THEORY OF MOLECULAR COLLISIONS IN THE PRESENCE OF A LASER FIELD

Thomas F. George, John R. Laing, Jian-Min Yuan and I. Harold Zimmerman
The University of Rochester
Department of Chemistry
Rochester, New York 14627 USA

Abstract

The reaction dynamics and mechanism of energy transfer in a gas-phase molecular collision system can be dramatically affected by an intense, external laser field. A rigorous theoretical treatment must consider explicitly the interaction of the field with the collision dynamics, where the absorption (and emission) of radiation and the molecular collision are viewed as a single process rather than separate, independent processes. The full quantum mechanical formulation yields a set of coupled equations, where the number of equations corresponds to the number of asymptotic channels (a given channel is identified by a field occupation number, vibrational, rotational, nuclear orbital angular momentum and electronic quantum numbers). A semiclassical formulation of the molecular dynamics involves the propagation of classical trajectories and their corresponding actions for nuclear motion on electronic-field potential surfaces, where each electronic-field surface depends on field-free, adiabatic electronic surfaces and radiative coupling (as functions of nuclear coordinates). Transitions between electronic-field surfaces are effected by trajectories propagating through intersection points between the surfaces analytically continued into the complex plane. Numerical results (S-matrix elements) from the quantum and semiclassical approaches have been obtained with model calculations on the process \( \text{Br} + \text{H}_2 \rightarrow \text{Br}_2 + \text{H}_2 \).

Introduction

The recent rapid development of laser systems and their use as investigative tools has led to a resurgence of interest in the interaction of matter and radiation. An understanding of this interaction at the microscopic level is necessary if the full potential of laser systems is to be realized. Recent experimental studies on atom-atom collisions have suggested enhancement of inelastic collisional cross sections due to intense optical radiation. A theoretical model of this phenomenon must treat the collision dynamics of the atoms and their interaction with radiation on the same level of approximation for the following reasons: 1) in ordinary molecular beams collisions occur in approximately \( 10^{-12} \) second, or the cycle of an infrared laser, so the collision and the absorption or emission may not be viewed as separate, distinct processes; and 2) for intense fields and/or multi-photon processes time-dependent perturbation theory is not valid.

In this paper we focus on atom-atom and atom-diatom collision processes in the presence of a laser field. The theory can be described molecular systems with a large number of electronic states and multi-mode lasers, but for clarity of presentation, we restrict ourselves to two electronic states and a single mode laser. Since our background lies in molecular scattering, we are most interested in the effects of the radiation field on the molecular collision dynamics.

Within the two-(electronic)state approximation both a quantum mechanical theory and a semiclassical theory of molecular scattering in a laser field have been developed, and the essence of these are discussed in the following section. In the third section some numerical results for the process

\[
\text{Br}(2\text{P}_{3/2}) + \text{H}_2(\text{u}=0) + \text{Br}(2\text{P}_{1/2}) + \text{H}_2(\text{u}=0)
\]

(1.1)

are discussed. The description of this process involves the construction of electronic-field potential energy surfaces from the original field-free adiabatic surfaces and electric dipole (sometimes magnetic dipole or electric quadrupole) transition matrix elements between electronic states as a function of nuclear coordinates.

Research supported by the Air Force Office of Scientific Research (contract No. F44620-74-C-0073) and the National Science Foundation.

Camille and Henry Dreyfus Teacher-Scholar; Alfred P. Sloan Research Fellow.
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Theory

A molecular collision process in an electromagnetic field may be described by the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \Psi(x,q,t)}{\partial t} = \hat{H}(x,q,t) \Psi(x,q,t),$$

(2.1)

where the total Hamiltonian is:

$$\hat{H}(x,q,t) = \hat{T}_{q} + \hat{H}_{el}(x,q) + \hbar \omega \hat{a}^\dagger \hat{a} + \hat{H}_{int}(x,q,t),$$

(2.2)

where $T_q$ and $q$ represent electronic and nuclear coordinates, respectively, and $\hat{a}$ ($\hat{a}^\dagger$) are the photon annihilation (creation) operators for the single-mode field of frequency $\omega$. The field-free electronic Hamiltonian, $\hat{H}_{el}(x,q)$, contains the electronic kinetic energy as well as the Coulomb potentials among electrons and nuclei. $\hat{H}_{int}$ is the Hamiltonian for the interaction between the radiation field and the molecular system and includes all multipole interactions. In practice the dipole approximation is invoked, such that

$$\hat{H}_{int}(x,q,t) = \mu(x,q) \cdot \mathbf{E}(t),$$

(2.3)

where $\mu(t)$ is the electric field, and the transition dipole operator is

$$\mu = \sum_{j} e_{j} \mathbf{Q}_{j},$$

(2.4)

in which $e_{j}$ and $\mathbf{Q}_{j}$ are charges and coordinates of electrons and nuclei.

The total wave function $\Psi(x,q,t)$ is expanded in terms of field-free adiabatic surfaces, $\phi_{k}(x,q)$ as

$$\Psi(x,q,t) = \sum_{k=1}^{2} a_{k}(q) e^{i \int_{\Sigma_1}^{\Sigma_2} \phi_{k}(x,q) \cdot \mathbf{E}(t) \, dt},$$

(2.5)

where we have made the two-(electron) state approximation. Substituting (2.5) into (2.1), multiplying by $\phi_{j}(x,q)$ and integrating over $x$ yields a set of coupled equations which may be written in matrix form as

$$\left( \hat{H} + \gamma \right) a_{k} = E_{k} a_{k},$$

(2.6)

where:

$$\hat{H} = \begin{pmatrix} \hat{T}_{q} & \hat{T}_{q}^{\dagger} T_{q} \hat{T}_{q} & 0 \\ 0 & \hat{T}_{q}^{\dagger} T_{q} \hat{T}_{q} & \hat{T}_{q}^{\dagger} T_{q} \hat{T}_{q}^{\dagger} T_{q} \hat{T}_{q} \hat{T}_{q}^{\dagger} T_{q} \hat{T}_{q} \hat{T}_{q} + \hat{H}_{el}(x,q) \end{pmatrix},$$

(2.7)

$$\gamma = \begin{pmatrix} \gamma_{1,1} \gamma_{1,2} \gamma_{2,1} \gamma_{2,2} \end{pmatrix},$$

(2.8)

$$\gamma_{ij} = \begin{pmatrix} \gamma_{ij} \\ \gamma_{ij} \end{pmatrix},$$

(2.9)

and $\mathbf{E}$ is the time-independent amplitude of the electric field in its polarization direction, and the rotating wave approximation has been made. The adiabatic surfaces $\Sigma_1$ and $\Sigma_2$ are strongly coupled through the radiative coupling, so the scattering equations are most appropriately cast in terms of electronic-field surfaces, which are given as

$$E_{j} = \frac{1}{2} \left( V_{1}^{2} + V_{2}^{2} + \hbar \omega \right) + \left( \frac{\gamma_{ij}}{2} \right) \left[ \left( V_{2} - V_{1} \right)^{2} + \left( V_{12} \right)^{2} \left( V_{21} \right)^{2} \right] 1/2$$

(2.10)

This transformation yields an alternate representation of Eq. (2.6) which may be integrated numerically. The scattering transition amplitude (S-matrix) is then obtained by applying appropriate boundary conditions to the integrated solution matrix.

Semiclassical S-matrix elements for a transition from initial state $i$ to final state $f$, derived from a path
Our work involves the study of electronic-to-vibrational resonance, where upon the presence of a field, the probability of electronic transition increases very rapidly with field strength from threshold at \(5 \times 10^5\) volts/cm to .85 at \(5 \times 10^7\) volts/cm. The electronic-to-vibrational probability falls from .3 to .17 in the same range of field strength. Transition probabilities are also calculated within the vibronic approximation. This model requires only two channels whereas the more general treatment employs eight channels together. However, the results are surprisingly close, and the semiclassical calculations employing the vibronic model are also in excellent agreement with the full quantum probabilities.

### Discussion and Conclusion

Both a semiclassical model and a coupled-channel quantum mechanical formulation of the field-plus-molecular scattering process have been derived in which the nonadiabatic and radiative coupling are treated equally. Our sample calculation reveals that molecular dynamics are greatly affected by the presence of an intense field, with some cross sections being enhanced while others are damped. Thus a laser field impinging on a scattering region may be tuned to yield products in selected final states.

The electronic-field surfaces, which are characteristic of both the molecular system and the applied laser
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field, may support a new spectrum and thus lead to absorptions and emissions not present in the absence of the field. These surfaces may also contain wells able to support metastable states. Preliminary investigations of these effects are underway in our laboratory.

References

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