\frac{8\pi}{c}I\,|D_{mj}|^2<<(|E_m-E_j|-\hbar\omega)^2 \tag{A11}$$

holds. Similar equations are obtained for $b_{rN'}$ by starting from Eq. (A2),

$$\frac{db_{rN'}}{dt}=-\frac{\gamma_r'}{2}b_{rN'}-i\delta_r b_{rN'}-\frac{i}{\hbar}H_{rN'iN}'b_{iN}e^{i\Delta_{ri}t}\ , \tag{A12}$$

with γ_r' and δ_r defined similarly as in Eqs. (A9) and (A10). In particular, γ_r' includes γ_{fr} as described by Eq. (2.14).

Letting $b_{iN}=b_{iN}'e^{-i\delta_i t}$ and $b_{rN'}=b_{rN'}'e^{-i\delta_r t}$, one obtains from Eqs. (A7) and (A12) the following equations describing the interaction between the perturbed (broadened and shifted) states:

$$\frac{db_{iN}'}{dt}=-\frac{\gamma_i'}{2}b_{iN}'-\frac{i}{\hbar}H_{iNrN'}'b_{rN'}'e^{-i\Delta_{ri}'t} \tag{A13}$$

and

$$\frac{db_{rN'}'}{dt}=-\frac{\gamma_r'}{2}b_{rN'}'-\frac{i}{\hbar}H_{rN'iN}'b_{iN}'e^{i\Delta_{ri}'t}\ , \tag{A14}$$

where the new frequency detuning is

$$\Delta_{ri}'\equiv\omega_r+\delta_r-\omega_i-\delta_i\mp\omega\ . \tag{A15}$$

As referred to in Sec. III, this quantity Δ_{ri}' could become zero whereas the original unperturbed detuning Δ_{ri} is not. The initial-value conditions, $b_{iN}'(0)=1$ and $b_{rN'}'(0)=0$, are the same as Eq. (2.16) for b_i and b_r. By comparison of Eqs. (A13) and (A14) with Eqs. (2.12) and (2.13) with the aid of Eq. (2.8), one obtains the substitution rules Eq. (3.1).

Note also that by substituting the above definition of $b_{rN'}'$ into Eq. (2.17), one obtains a similar equation with a modified $\Delta_{rf}'\equiv\omega_r+\delta_r-\omega_f\mp\omega$ in place of Δ_{rf}. With manipulations similar to those leading up to Eq. (2.22) the energy conservation condition is now given by $\omega_f=\omega_i+\delta_i$, instead of $\omega_f=\omega_i$. Therefore, the subsequent solutions of Eqs. (A13), (A14), and the modified (2.17) are identical to those in Sec. II, and we have proven our assertion.

The above procedure of including the laser-stimulated decays and optical Stark shifts can be extended to include multiphoton transition rates and higher-order optical Stark shifts, if they are needed.

APPENDIX B. ROTATIONAL TRANSITION STRENGTHS FOR LINEAR POLARIZED LIGHT

In this Appendix, the rotational transition strengths for the PC predissociation of symmetric-top molecules with a linearly polarized laser are given.

The wave functions[32] of a symmetric top molecule can be written as $|s\alpha vJKM\rangle$,

$$|\pm\alpha vJKM\rangle=\frac{1}{\sqrt{2}}(|\alpha vJKM\rangle\pm|\alpha vJ,-K,M\rangle)\quad\text{for } K\neq 0\ ,$$

and

$$|\pm\alpha vJ0M\rangle=|\alpha vJ0^{\pm}M\rangle\quad\text{for } K=0\ , \tag{B1}$$

where s stands for either + or − sign, α is the electronic state label, v stands for all labels for the vibrational states, J is the quantum number of the total angular momentum $\vec{J}$, M is the quantum number of its component along the space-fixed quantization axis, and K is the quantum number of component $\vec{K}$ of the angular momentum $\vec{J}$ along the symmetric-top axis. By convention, K is always positive. In general, for symmetric-top polyatoms, $\vec{\mathrm{K}}$ may have contributions from rotational, vibrational, and electronic angular momenta.[33] In diatoms, $\hbar K$ is the magnitude of the electronic orbital angular momentum along the internuclear axis and is usually denoted by $\hbar\Lambda$. It is well known that the states $|s\alpha vJKM\rangle$ for different M values are $(2J+1)$-fold degenerate. In addition, for $K\neq 0$, the states with K and $-K$ values are doubly degenerate. The question, therefore, arises whether the analytic formulas in Secs. II B – II D are applicable, since in the analytic solution Eqs. (2.30) – (2.32), it has been assumed that for each initial state there is only one resonant intermediate state.

Since the laser bandwidth is usually narrow compared to the rotational energy separation between the P,Q,R transitions from a given initial state, one can select a particular J' level as near resonant. Then for a given initial state $|s\alpha vJKM\rangle$ and a given $\alpha'v'J'$ level, it can be shown that the initial state is coupled to only one state out of the $2(2J'+1)$-fold degenerate states $|s'\alpha'v'J'K'M'\rangle$ for $K'\neq 0$; or one out of the $(2J'+1)$-fold degenerate state for $K'=0$. To see this, we note first that the selection rule for electric-dipole transition induced by linear-polarized light is $M'-M=0$, if the space-fixed quantization axis is chosen along the polarization direction $\hat{\epsilon}$. This means that for $K'=0$, only one intermediate state $M'=M$ is coupled and that for $K'\neq 0$, only two $M'=M$ states corresponding $s'=s$ and $s'=-s$ are coupled. For the latter case, only one state has the opposite parity as the initial state and is therefore allowed by electric-dipole selection rules; the other state has the same parity and is forbidden. This can be seen explicitly using the property under the spatial inversion $\vec{\mathrm{r}}'_l \rightarrow -\vec{\mathrm{r}}'_l$,

$$|s\alpha vJKM\rangle \rightarrow (-1)^{\delta_{s}-}(-1)^{K+J}|s\alpha vJKM\rangle\ , \tag{B2}$$

one obtains with spatial inversion invariance for the electric-dipole matrix element,

$$\langle s'\alpha'v'J'K'M'|\sum_l q_l\vec{\mathrm{r}}'_l|s\alpha vJKM\rangle=(-1)^{\delta_{s's}+J'+K'+J+K}\langle s'\alpha'v'J'K'M'|\sum_l q_l\vec{\mathrm{r}}'_l|s\alpha vJKM\rangle\ , \tag{B3}$$

where $\delta_{s's}$ equals 1 if s' and s are of the same sign and equals 0 if s' and s are opposite signs. It is, therefore, seen that for nonvanishing matrix elements, a given state $|s\alpha vJKM\rangle$, and given quantum numbers $\alpha'v'J'K'M'$, only one value s' is possible.

From Eq. (2.1) with substitutions from Eqs. (2.38), (2.15), and (2.8), the probability P of the PC predissociation in the long-time case is given by

$$P=\frac{2^5\pi^3}{\hbar^3c^2}I^2\sum_i g_i\sum_f{}'\rho_f\frac{\beta_{ri}\tau_{ri}|D_{fr}|^2|D_{ri}|^2}{\Delta_{ri}^2+\frac{1}{4}\gamma_{ri}^2+(8\pi I\beta_{ri}|D_{ri}|^2/\hbar^2c)}\ , \tag{B4}$$

where i stands for $s\alpha vJKM$, $r\equiv s'\alpha'v'J'K'M$, and $f\equiv s''\alpha''v''J''K''M$. The calculation becomes simpler when the transition matrix elements D's are expressed in terms of $|\alpha vJKM\rangle$ only [i.e., free of the $|\alpha vJ,-K,M\rangle$ component in Eq. (B1) for $K\neq 0$]. This is accomplished by using the relationship

$$\langle s'\alpha'v'J'K'M|\sum_l q_l\vec{\mathrm{r}}'_l|s\alpha vJKM\rangle=l_{K'K}[1+(-1)^{\delta_{s's}+J'+K'+J+K}]\langle\alpha'v'J'K'M|\sum_l q_l\vec{\mathrm{r}}'_l|\alpha vJKM\rangle\ , \tag{B5}$$

where

$$l'_{KK}=\begin{cases}\dfrac{1}{\sqrt{2}} & \text{if } (K'=0,\ \ K=1) \text{ or } (K'=1,\ \ K=0)\ ,\\ \frac{1}{2} & \text{in all other cases}\ .\end{cases}$$

Each of the wave functions $|\alpha vJKM\rangle$ can be written as a product of an electronic and vibrational part $|\alpha KvJ\rangle$ and a rotational wave function $|JKM\rangle$,

$$|\alpha vJKM\rangle=|\alpha KvJ\rangle|JKM\rangle\ . \tag{B6}$$

Thus, the matrix elements $\langle\alpha'v'J'K'M|\ \sum q_l\vec{\mathrm{r}}'_l|\alpha vJKM\rangle\cdot\hat{\epsilon}$ can be written as

$$\langle \alpha' v' J' K' M \,|\, \sum q_l \vec{r}\,'_l \,|\, \alpha v J K M \rangle \cdot \hat{\epsilon} = \mu_{r'i'} A_{J'K'MJKM} \ , \tag{B7}$$

where $\mu_{r'i'}$ is the electronic-vibrational electric-dipole matrix element defined in Table I and A is a rotational factor. These angular factors A are known[34] and can be expressed as a product of three factors,

$$A_{J'K'MJKM} = N_{J'J} C_{J'MJM} B_{J'K'JK} \ , \tag{B8}$$

where N, C, and B are given in Table II for convenience of reference. Substitution of Eqs. (B5) and (B7) into Eq. (B4), one has

$$P = \left[\frac{8\pi}{\hbar}\right]^3 \left[\frac{I}{c}\right]^2 \sum_i g_i \sum_{f'}{}' \rho_f \beta_{ri} \tau_{ri} l^2_{K''K'} l^2_{K'K} \frac{|\mu_{f'r'}\mu_{r'i'}|^2 A^2_{J''K''JM'K'M} A^2_{J'K'MJKM}}{\Delta^2_{ri} + \frac{1}{4}\gamma^2_{ri} + (2^5 \pi I \beta_{ri} l^2_{K'K} |\mu_{r'i'}|^2 A^2_{J'K'MJKM}/\hbar^2 c)} \ , \tag{B9}$$

where i, r, and f now stand for $\alpha vJKM$, $\alpha' v' J' K' M$, and $\alpha'' v'' E_f J'' K'' M$, respectively; i', r', and f' stands for $\alpha K v J$, $\alpha' K' v' J'$, and $\alpha'' K'' v'' J''$, respectively; and J' may take either one of the values $J-1$, J, $J+1$ while the summation over J'' include all three values $J'-1$, J', $J'+1$. Equation (B9) is the general result of this section. It differs from Eq. (B4) in that the sums over s, s', and s'' have been performed, and it exhibits the rotational transition factors A given by Eq. (B8) and Table II.

In the following, we shall consider the expression P for the unsaturated regime and the coherently saturated regime. Since the Rabi flopping frequency X_{ri} [or the third term in the denominator in Eq. (B9)] differs for different pair of $|i\rangle$ and $|r\rangle$ states, the condition (2.49) for nonsaturation and the condition (2.44) for coherent saturation must be satisfied for all the significantly populated states $|i\rangle$. The following results in Eqs. (B12) and (B15) for the two regimes are also further simplified in that the summation over M in $\sum_i$ has been performed. In order to perform this summation, two simplifying assumptions have been made. The first one is that γ'_r [also Δ'_{ri} and γ'_i if Eq. (3.1) is used] are weakly dependent on M so that they can be treated as M independent. The second one is that the initial population distribution is isotropic, i.e.,

$$g_{\alpha vJKM} = \frac{1}{2J+1} g_{\alpha vJK} \ , \tag{B10}$$

for all M. Another approximation, but an excellent one, is that the densities of final states $\rho_{J''}$ and transition matrix elements $\mu_{f'r'}$ for *adjacent* rotational states are equal, i.e.,

$$\rho_{J'} |\mu_{J'J'}|^2 = \rho_{J'-1} |\mu_{J'-1J'}|^2 = \rho_{J'+1} |\mu_{J'+1J'}|^2 \ . \tag{B11}$$

Under these assumptions, the result P for near-resonant intermediate transition but before coherent saturation is

$$P = \left[\frac{8\pi}{\hbar}\right]^3 \left[\frac{I}{c}\right]^2 \sum_{i'} g_{i'} \sum_{\alpha''K''v''} \rho_{\alpha''K''v''J'} \beta_{r'i'} \tau_{r'i'} l^2_{K''K'} l^2_{K'K} \frac{|\mu_{\alpha''K''v''J',r'} \mu_{r'i'}|^2}{\Delta^2_{r'i'} + \frac{1}{4}\gamma^2_{r'i'}} R_{K''J'K'JK} \ , \tag{B12}$$

TABLE I. Definitions of the electronic-vibrational electric-dipole matrix element $\mu_{\alpha' K' v' J' \alpha K v J}$ in Eq. (B7). The evaluation of these matrix elements involve integration over the coordinates $\vec{r}_l$ in the molecular body-fixed coordinate system.

K'	$\mu_{\alpha' K' v' J' \alpha K v J}$
$K+1$	$\langle \alpha', K+1, v' J' \,|\, \sum_l q_l (x_l + i y_l) \,|\, \alpha K v J \rangle$
K	$\langle \alpha' K v' J' \,|\, \sum_l q_l z_l \,|\, \alpha K v J \rangle$
$K-1$	$\langle \alpha', K-1, v' J' \,|\, \sum_l q_l (x_l - i y_l) \,|\, \alpha K v J \rangle$

TABLE II. Expressions of the factors $N_{J'J}$, $C_{J'M'JM}$, and $B_{J'K'JK}$ in Eq. (B8). The $C_{J'MJM}$ are valid only for linear polarization $\hat{\epsilon}$ chosen as the rotational quantization space-fixed axis $\hat{z}$. Other than notational differences and factors of $\frac{1}{2}$ in the definition of the B's, these factors are the same as those in Ref. 34.

	$J'=J+1$	$J'=J$	$J'=J-1$
$N_{J'J}$	$(J+1)^{-1}[(2J+1)(2J+3)]^{-1/2}$	$[J(J+1)]^{-1}$	$J^{-1}(4J^2-1)^{-1/2}$
$C_{J'MJM}$	$[(J+1)^2-M^2]^{1/2}$	M	$[J^2-M^2]^{1/2}$
$B_{J'K+1JK}$	$-\frac{1}{2}[(J+K+1)(J+K+2)]^{1/2}$	$\frac{1}{2}[J(J+1)-K(K+1)]^{1/2}$	$\frac{1}{2}[(J-K)(J-K-1)]^{1/2}$
$B_{J'KJK}$	$[(J+1)^2-K^2]^{1/2}$	K	$[J^2-K^2]^{1/2}$
$B_{J'K-1JK}$	$\frac{1}{2}[(J-K+1)(J-K+2)]^{1/2}$	$\frac{1}{2}[J(J+1)-K(K-1)]^{1/2}$	$-\frac{1}{2}[(J+K)(J+K-1)]^{1/2}$

where the rotational transition strength R is given by

$$\begin{aligned} R_{K''J'K'JK} = {} & B^2_{J'+1,K''J'K'}B^2_{J'K'JK}G_{J'+1,J'J} \\ & +B^2_{J'K''J'K'}B^2_{J'K'JK}G_{J'J'J} \\ & +B^2_{J'-1,K''J'K'}B^2_{J'K'JK}G_{J'-1,J'J} \ , \end{aligned} \tag{B13}$$

and the quantities G's are defined by

$$G_{J''J'J} \equiv \frac{N^2_{J''J'}N^2_{J'J}}{(2J+1)} \sum_{M=-J_m}^{J_m} C^2_{J''MJ'M}C^2_{J'MJM} \ , \tag{B14}$$

where J_m is the smallest of J'', J', and J. These G's are evaluated and the results are tabulated in Table III.

Under the same assumptions, the result P for near resonance with intermediate states after coherent saturation is

$$\begin{aligned} P = \frac{2^4\pi^2}{\hbar c} I \sum_{i'} g_{i'} \sum_{\alpha''K''v''} & \rho_{\alpha''K''v''J'}\tau_{r'i'}l^2_{K''K'} \\ & \times |\mu_{\alpha''K''v''J'r'}|^2 R_{K''J'K'} \ , \end{aligned} \tag{B15}$$

where

$$\begin{aligned} R_{K''J'K'} = {} & B^2_{J'+1,K''J'K'}G_{J'+1,J'}+B^2_{J'K''J'K'}G_{J'J'} \\ & +B^2_{J'-1,K''J'K'}G_{J'-1,J'} \ , \end{aligned} \tag{B16}$$

and $G_{J''J'}$ are defined by

$$G_{J''J'} = \frac{N^2_{J''J'}}{2J+1} \sum_{M=-J_m}^{J_m} C^2_{J''MJ'M} \ . \tag{B17}$$

TABLE III. The $G_{J''J'J}$ factors defined in Eq. (B14) and used in Eq. (B13) for the calculation of rotational transition strengths of the PCE in the nonsaturated case.

	$J''=J'+1$	$J''=J'$	$J''=J'-1$
$J'=J+1$	$\frac{2}{15(J+1)(J+2)(2J+1)(2J+3)}$	$\frac{J}{15(J+1)^3(J+2)(2J+1)}$	$\frac{4(J+1)^2+1}{15(J+1)^3(2J+1)^2(2J+3)}$
$J'=J$	$\frac{J+2}{15J(J+1)^3(2J+1)}$	$\frac{3J(J+1)-1}{15J^3(J+1)^3}$	$\frac{J-1}{15J^3(J+1)(2J+1)}$
$J'=J-1$	$\frac{4J^2+1}{15J^3(2J-1)(2J+1)^2}$	$\frac{J+1}{15J^3(J-1)(2J+1)}$	$\frac{2}{15J(J-1)(4J^2-1)}$

TABLE IV. The $G_{J''J'}$ factors defined in Eq. (B17) and used in Eq. (B16) for the calculation of the rotational transition strengths of the PCE in the coherently saturated case.

	$J''=J'+1$	$J''=J'$	$J''=J'-1$
$J'=J+1$	$\frac{J+4}{3(J+2)^2(2J+5)}$	$\frac{J}{3(J+1)(J+2)^2}$	$\frac{1}{3(2J+1)(J+1)}$
$J'=J$	$\frac{1}{3(J+1)(2J+1)}$	$\frac{1}{3J(J+1)}$	$\frac{1}{3J(2J+1)}$
$J'=J-1$	$\frac{1}{3J(2J+1)}$	$\frac{2J-1}{3J(J-1)(2J+1)}$	$\frac{1}{3(J-1)(2J+1)}$

The results for $G_{J''J'}$ are tabulated in Table IV.

With these analytic results, one can now calculate the rotational transition strengths in the PC predissociation of symmetric-top molecules induced by a linearly polarized laser by the simple substitution of the rotational quantum numbers for the states of interest.

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