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Computational study of a molecular collision process in the presence of an intense radiation field: Enhanced quenching of F by Xe in the 248-nm light of the KrF laser

Paul L. DeVries, Maurice S. Mahlab, and Thomas F. George
Department of Chemistry, The University of Rochester, Rochester, New York 14627

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A model is developed to describe collisional quenching in the presence of a radiation field within a close-coupled formalism. In this model the collision dynamics are treated in a simplified manner, ignoring Coriolis and angular-potential coupling, thus reducing the computational complexity of the problem. The model hence focuses on the radial coupling of the collision system to the radiation field. The process investigated with this model is the quenching of fluorine by xenon in the 248-nm radiation field of a KrF laser. The mechanism for the radiative contribution to the quenching cross section is absorption of a photon by XeF followed by stimulated emission of a photon to the XeF ground state, the intermediate state being an excimer state of the XeF molecule. Thus, there is no net loss of photons from the radiation field and (in the language of perturbation theory) the process is of second order. The quenching cross section is calculated for collision energies in the range 0.05 to 0.25 eV and for field intensities of 0, 10, 100, and 1000 GW/cm^2. Results indicate that field intensity of 10–100 GW/cm^2 should have an experimentally observable effect on the quenching of fluorine by xenon at thermal collision energies.

I. INTRODUCTION

In recent years the study of the intense radiation fields of lasers interacting with dynamic molecular processes has gained substantial interest from both theorists[1-24] and experimentalists,[25-28] and such effects have been experimentally observed in at least three distinct physical processes.[26-28] various theoretical efforts have been made, presenting both semiclassical and quantum-mechanical formalisms. However, the key question of the magnitude of the radiation intensity required for these effects has not been thoroughly answered. The present paper addresses itself to this question.

The process under consideration is the quenching of fluorine by xenon in the 248-nm radiation field of a KrF laser. Since quenching is an allowed process in the absence of the field, the effect of the radiation field can be viewed as an additional contribution to the quenching cross section, and its importance can be readily determined. The mechanism for the radiative contribution is absorption of a photon by the XeF* excited electronic state [correlating to Xe + F($^2P_{1/2}$)] followed by stimulated emission of a photon to the XeF ground electronic state [correlating to Xe + F($^2P_{3/2}$)], the intermediate electronic state being an excimer state of the XeF molecule (correlating to Xe$^+$ + F$^-$). Thus there are no net photons involved and, in the language of perturbation theory, this is a second-order process. The KrF laser was chosen for this study both because the XeF excimer states are energetically accessible via a single-photon absorption, and because of the high intensities possible with this laser. We note that the radiation field is resonant with the molecular system only in the collision region, so that we are indeed investigating a radiation-affected collision process.

In Sec. II the model employed in this investigation is discussed. The calculations and results are presented in Sec. III, and Sec. IV contains a brief conclusion.

II. MODEL

In a previous paper,[29] we have presented a rigorous treatment of an atom-atom collision in the presence of an intense radiation field. This rigor is, however, inappropriate for the current study in which we simply wish to ascertain an order-of-magnitude estimate of the field strengths required for observable effects. We are thus justified in employing several approximations to the collision dynamics of the system and to the Hamiltonian, although *ab initio* information is used for the construction of the electronic Hamiltonian matrix (i.e., the potential) and the off-diagonal elements of the interaction Hamiltonian matrix (i.e., the electric dipole transition moments).

The total Hamiltonian is written

$$\mathcal{H} = -(\hbar^2/2m)\,\nabla^2_{\vec{R}} + H^{\mathrm{el}} + H^{\mathrm{so}} + H^{\mathrm{rad}} + H^{\mathrm{int}}\,, \qquad (1)$$

where $\vec{R}$ is the internuclear separation vector, m the reduced mass, and H^{el}, H^{so}, H^{rad}, and H^{int} are the electronic, spin-orbit, pure radiation, and matter-radiation interaction Hamiltonians, respectively. The total wave function of the system can be written as a sum of products of eigenfunctions

$$\Psi = \sum_{j\beta} \tilde{\phi}_j |\beta\rangle \tilde{\psi}_{j\beta}(\vec{R}) \,, \tag{2}$$

where $\tilde{\phi}_j$ is an eigenfunction of H^{el}, $|\beta\rangle$ is the number state representation[3,30] of an eigenfunction of H^{rad}, and $\tilde{\psi}_{j\beta}(\vec{R})$ is the nuclear wave function. With this expansion for Ψ, the close-coupled equations are easily found to be

$$\sum_{j\beta} \left[\delta_{i\alpha,j\beta} \left(-\frac{\hbar^2}{2m} \nabla^2_{\vec{R}} - E \right) + \tilde{H}^{\mathrm{el}}_{i\alpha,j\beta} + \tilde{H}^{\mathrm{so}}_{i\alpha,j\beta} + \tilde{H}^{\mathrm{rad}}_{i\alpha,j\beta} + \tilde{H}^{\mathrm{int}}_{i\alpha,j\beta} \right] \tilde{\psi}_{j\beta}(\vec{R}) = 0 \,, \tag{3}$$

where

$$\tilde{H}_{i\alpha,j\beta} \equiv \langle \tilde{\phi}_i \alpha | H | \tilde{\phi}_j \beta \rangle \tag{4}$$

and

$$\tilde{H}^{\mathrm{rad}}_{i\alpha,j\beta} = \delta_{i\alpha,j\beta}\, \alpha \hbar \omega \,, \tag{5}$$

ω being the frequency of the (monochromatic) radiation field. In the derivation of Eq. (3), the electronic (field free) nonadiabatic coupling has been totally neglected. The matrix $\tilde{H}^{\mathrm{el}}_{i\alpha,j\beta}$ is diagonal in this basis although $\tilde{H}^{\mathrm{so}}_{i\alpha,j\beta}$ is not. It will prove convenient to introduce $\{\phi_l\}$ which is related to the $\{\tilde{\phi}_j\}$ basis by a constant unitary transformation

$$\phi_l = \sum_j \Gamma_{lj} \tilde{\phi}_j \,, \tag{6}$$

and whose members are eigenfunctions of $H^{\mathrm{el}} + H^{\mathrm{so}}$ asymptotically. Assuming that H^{so} is independent of R, Eq. (3) is written in the new basis as

$$\sum_{j\beta} \left[\delta_{i\alpha,j\beta} \left(-\frac{\hbar^2}{2m} \nabla^2_{\vec{R}} - E + E_{i\alpha} \right) + V_{i\alpha,j\beta} + H^{\mathrm{int}}_{i\alpha,j\beta} \right] \psi_{j\beta}(\vec{R}) = 0 \,, \tag{7}$$

where

$$H_{i\alpha,j\beta} \equiv \langle \phi_i \alpha | H | \phi_j \beta \rangle \,, \tag{8}$$

$$V_{i\alpha,j\beta} \equiv H^{\mathrm{el}}_{i\alpha,j\beta} + H^{\mathrm{so}}_{i\alpha,j\beta} + H^{\mathrm{rad}}_{i\alpha,j\beta} - \delta_{i\alpha,j\beta} E_{i\alpha} \,, \tag{9}$$

and

$$E_{i\alpha} \equiv \langle \phi_i \alpha | H^{\mathrm{el}} + H^{\mathrm{so}} | \phi_i \alpha \rangle_{R=\infty} + \alpha \hbar \omega \,. \tag{10}$$

The approximation is now made that both $V_{i\alpha,j\beta}$ and $H^{\mathrm{int}}_{i\alpha,j\beta}$ depend only upon the radial coordinate, thus ignoring angular and Coriolis coupling while greatly simplifying the collisional dynamics of the system. The nuclear wave function can then be expanded in terms of spherical harmonics,

$$\psi_{j\beta}(\vec{R}) = \sum_{lm} Y_{lm}(\hat{R}) R^{-1} \psi^{lm}_{j\beta}(R) \,, \tag{11}$$

and Eq. (7) can be written

$$\sum_{j\beta} \left[\delta_{i\alpha,j\beta} \left(\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} + K^2_{i\alpha} \right) - W_{i\alpha,j\beta} \right] \psi^{lm}_{j\beta}(R) = 0 \,, \tag{12}$$

where we have introduced the notation

$$K^2_{i\alpha} \equiv (2m/\hbar^2)(E - E_{i\alpha}) \,, \tag{13}$$

and

$$W_{i\alpha,j\beta} \equiv (2m/\hbar^2)(V_{i\alpha,j\beta} + H^{\mathrm{int}}_{i\alpha,j\beta}) \,. \tag{14}$$

Consistent with this approximation, the matrix elements of the interaction Hamiltonian are taken to be

$$H^{\mathrm{int}}_{i\alpha,j\beta} = \delta_{\alpha\pm1,\beta}\, \epsilon \mu_{ij} \,, \tag{15}$$

where ϵ is the electric field strength and μ_{ij} is the Z component of the electric dipole moment between the states ϕ_i and ϕ_j.

For xenon fluoride, the transition dipole moments between all states of interest vanish asymptotically, as does $V_{i\alpha,j\beta}$. Equation (12) thus reduces to a set of uncoupled equations which enables scattering boundary condtions to be imposed and an S matrix defined in the usual manner. The total cross section for an inelastic process is then

$$\sigma_{f\leftarrow i} = \frac{\pi}{K^2_i} \sum_{l=0}^{\infty} (2l+1) |S^l_{fi}|^2 \,, \tag{16}$$

where $i(f)$ is a collective index denoting the initial (final) state.

The wave-function expansion of Eq. (2) is truncated to include only the six states corresponding to Xe + F(^2P) + ($n+1$) photons and Xe$^+$(^2P) + F$^-$ + n photons. Inherent in this truncation is the application of the rotating wave approximation and the neglect of any permanent dipole moments as well as other possible effects, such as multiphoton absorption. These purely electronic states $\{\tilde{\phi}\}$ are indexed by Λ, the projection of electronic angular momentum upon the internuclear axis. By transforming to the electronic plus spin-orbit basis [Eq. (6)], the projection of spin Σ has been coupled to Λ so that the basis $\{\phi\}$ is indexed by the total angular momentum projection Ω, which can have the values $\frac{1}{2}$ or $\frac{3}{2}$. (Actually, Ω is the absolute value of the total angular momenta projections, the states $\pm\Omega$ being degenerate.) Ω is a good quantum number with respect to $H^{\mathrm{el}} + H^{\mathrm{so}}$, and the interaction Hamiltonian of Eq. (15) couples only those states having the same value of Ω. Thus the six-state problem reduces to a two-state problem ($\Omega = \frac{3}{2}$) and a four-state problem ($\Omega = \frac{1}{2}$) which can be solved separately. However, the state asymptotically corresponding to Xe $+\mathrm{F}(^2P_{1/2})$ has $\Omega = \frac{1}{2}$, so that the quenching process is entirely determined by consideration of the four state ($\Omega = \frac{1}{2}$) problem. (For a more complete discussion of the angular momentum considerations for a rare-gas monohalide, see the excellent article by Hay and Dunning.[31])

III. CALCULATIONS AND RESULTS

The adiabatic potential curves for the six energetically lowest states of XeF (derived from the Hamiltonian $H^{el}+H^{so}$) are presented in Fig. 1. These curves as well as the electric dipole transition moments are taken from *ab initio* calculations performed by Dunning.[32] The covalent states are all essentially repulsive (although regions of very small attraction have been predicted from experimental observations,[33] and have been confirmed by Dunning's work), while the excimer states have substantial wells. These features are clearly responsible for the interest in XeF (and similar systems) as laser systems. In Fig. 2 the four $\Omega = \frac{1}{2}$ states of interest are presented (derived from the Hamiltonian $H^{el}+H^{so}+H^{rad}$). The excimer states are shifted by the energy of one KrF photon (248 nm), since these states correspond to an absorption of a photon (and hence have $\hbar\omega$ less energy in the radiation field than the covalent states). The distortion of the potential curves near the field-free crossings due to the interaction with a radiation field of intensity 100 GW/cm^2 is shown by the dotted curves in the inset. The variations of the quenching cross section with field intensity is a consequence of these distortions.

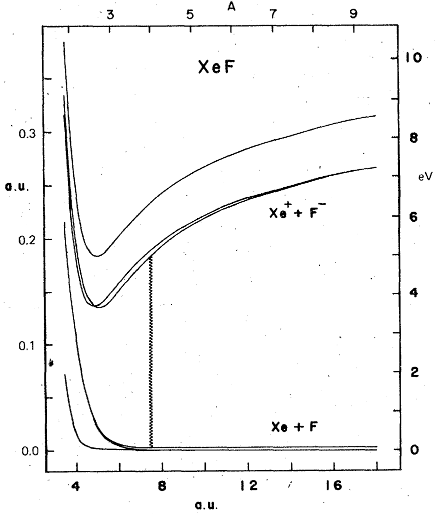

FIG. 1. Potential-energy curves for the XeF system. The vertical line corresponds to the 248-nm line of the KrF laser.

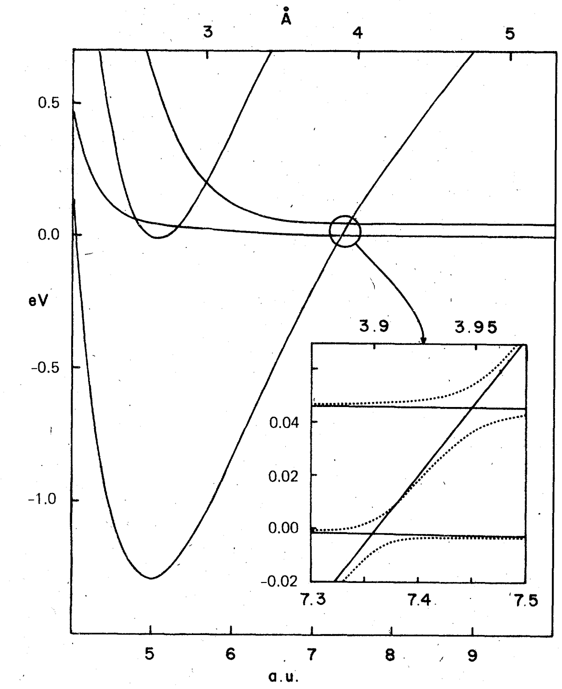

FIG. 2. Four $\Omega = \frac{1}{2}$ potential curves used in the calculation where the upper two are shifted downward in energy by $\hbar\omega$. Inclusion of radiative coupling results in avoided crossings, shown in the inset as dotted curves for the case when the field strength is 100 GW/cm^2.

The close-coupled equations of Eq. (12) were numerically solved by the R-matrix method of Light and Walker.[34] In passing, we note that the method for selecting step sizes originally proposed by Light[35] proved unsatisfactory for this calculation, requiring a very large number of steps to obtain convergence. This was apparently due to the existence of the rather large well. The step-selection algorithm was replaced by a fixed step size within a given interval, and the total integration region divided into seven such intervals. Convergence was then obtained with about $\frac{1}{10}$ the computational effort of the original method. Convergence of the partial cross sections was tested with respect to these fixed step sizes, as well as to initial and final integration points. The summation for the total cross section, Eq. (16), was then performed containing a sufficient number of partial waves to achieve convergence, as many as 225 at the largest energy.

The cross section for quenching of $\mathrm{F}(^2P_{1/2})$ was calculated for various values of the initial collision energy and radiation intensity. These results appear in Fig. 3. The effect of the radiation field is clearly evident, and is largest at small

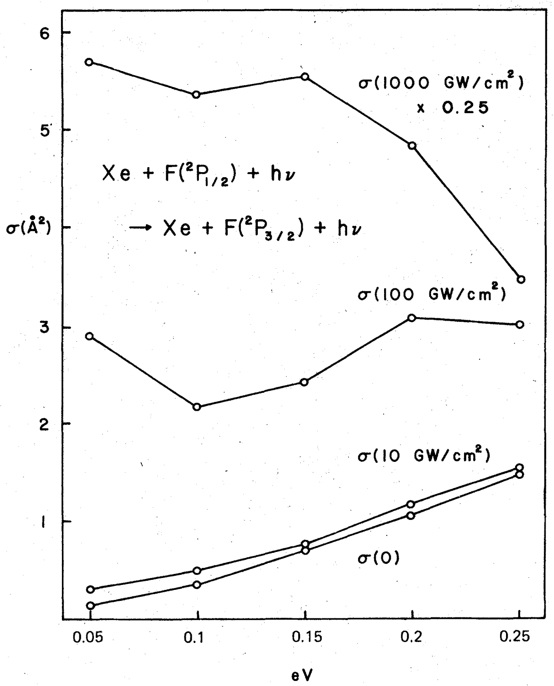

FIG. 3. Calculated quenching cross sections for various field strengths as functions of initial collision energy for the process. $Xe + F(^2P_{1/2}) + \hbar\omega \rightarrow Xe + F(^2P_{3/2}) + \hbar\omega$.

collision energies. At the lowest energy reported, the quenching cross section is enhanced 100% by a radiation field of 10 GW/cm^2, and order-of-magnitude enhancement is calculated at 100 and 1000 GW/cm^2.[36]

IV. DISCUSSION

The quenching of fluorine by xenon in the radiation field of a KrF laser is illustrated schematically in Fig. 4 from a localized classical argument. As the system, initially in the $Xe + F(^2P_{1/2})$ state, collides an internuclear separation is reached at which the system can easily absorb a photon (i.e., near resonance) and make the transition to an excimer state. As the collision proceeds, another near-resonant situation is achieved, but between the excimer state and the $Xe + F(^2P_{3/2})$ state. Again, the system can undergo a transition (by stimulated emission). The net result is a transition from the $Xe + F(^2P_{1/2})$ state to the $Xe + F(^2P_{3/2})$ state with no photons lost from the radiation field, that is, radiation-enhanced collisional quenching. Since two photons are involved, this is a second-order process in the radiation field (using the language of perturbation theory). It is particularly interesting to note that the external field is not in resonance anywhere with the actual curves correlating to $Xe + F(^2P_{3/2})$ and $Xe + F(^2P_{1/2})$.

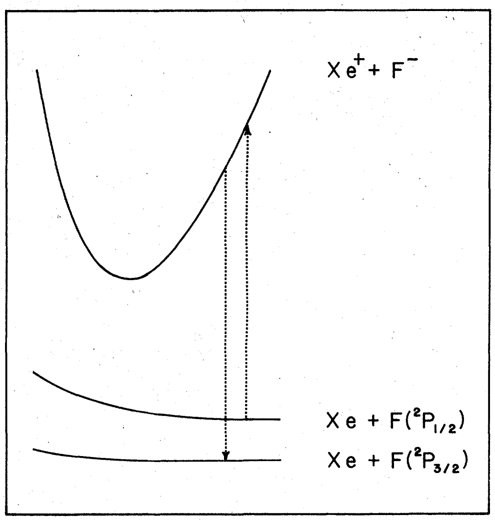

FIG. 4. Schematic illustration of absorption and stimulated emission resulting in radiative quenching, involving two covalent potential curves and one excimer curve in a region of resonance with $\hbar\omega$.

In this paper we have presented a close-coupled formalism for the description of this quenching process and employed it to calculate the cross section as a function of collision energy and field intensity. A marked dependence of the cross section on the field intensity in the thermal collision energy range was found. Although several approximations were made and possible competitive processes (such as Raman emission or multiphoton absorption) were ignored, these results clearly indicate that a substantial enhancement of the quenching cross section should be experimentally observable at thermal energies in a field with intensity on the order of 10–100 GW/cm^2.

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