Resonant Photocatalytic Effect in Laser-Induced Unimolecular Decomposition

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The probability rate of photon-catalyzed molecular predissociation (or unimolecular reaction) is shown to increase by many orders of magnitude in the case of (near-) resonance of the laser frequency with intermediate discrete molecular states. As a result, the photocatalytic effect is important even at unexpectedly low laser power. Both the resonant and the nonresonant photocatalytic effects can be demonstrated by experiments with alkali-metal dimers (e.g., Na_2).

It is shown in this Letter that *photon-catalyzed* molecular predissociation (or unimolecular reaction) can occur with significant probability rate at laser intensity many orders of magnitude smaller than those expected from previous studies.[1-3] This reduction in the required laser power is made possible by the huge resonance enhancement (e.g., $\gtrsim 10^4$) in the probability rate (or unimolecular rate "constant") when the laser frequency is resonant with the initial and some intermediate molecular states. In this process, a molecule in the vibrational bound state $(AB)^*$ makes a transition to a nearby vibrational continuum via intermediate states by *simultaneous* absorption of one photon and stimulated emission of another photon of the same mode (see Fig. 1),

$$(AB)^* \xrightarrow{\text{laser}} A+B, \tag{1}$$

where A and B may be atoms or molecules. Since the laser photons are *not* consumed in this channel of Reaction (1) and yet can increase its rate constant, the photons are acting like catalysts. As a result of the low power requirement found here, this interesting photocatalytic effect will be much more amenable to laboratory studies and practical applications. To underscore this physical significance, this novel effect is called *resonant* photocatalysis and is distinguished from the previous *nonresonant* photocatalytic effect.[1,2] In the latter, because of the large difference of the laser frequency from resonance with any intermediate states, only *virtual* absorption and emission of the laser photons are involved.

The alkali-metal dimers (e.g., Na_2) are suggested here for the experimental demonstration of both the resonant and the nonresonant photocatalytic effects. This is the first time any molecular system has been identified where these effects are clearly dominant.

Nonradiative molecular predissociation is an important process for the study of the spectra and structure of molecules.[4] It is also the basic mechanism in the decomposition (or bond-breaking) step of nearly all unimolecular reactions.[5] In the nonradiative predissociation, the direct transition from the initial molecular state to the adjacent vibrational continuum (see Fig. 1)

$$(AB)^* \to A+B \tag{2}$$

is due to intramolecular interactions.[4-7] Numerous recent works[7,8] have used laser excitation to prepare molecular population in the initial bound state for studying process (2). In the active area of infrared multiphoton dissociation of polyatomic molecules,[9] the molecules are energized into excited bound states by absorbing laser photons in the pump mode but it is assumed that the intense laser radiation does not induce any decomposition from these states in addition to the nonradiative component.

Lau and Rhodes[1,2] were the first to study how the intense laser radiation may modify and contribute to the predissociation dynamics itself. It was found that depending on the symmetries (if any) of the initial and final states, the laser radiation can induce a radiative predissociation by absorption (or stimulated emission) of the laser photons[3] or by the *nonresonant* photocatalytic effect.[1,2] When the symmetries forbid single-photon absorption or stimulated emission, the photocatalytic effect can become the dominant process.

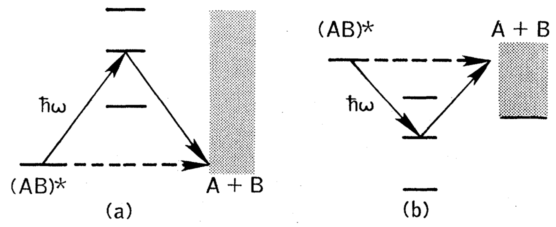

FIG. 1. Resonant photocatalytic predissociation (solid arrows) due to (a) higher- and (b) lower-lying intermediate levels. Nonradiative predissociation is indicated by dashed arrow.

Now I want to give the theory of resonant photocatalytic effect. Since the molecular symmetries may allow both the laser-induced photocatalytic effects (1) and the nonradiative predissociation (2), the total decomposition rate per second per molecule is given by

$$\gamma = (2\pi/\hbar)\textstyle\sum_i g_i \sum_f \rho_f \,|\, T_{fi} + S_{fi}\,|^2 ,$$

where

$$S_{fi} = (2\pi/c)I \int d\omega\, g(\hbar\omega - \hbar\bar{\omega})\textstyle\sum_n D_{fn} D_{ni}\{[(\Delta_{ni-}{}^2 + \chi_{ni}{}^2)^{1/2} - i\,\tfrac{1}{2}\gamma_{ni}]^{-1} + [(\Delta_{ni+}{}^2 + \chi_{ni}{}^2)^{1/2} - i\,\tfrac{1}{2}\gamma_{ni}]^{-1}\}. \tag{3}$$

In this expression, g_i gives the probability distribution in the initial states ψ_i so that $\sum g_i = 1$. The density of states for the vibrational continuum, ρ_f, is evaluated at $E_f = E_i$ (i.e., energy conservation) and the sum $\sum_f$ is carried over other discrete electronic ($k\Lambda$) and rotational (JM) quantum numbers of the final molecular states. The nonradiative predissociation is given by the known[4,6,7] matrix element T_{fi}. The photocatalytic effects are given by the matrix element S_{fi}. The laser, with integrated intensity I, has a spectral line shape $g(\hbar\omega - \hbar\bar{\omega})$ centered at $\bar{\omega}$ so that $\int d\omega\, \hbar(\hbar\omega - \hbar\bar{\omega}) = 1$. The sum $\sum_n$ is carried over the intermediate states of the molecule. The electric-dipole transition moments D_{jn} are given by $\langle \psi_j | \sum_l q_l \vec{r}_l \cdot \hat{\epsilon} \,|\, \psi_l \rangle$ with the continuum vibrational part of the final state ψ_f normalized as $\langle E_f | E_f{}' \rangle = \rho_f^{-1} \delta(E_f - E'_f)$. The frequency detunings are given by $\Delta_{ni\pm} \equiv (E_n - E_i \pm \hbar\omega)/\hbar$. The Rabi frequency $\chi_{ni} \equiv (8\pi I/c)^{1/2} D_{ni}/\hbar$ gives rise to power broadening due to coherent optical pumping and the full width at half maximum γ_{ni} includes *all* incoherent broadening mechanisms.

The magnitude of the *resonant* ($\Delta_{ni} \approx 0$) photocatalytic effect depends on the width of the laser spectral line shape relative to the full width $\delta_{ni} \equiv \chi_{ni} - i\frac{1}{2}\gamma_{ni}$ of the transitions. This is illustrated by the results for two simple special cases that are encountered frequently. The first is when the laser linewidth is much smaller than $|\delta_{ri}|$, where r are the resonant (or near-resonant) states. Then neglecting the much smaller contribution from far off-resonant states, one obtains

$$S_{fi} = (2\pi/c)I \textstyle\sum_r D_{fr} D_{ri}/\delta_{ri}. \tag{4}$$

The second case is when the laser width is much greater than $|\delta_{ri}|$; then it is obtained from Eq. (3) that

$$S_{fi} = i(2\pi^2/c)I \textstyle\sum_r D_{fr} D_{ri}\, g(\pm E_{ri} - \hbar\bar{\omega}). \tag{5}$$

We see that in the former case, Eq. (4) the molecular line-shape function comes into play whereas in the latter case, Eq. (5), it is the laser line-shape function.

Now I want to show the resonant enhancement by comparing with the *nonresonant* photocatalytic effect.[1,2] In the latter, the energy departure from resonance with *any* intermediate state is much larger than the molecular or laser linewidth; the probability rate formula is also given by Eq. (3) but with S_{fi} simplified to be[3]

$$S_{fi}{}' = (4\pi/c)I \textstyle\sum_n D_{fn} D_{ni} E_{ni} [E_{ni}{}^2 - (\hbar\bar{\omega})^2]^{-1}. \tag{6}$$

With the assumption that T_{fi} is negligible (e.g., by symmetry $\Delta\Lambda = 2$), an estimate of the order of magnitude of the resonance enhancement is given by the ratio of the resonant photocatalytic probability rate γ_R to the nonresonant photocatalytic probability rate γ_N,

$$\frac{\gamma_R}{\gamma_N} \sim \frac{|S_{fi}|^2}{|S_{fi}{}'|^2} \sim \left| \frac{(|E_{ni}| - \hbar\bar{\omega}) I_R}{\delta I_N} \right|^2 , \tag{7}$$

where $\delta \equiv \delta_{ri}$ for the case of Eq. (4) and $\delta \equiv [\pi g(0)]^{-1}$ for the case of Eq. (5); and I_R and I_N are the intensity of the laser used in the resonant and the nonresonant case, respectively. Using the same laser that can be tuned into and away from resonance, one has $\gamma_R/\gamma_N \sim (|E_{ni}| - \hbar\bar{\omega})^2/\delta^2$. For the typical range of off-resonance $|E_{ni}| - \hbar\bar{\omega} \sim 10$ to 10^4 cm^{-1}, and a typical molecular or laser linewidth $\delta \sim 0.1$ cm^{-1}, one obtains a huge enhancement factor of 10^4 to 10^{10}! If two different nontunable lasers are used in the resonant and nonresonant cases, the reduction in the resonant laser intensity I_R required to induce the same rates $\gamma_R = \gamma_N$ is given by $I_R/I_N \sim \delta/(|E_{ni}| - \hbar\bar{\omega})$. For the above typical numbers, $I_R/I_N \sim 10^{-2}$ to 10^{-5}.

A class of molecules has also been identified to demonstrate the photocatalytic effects. The previously suggested diatomic halogens such as I_2 and Br_2 have the difficulty that predissociation by laser-stimulated single-photon transitions from the bound $B\ 0_u{}^+$ states to the nearby repulsive 1_g and $0_g{}^+$ states would dominate over the photocatalytic effects.[3] However, the bound $a^3\pi_u$ state of the alkali-metal dimers (Li_2, Na_2, etc.) is free from any single-photon predissociation because it does not have any low-lying *repulsive gerade* states nearby. This is shown in Fig. 2.[10,11]

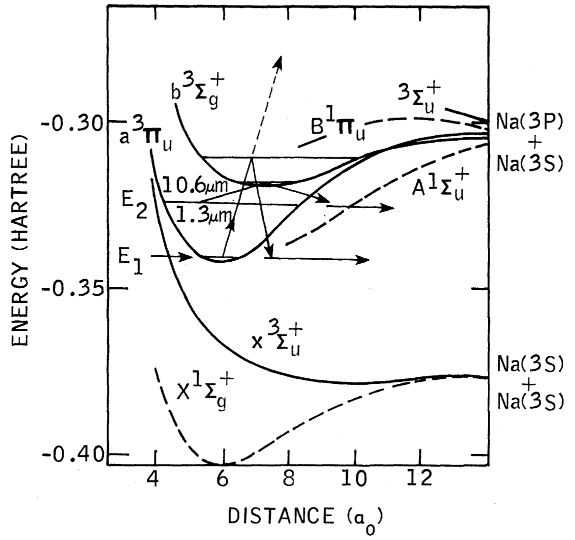

FIG. 2. Schematic diagram showing the resonant photocatalytic effect (solid arrows) applied to the lowest triplet states (solid curves) of Na_2.

Although the discussion below applies to other alkali-metal dimers as well, Na_2 is chosen for the amount of known information and for experimental advantages. Because of spin-orbit mixing with the $A^1\Sigma_u{}^+$ states,[12] populations in the $(a^3\pi_u v'J')$ states (lifetimes $\gtrsim 10^{-6}$ sec) can be prepared by dye-laser excitation from the ground $(X^1\Sigma_g{}^+ v''J'')$ states. A second infrared laser can photocatalytically predissociate these $(a^3\pi_u v'J')$ populations into the continuum of the $x^3\Sigma_u{}^+$ state with the $(b^3\Sigma_g{}^+ vJ)$ states acting as the dominant intermediate states:

$$\mathrm{Na}_2(a^3\pi_u v'J') \xrightarrow{\text{laser}} \mathrm{Na}(3s) + \mathrm{Na}(3s). \qquad (8)$$

In general, a CO_2 laser can be used for the nonresonant photocatalytic effect.[1,2] However to obtain resonance enhancement with a CO_2 laser here, one has to populate levels above E_2 in Fig. 2. For low-lying levels such as E_1 in Fig. 2, one may use the 1.318-μm line of the yttrium-aluminum-garnet laser to obtain resonant enhancement through the high-lying discrete levels of the $b^3\Sigma_g{}^+$ state. By tuning the pump dye laser or the ir laser (if tunable), one can optimize the $i \to r$ and $r \to f$ Franck-Condon factors to obtain large photocatalytic effect (now shown in Fig. 2). The predissociation probability rate per second per molecule in general can be estimated by

$$\gamma_R \approx 6.3\times 10^{-7}(I/\delta)^2 \rho_f D_{fr}{}^2 D_{ri}{}^2, \qquad (9)$$

where I is in watts per square centimeter, and δ is in inverse centimeters, ρ_f is the density of states per hartree, and D_{fr} and D_{ri} are in atomic units (1 a.u. = 2.54×10^{-18} esu). For Na_2, rough estimates of $\rho_f D_{fr}{}^2 \sim 0.9$ and $D_{ri}{}^2 \sim 0.9$ give a power-broadened $\delta \sim 1.9$ cm^{-1} and $\gamma_R \sim 1.2\times10^6$/sec at $I = 3\times10^6$ W/cm^2. A laser pulse of $\tau \sim 0.1$ μsec would decompose 12% of the population. To induce the same rate with an energy off resonance by ~ 100 cm^{-1} would require a laser intensity ~10^8 W/cm^2.[1,2] The proposed experiment uses an Na_2 molecular *beam* so that the decomposed fragments Na(3s) can be detected separately from the Na(3s) atoms present in the primary Na_2 beam.

The increase in the detected signals from the products Na(3s) with the infrared laser on, as compared to off, can distinguish the photocatalytic effects from the nonradiative predissociation (if any[10]). Note that the rate "constants" of the photocatalytic effects can become dominant by increasing the laser intensity whereas the nonradiative rate constant is fixed.[3,13] Another process, resonant Raman effect (or resonance fluorescence), may produce Na(3s) fragments but their kinetic energy distribution is more diffused than those of the resonant photocatalytic effect peaking at $E_f = E_i$ only. For the same values of the molecular and laser parameters as above, the resonant Raman effect depletes the initial population at a rate ($\lesssim 0.9\times10^6$ sec^{-1}) lower than the photocatalytic rate. More importantly, *further increase in laser intensity increases the photocatalytic rate linearly whereas the Raman rate remains constant*, because the $i \leftrightarrow r$ transition is already saturated in both cases. Therefore *the resonant photocatalytic effect can be distinguished from and dominate over the resonant Raman effect.* Another competing process, stimulated two-photon absorption, can also be discriminated. For the low-lying levels such as E_1 where an yttrium-aluminum-garnet laser is used, even if there were significant two-photon absorption into a higher electronic repulsive states, the product, excited Na*, would fluoresce. See Fig. 2. The relative kinetic energy of the dissociated fragments is also distinct from that of photocatalytic fragments. For the high-lying levels such as E_2, where the CO_2 laser is used, predissociation by laser-stimulated two-photon absorption and emission into the continuum of the $x^3\Sigma_u{}^+$ state can occur. But the Na(3s) products of these processes can be resolved from those from the photocatalytic effects because their relative kinetic energy differs by $\pm 2\hbar\omega$. Finally the probability rate for stimulated two-photon emission is further reduced by orders of magnitude because of its large departure from resonance with the intermediate states. Thus it is likely that the photocatalytic effects can be unambiguously demonstrated using Na_2 (or other alkali-metal dimers).

Photons have always been thought of as being absorbed or emitted in photochemistry and laser-induced chemistry. The significance of the above experiment is to demonstrate the predicted new role of the photons as "catalysts" and a new channel of laser-induced unimolecular decomposition. This also makes more attractive the attempt to demonstrate this effect in the more complex laser-controlled collisional or reactional process. Theory shows that the same principle governs the two kinds of processes.[1-3]

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