General Laser Interaction Theory in Atom−Diatom Systems for Both Adiabatic and Nonadiabatic Cases†

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This paper develops the general theory for laser fields interacting with bimolecular systems. In this study, we choose to use the multipolar gauge on the basis of gauge invariance. We consider both the adiabatic and nonadiabatic cases and find they produce similar interaction pictures. As an application of this theory, we present the study of rovibrational energy transfer in Ar + CO collisions in the presence of an intense laser field.

I. Introduction

The study of dynamic molecular processes in the presence of an electromagnetic field is important to both experimentalists and theorists. We are particularly interested in molecular rearrangement dynamics and quantum coherent control of bimolecular chemical reactions in the presence of an electromagnetic field.

As discussed by Light and co-workers (ref 1 and references therein):

Intense laser radiation can affect kinetic processes in gas mixtures in two distinct ways: It can alter the Boltzmann population of the internal states of the atoms and molecules in the system, thus inducing kinetics of excited species, and in some circumstances, it can alter the dynamics of the collision events themselves even in the absence of prior population changes. The theoretical approaches to these two classes of processes are quite different, the first requiring detailed rate constants or cross sections for the excited initial states and the second requiring that the laser field be included in the dynamics of the collision process itself. The spectrum of different collision processes which could be influenced by the laser field is as broad as the collision process itself, including collision induced absorption, laser induced collisional energy transfer, ionization, and chemical reaction.

This is because the collision system in the presence of a laser field has a much richer range of phenomena than in the absence of the laser field. When the laser field is included, photons can be absorbed or emitted during the collision process due to additional photon-system couplings. If the initial and final states are not in resonance with the laser field, then the induced transitions must be associated with the short-range interaction. The dynamics of the colliding system are thus greatly affected by the presence of the laser field, and a full quantum mechanical treatment of the problem should be used. George and collaborators have shown the necessity of this approach.[2−4]

Another important example is the coherent control of bimolecular reactions, which can be implemented by methods similar to those used by Brumer and Shapiro to control collinear chemical reactions.[5] In these methods, coherent control of a bimolecular collision is accomplished by photoassociating the mixed atom−diatom system to form a triatomic complex of excited states. The first excitation step, the pump phase, uses a picosecond laser pulse to create a coherent superposition of excited rovibrational states of the triatomic complex. The excited wave packet created by the pump pulse then evolves for a variable time. A second laser pulse, the dump pulse, stimulates a transition to the ground state that preferentially favors a particular reactive or nonreactive channel. The experimental control parameters are the relative detuning of the pump pulse from the superposed excited state levels and the time delay between the pump and dump pulses. Brumer and Shapiro showed that, theoretically, nearly 100% control may be obtained using their collinear model for the H + HD bimolecular collision. They use the shape of the pulses (the excitation centerline energy and pulse width) to control the dynamics leading to the breaking of one bond and the formation of another.

This paper is the first of a series showing the effects of laser fields on atom−diatom molecular collisions. Many researchers have shown great interest in atom−radiation interactions, and different derivations have been established for different applied gauges. In 1979, Kobe advocated the use of the multipolar gauge on the basis of gauge invariance.[6,7] However, the general theory was not established specifically for an atom−diatom system interacting with a laser field. What is more, nonadiabatic collisions have interested many researchers and will be important for some systems. It will be a challenge to include the nonadiabatic terms in the atom−radiation interaction. We herein provide the theory approach including nonadiabatic effects in the atom−diatom collision system with a laser field.

In section II of this paper, we develop the general theory for using the multipolar gauge to deal with the atom−radiation interaction (ARI). Adiabatic and nonadiabatic cases will both be developed. If the electromagnetic field is intense, then one must also quantize the photon field. An application of the theory to the strong laser field case is included in section III. The particular application studied in the current paper is that of

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rovibrational energy transfer in Ar + CO collisions in the presence of an intense laser field. Subsequent publications will treat reactive molecular collisions in the presence of an electromagnetic field. Results for this system will be presented in section IV, and concluding remarks will be provided in section V.

II. General Theory

A. ARI in a Three-Atom System. The main problem we are dealing with is the behavior of an atom−diatom collision system in a laser field. Our derivation of this problem begins with the time-dependent Schrödinger equation (TDSE)

$$\hat{H}\Psi = i\hbar \frac{\partial}{\partial t}\Psi \tag{1}$$

where the full Hamiltonian is

$$\hat{H} = \sum_{\alpha}^{N}\left\{\frac{1}{2m_\alpha}[\vec{p}_\alpha - q_\alpha\vec{A}(\vec{r}_\alpha,t)]^2 + q_\alpha\phi(\vec{r}_\alpha,t)\right\} + V_0(\vec{r}_1,r_2, ...,\vec{r}_N) \tag{2}$$

The sum runs over both the nuclei and the electrons, $\vec{p}_\alpha = -i\hbar\nabla_{\vec{\alpha}}$, V_0 is the usual interparticle Coulombic potential energy for the whole system, $\vec{A}$ is the vector potential, ϕ is the external scalar potential, q_α is $-e$ for an electron and $+Z_\alpha e$ for nuclei, and m_α are the masses of the particles.

Here, we want to specify that $\phi(\vec{r}_\alpha,t)$ is the scalar potential for the external field but not the total scalar potential for the molecular system and the field. The total scalar potential is

$$\phi_{\text{total}} = \sum_{\alpha}^{N}\phi_{\text{total}}(\vec{r}_\alpha,t) = \sum_{\alpha}^{N}[\phi(\vec{r}_\alpha,t) + \phi_{\text{sys}}(\vec{r}_\alpha,t)] \tag{3}$$

where the interparticle Coulombic potential energy is $V_0 = \sum_\alpha^N q_\alpha\phi_{\text{sys}}(\vec{r}_\alpha,t)$, which depends on the scalar potential of the atom−diatom system.

To simplify the problem, we will partition the Hamiltonian. The total Hamiltonian is the sum of the molecular Hamiltonian (field-free Hamiltonian) $\hat{H}_0$ and the interaction Hamiltonian $\hat{H}_{\text{int}}$

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}} \tag{4}$$

where the $\hat{H}_0$ and $\hat{H}_{\text{int}}$ terms are chosen differently based on the associated gauges, and H_0 always contains the interparticle Coulombic V_0 term.

B. Multipolar Gauge in ARI Without Nonadiabatic Coupling. We use the multipolar gauge to simplify the full Hamiltonian and so that the Hamiltonian will have the proper gauge invariance.[7] In this subsection, the derivation is limited to an adiabatic case, and we will use a Born−Oppenheimer expansion to include the nonadiabatic terms in the next subsection.

The multipolar gauge is defined as follows[8]

$$\vec{r}\cdot\vec{A}_{\text{M}}(\vec{r},t) = 0 \tag{5}$$

with a boundary condition for the gauge transformation function $\chi_{\text{M}}(\vec{r},t)$ at the origin

$$\phi(0,t) - \frac{\partial}{\partial t}\chi_{\text{M}}(0,t) = 0 \tag{6}$$

where the subscript "M" denotes the multipolar gauge. In eqs 5 and 6, we neglect the subscript α for simplicity.

Using the multipolar gauge, we can express the vector potential and the scalar potential in terms of the $\vec{E}$ and $\vec{B}$ fields

$$\vec{A}_{\text{M}}(\vec{r},t) = -\vec{r} \times \int_0^1 u\vec{B}(u\vec{r},t)\,\text{d}u \tag{7}$$

$$\phi_{\text{M}}(\vec{r},t) = -\vec{r}\cdot\int_0^1 \vec{E}(u\vec{r},t)\,\text{d}u \tag{8}$$

and we know that both $\vec{E}$ and $\vec{B}$ must be gauge invariant.

A multipole expansion of the potentials in eq 7 and eq 8 can be made by expanding the fields about the origin (center-of-mass of the system). Here, we employ the long wavelength approximation (LWA), where only the first few terms of the expansion need to be included because the laser wavelength is much longer than the scale of the atom or diatom

$$\vec{A}_{\text{M}}(\vec{r},t) = -\frac{1}{2}\vec{r} \times \vec{B}(0,t) + \cdots \tag{9}$$

$$\phi_{\text{M}}(\vec{r},t) = -\vec{r}\cdot\vec{E}(0,t) - \sum_i\sum_j\frac{1}{2}r_ir_j\partial'_jE_i(\vec{r}\,',t)|_{\vec{r}\,'=0} + \cdots \tag{10}$$

where the definition of the derivative is $\partial'_j = \partial/\partial r'_j$, and r_j values are the Cartesian components of the vector $\vec{r}$.

In this expansion, the first term in $\vec{A}_{\text{M}}$ is the magnetic dipole moment, the first term in ϕ_{M} is the electric dipole moment, and the second term in ϕ_{M} is the electric quadrupole term. It should be specified that the electric quadrupole and magnetic dipole terms are of the same order in their contribution to the electromagnetic field.[9] By neglecting these two terms, we rewrite the equations for $\vec{A}_{\text{M}}$ and ϕ_{M} as

$$\vec{A}_{\text{M}}(\vec{r},t) \approx 0 \tag{11}$$

$$\phi_{\text{M}}(\vec{r},t) \approx -\vec{r}\cdot\vec{E}(0,t) \tag{12}$$

This approximation is called the electric dipole approximation (EDA).

Here, we need to specify that the application of the LWA and EDA is valid only in the following situation: the subsystem, which would be excited by the laser field, should be confined in a region that is much smaller than the laser wavelength. For a larger subsystem, we argue that the electric quadrupole and magnetic dipole terms should be taken into consideration. In this case of the diatom subsystem, this condition is met and the two approximations are valid.

Therefore, with the LWA and the EDA, the Hamiltonian becomes

$$\hat{H} = \sum_\alpha \frac{1}{2m_\alpha}{p_\alpha}^2 + V_0 - \hat{\mu}\cdot\vec{E}(t) = \hat{H}_0 - \hat{\mu}\cdot\vec{E}(t) \tag{13}$$

where

$$\hat{\mu} = \sum_\alpha q_\alpha\vec{r}_\alpha \tag{14}$$

is the dipole moment operator. The time-independent part of the Hamiltonian, $\hat{H}_0$, is

$$\hat{H}_0 = \sum_\alpha \frac{1}{2m_\alpha}{p_\alpha}^2 + V_0 \tag{15}$$

Since the interaction part in the Hamiltonian under the multipolar gauge transformation has an $\vec{r}$ term, it is said that the multipolar gauge has a "length form".

The term containing the dipole operator is responsible for coupling the states of the system, and the coupling matrix element for the multipolar gauge can be written as

$$\begin{aligned} V_{kl} &= \langle k|\,\hat{H}_{\mathrm{int}}|l\rangle \\ &= -\langle k|\vec{E}\cdot\hat{\vec{\mu}}|l\rangle \end{aligned} \qquad (16)$$

where the indices "k" and "l" represent different states of the whole system.

C. Multipolar Gauge in ARI with Nonadiabatic Coupling. It will be necessary to include nonadiabatic terms for systems that have conical intersections in the relevant energy states. In this situation, the full Hamiltonian in eq 2 can be partitioned into three parts

$$\hat{H} = \hat{H}_{\mathrm{n}} + \hat{H}_{\mathrm{e}} + V_0 \qquad (17)$$

where

$$\hat{H}_{\mathrm{n}}(\vec{R}) = \sum_{\alpha}^{\mathrm{n}} \left\{ \frac{1}{2m_\alpha} [\vec{p}_\alpha - q_\alpha \vec{A}(\vec{R}_\alpha,t)]^2 + q_\alpha \phi(\vec{R}_\alpha,t) \right\} \qquad (18)$$

and

$$\hat{H}_{\mathrm{e}}(\vec{r};\vec{R}) = \sum_{\alpha}^{\mathrm{e}} \left\{ \frac{1}{2m_\alpha} [\vec{p}_\alpha - q_\alpha \vec{A}(\vec{r}_\alpha,t)]^2 + q_\alpha \phi(\vec{r}_\alpha,t) \right\} \qquad (19)$$

The symbol "n" denotes nuclei, and the symbol "e" denotes electrons. Here, α in eq 18 runs over all the nuclei, and α in eq 19 runs over all the electrons. The $\vec{R}$ terms are the nuclear coordinates, and the $\vec{r}$ terms are the electronic coordinates.

If we introduce the basis $\Phi(\vec{r};\vec{R})$ (the eigenfunctions of the electronic Hamiltonian) and use a Born−Oppenheimer expansion, then we will end up with the following Hamiltonian after integration over the electronic space "**r**"

$$\hat{H}(\vec{R})_{ij} = \langle \Phi_i|\hat{H}_{\mathrm{n}}|\Phi_j\rangle_{\vec{r}} + \langle \Phi_i|\hat{H}_{\mathrm{e}}|\Phi_j\rangle_{\vec{r}} + \langle \Phi_i|V_0|\Phi_j\rangle_{\vec{r}} \qquad (20)$$

The first part of the full Hamiltonian in the nuclear space "**R**" is

$$\langle \Phi|\hat{H}_{\mathrm{n}}|\Phi\rangle_{\vec{r}} = \sum_{\alpha}^{\mathrm{n}} \left\{ \frac{1}{2m_\alpha} \left[\frac{\hbar}{i}\nabla_{\vec{\alpha}} - q_\alpha \vec{A}(\vec{R}_\alpha,t) + \frac{\hbar}{i}\vec{F} \right]^2 + q_\alpha \phi(\vec{R}_\alpha,t) \right\} \qquad (21)$$

where the nonadiabatic term $\vec{F}$ is

$$\vec{F}_{ij} = \langle \Phi_i|\vec{\nabla}|\Phi_j\rangle_{\vec{r}} \qquad (22)$$

For simplicity, the sum is implied, and we will rewrite eq 21 as

$$\langle \Phi|\hat{H}_n|\Phi\rangle_{\vec{r}} = \frac{1}{2m} \left[\frac{\hbar}{i}\vec{\nabla} - q\vec{A}(\vec{R},t) + \frac{\hbar}{i}\vec{F} \right]^2 + q\phi(\vec{R},t) \qquad (23)$$

Notice that these operators are matrixes in the electronic state basis.

If we apply the EDA to the multipolar gauge, then $\vec{A} = 0$ and the total Hamiltonian in the nuclear space "**R**" will be

$$\begin{aligned} \vec{H}_{\mathrm{M}}(\vec{R}) &= \frac{1}{2m} \left[\frac{\hbar}{i}\nabla_{\vec{R}} + \frac{\hbar}{i}\vec{F} \right]^2 - \hat{\vec{\mu}}\cdot\vec{E} + V_{\mathrm{e}} \\ &= -\frac{\hbar^2}{2m} [\nabla_{\vec{R}} + \vec{F}]^2 - \hat{\vec{\mu}}\cdot\vec{E} + V_{\mathrm{e}} \end{aligned} \qquad (24)$$

where $\vec{\mu}$ is the dipole operator and

$$V_{\mathrm{e}} = \langle \Phi|\hat{H}_{\mathrm{e}}|\Phi\rangle + \langle \Phi|V_0|\Phi\rangle \qquad (25)$$

If we choose to let the molecular Hamiltonian be

$$\hat{H}_0 = -\frac{\hbar^2}{2m} [\nabla_{\vec{R}} + \vec{F}]^2 + V_{\mathrm{e}} \qquad (26)$$

then the coupling matrix element for the multipolar gauge is

$$V_{kl} = -\langle k|\vec{E}\cdot\hat{\vec{\mu}}|l\rangle \qquad (27)$$

We notice here that the interaction Hamiltonian has the same form as in the adiabatic case. However, the basis functions are different because the different basis-determining Hamiltonian now includes the nonadiabatic terms $\vec{F}$.

III. Atom−Diatom Collisions in a Laser Field

In this section, we apply the theory of section II to a problem of an S-state, structureless atom colliding with a Σ-state diatomic molecule in the presence of an intense laser field. We want to specify that we will not consider the nonadiabatic terms in this study for now; we will limit our focus to the adiabatic case. This limitation is valid for the collision energies and laser frequency used herein.

We use the center-of-mass of the atom (A)−diatom (BC) as our coordinate origin, and we ignore the center-of-mass motion. The position vectors $\vec{r}$ and $\vec{R}$ are measured from the center-of-mass of the diatom BC to the atom A and from the atom B to the atom C, respectively. The angle between $\vec{r}$ and $\vec{R}$ is denoted by θ. In the space-fixed (SF) theory, the angles (θ_r,ϕ_r) and (θ_R,ϕ_R) define the directions of the position vectors $\vec{r}$ and $\vec{R}$, where θ and ϕ are the polar and azimuthal angles, respectively.

A. SF Theory. First, let us discuss the Hamiltonian of the atom−diatom collision in the presence of a strong laser field in an SF set of coordinates. The body-fixed (BF) formulation has been defined elsewhere.[10] The total Hamiltonian $\hat{H}$ of the collision system in the presence of a laser field with a total energy E satisfies the time-independent Schrödinger equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \qquad (28)$$

where the Dirac notation $|\Psi\rangle$ represents the wave function of the whole system. The total Hamiltonian $\hat{H}$ of the system includes three terms

$$\hat{H} = \hat{H}_0 + \hat{H}_{\mathrm{rad}} + \hat{H}_{\mathrm{int}} \qquad (29)$$

The first term, the field-free Hamiltonian $\hat{H}_0$, is the Hamiltonian for the collision system in the absence of the laser field; the second term, the radiation Hamiltonian $\hat{H}_{\mathrm{rad}}$, is the Hamiltonian for a radiation field; the last term, the radiative interaction Hamiltonian $\hat{H}_{\mathrm{int}}$, is the Hamiltonian for the interaction of the laser radiation field with the system. This derivation is slightly different from that in section II, but the theory is equivalent.

In the center-of-mass coordinate system, the field-free Hamiltonian $\hat{H}_0$ (in cgs units) can be written as

$$\begin{aligned}\hat{H}_0 &= -\frac{\hbar^2}{2\mu}\nabla_r{}^2 + \hat{H}_{BC} + V(r,R,\theta)\\ &= -\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right) + \frac{\vec{L}^2}{2\mu r^2} + \hat{H}_{BC} + V(r,R,\theta)\end{aligned} \tag{30}$$

with

$$\vec{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta_r}\frac{\partial}{\partial\theta_r}\left(\sin\theta_r\frac{\partial}{\partial\theta_r}\right) + \frac{1}{\sin^2\theta_r}\frac{\partial^2}{\partial\phi^2{}_r}\right] \tag{31}$$

where $\vec{L}$ is the orbital angular momentum operator of the atom A relative to the diatomic molecule BC, V is the intermolecular potential energy, μ is the atom−diatom reduced mass

$$\mu = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C} \tag{32}$$

and $\hat{H}_{BC}$ is the Hamiltonian of the isolated diatom BC. In the center-of-mass coordinate system of the diatomic molecule, the Hamiltonian $\hat{H}_{BC}$ can be written as

$$\begin{aligned}\hat{H}_{BC} &= -\frac{\hbar^2}{2\mu_{BC}}\nabla_R{}^2 + V_{BC}(R)\\ &= \frac{\hbar^2}{2\mu_{BC}}\left(\frac{1}{R}\frac{\partial^2}{\partial R^2}R\right) + \frac{\vec{\mathscr{J}}^2}{2\mu_{BC}R^2} + V_{BC}(R)\end{aligned} \tag{33}$$

where $\vec{\mathscr{J}}$ is the rotational angular momentum operator of the vibrating rotating diatomic molecule BC, V_{BC} is the intramolecular potential energy of diatom BC, and μ_{BC} is the reduced mass of diatom BC

$$\mu_{BC} = \frac{m_B m_C}{m_B + m_C} \tag{34}$$

The eigenfunctions of $\hat{H}_{BC}$ must satisfy[11]

$$(\hat{H}_{BC} - \epsilon_{j\nu})\chi_{j\nu}(R)Y_{jm_j}(\hat{R}) = 0 \tag{35}$$

where $\hat{R} \equiv (\theta_R,\phi_R)$, $\chi_{j\nu}$ is a vibrational wave function, Y_{jm_j} is a spherical harmonic, and the $\epsilon_{j\nu}$ are the rotation−vibration energy levels.

The radiation Hamiltonian $\hat{H}_{rad}$ can be expressed as

$$\hat{H}_{rad} = \sum_{\mathbf{k},\sigma}\hbar\omega_k\hat{N}_{\mathbf{k}\sigma} = \sum_{\mathbf{k},\sigma}\hbar\omega_k\hat{a}^{\ddagger}_{\mathbf{k}\sigma}\hat{a}_{\mathbf{k}\sigma} \tag{36}$$

Since each mode of the radiation field is specified by the wavevector **k** and the polarization σ, the sum of **k** and σ is therefore a sum over a complete set of modes of the radiation field.

The creation operator $\hat{a}^{\ddagger}_{\mathbf{k}\sigma}$ and annihilation operator $\hat{a}_{\mathbf{k}\sigma}$ are defined by[12]

$$\hat{a}^{\ddagger}_{\mathbf{k}\sigma}|\cdots, n_{\mathbf{k}\sigma},\cdots\rangle = \sqrt{n_{\mathbf{k}\sigma}+1}\,|\cdots, n_{\mathbf{k}\sigma}+1,\cdots\rangle \tag{37}$$

$$\hat{a}_{\mathbf{k}\sigma}|\cdots, n_{\mathbf{k}\sigma},\cdots\rangle = \sqrt{n_{\mathbf{k}\sigma}}\,|\cdots, n_{\mathbf{k}\sigma}-1,\cdots\rangle, \tag{38}$$

where we use the Dirac notation $|\cdots, n_{\mathbf{k}\sigma},\cdots\rangle$ to describe a many-photon radiation field with $n_{\mathbf{k}\sigma}$ photons in the mode **k** and polarization σ.

The number operator $\hat{N}_{\mathbf{k}\sigma}$ satisfies the eigenvalue equation

$$\hat{N}_{\mathbf{k}\sigma}|\cdots, n_{\mathbf{k}\sigma},\cdots\rangle = n_{\mathbf{k}\sigma}|\cdots, n_{\mathbf{k}\sigma},\cdots\rangle \tag{39}$$

The operator $\hat{H}_{rad}$, defined in eq 36, can thus be considered the Hamiltonian of the radiation field and obeys the eigenvalue equation

$$\hat{H}_{rad}|\cdots, n_{\mathbf{k}\sigma},\cdots\rangle = \sum_{\mathbf{k},\sigma}\hbar\omega_k n_{\mathbf{k}\sigma}|\cdots, n_{\mathbf{k}\sigma},\cdots\rangle \tag{40}$$

The interaction Hamiltonian $\hat{H}_{int}$ can be written as

$$\hat{H}_{int} = -\hat{\mu}\cdot\vec{E} \tag{41}$$

where $\hat{\mu}$ is the electric dipole moment formed by the charges making up the atom−diatom system, and $\vec{E}$ is the electric field strength of the laser field. The main derivation of the interaction Hamiltonian is developed in section II.

The electric dipole moment $\hat{\mu}$ can be separated into two terms

$$\hat{\mu} = \hat{\mu}_{BC}(R) + \hat{\mu}^{ind}_{A,BC}(r,R,\theta) \tag{42}$$

The first term $\hat{\mu}_{BC}$ is a function of the internuclear distance R, and it represents the electric dipole moment of the isolated diatom BC. The second term $\hat{\mu}^{ind}_{A,BC}$, caused by the presence of the collision particle (atom A) which distorts the charge distribution of the atom−diatom system, is called the induced electric dipole moment of the system. The term $\hat{\mu}^{int}_{A,BC}$ is a function of the translational distance r, the internuclear distance R, and the angle θ between $\vec{r}$ and $\vec{R}$. For simplicity, we assume the collision particle and the diatom have small polarizabilities; they can only slightly distort the charge distribution of the whole system, and therefore the induced electric dipole moment, $\hat{\mu}^{ind}_{A,BC}$, is much weaker than the electric dipole moment $\hat{\mu}_{BC}$. Under this assumption, the induced dipole moment $\hat{\mu}^{ind}_{A,BC}$ can be neglected, and $\hat{H}_{int}$ becomes

$$\hat{H}_{int} \approx -\hat{\mu}_{BC}\cdot\vec{E} \tag{43}$$

The electric field strength $\vec{E}$, which interacts with the collision system (in spherical coordinates), is given by[13]

$$\vec{E} = \sum_{k,\sigma}E_0(\hat{e}_{k\sigma}a_{k\sigma}e^{i\mathbf{k\cdot r}} - \hat{e}^*_{k\sigma}a^+_{k\sigma}e^{-i\mathbf{k\cdot r}}) \tag{44}$$

with

$$E_0 = i\sqrt{\frac{2\pi\hbar\omega_k}{V}} \tag{45}$$

where $\hat{e}_{k\sigma}$ is the unit vector in the mode **k** and polarization σ, and V is the quantization volume of the laser field. For the electric dipole interaction, the electric field strength can be written as

$$\vec{E} \approx \sum_{k,\sigma}E_0(\hat{e}_{k\sigma}a_{k\sigma} - \hat{e}^*_{k\sigma}a^+_{k\sigma}) \tag{46}$$

Equation 46 is obtained by applying the EDA.

For simplicity, we assume the laser field contains only one frequency ω (single mode) with polarization σ. Because the collision system now interacts with the laser field, the wave functions of the system are then a sum of direct products including the photon state $|n_\sigma\rangle$

$$\Psi^{JMj\ell\nu n_\sigma} = \sum_{J''M''j''\ell''\nu''n_\sigma''} r^{-1} G^{JMj\ell\nu n_\sigma}_{J''M''j''\ell''\nu''n_\sigma}(r)|j''\nu''\rangle|J''M''j''\ell''\rangle|n_\sigma''\rangle \quad (47)$$

where J is the total angular momentum, M is the eigenvalue of the $\vec{J}_z$ component, and G is the expansion coefficient.

The time-independent Schrödinger equation for the collision system in a laser field is

$$(\hat{H} - E)\Psi^{JMj\ell\nu n_\sigma} = 0 \quad (48)$$

where $\hat{H}$ is the total Hamiltonian defined in eq 28 and E is the total energy of the whole system. The coupled-channel equations in a laser field (using the Floquet Hamiltonian[14]) are then given as

$$\sum_{J''M''j''\ell''\nu''n_\sigma''} \langle n_\sigma'\,|\langle J'M'j'\ell'|\langle j'\nu'|\hat{H} - E|j''\nu''\rangle|J''M''j''\ell''\rangle|\,n_\sigma''\rangle \times r^{-1} G^{JMj\ell\nu n_\sigma}_{J''M''j''\ell''\nu''n''_\sigma}(r) = 0 \quad (49)$$

The matrix elements of the relative kinetic energy, $\hat{H}_{\mathrm{BC}}$ and $V(r,R,\theta)$ are

$$\left\langle n_\sigma'\,\middle|\left\langle J'M'j'\ell'\middle|\left\langle j'\nu'\middle| -\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right) + \frac{\vec{L}^2}{2\mu r^2}\middle|j''\nu''\right\rangle\middle|J''M''j''\ell''\right\rangle\middle|\,n_\sigma''\right\rangle = \delta_{n'_\sigma n''_\sigma}\delta_{J'J''}\delta_{M'M''}\delta_{j'j''}\delta_{\ell'\ell''}\delta_{\nu'\nu''}\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right) + \frac{\ell'(\ell'+1)\hbar^2}{2\mu r^2}\right] \quad (50)$$

$$\langle n_\sigma'\,|\langle J'M'j'\ell'|\langle j'\nu'|\hat{H}_{\mathrm{BC}}|j''\nu''\rangle|J''M''j''\ell''\rangle|\,n''_\sigma\rangle = \delta_{n'_\sigma n''_\sigma}\delta_{J'J''}\delta_{M'M''}\delta_{j'j''}\delta_{\ell'\ell''}\delta_{\nu'\nu''}\epsilon_{j''\nu''} \quad (51)$$

$$\langle n_\sigma'\,|\langle J'M'j'\ell'|\langle j'\nu'|V(r,R,\theta)|j''\nu''\rangle|J''M''j''\ell''\rangle|\,n_\sigma''\rangle = \delta_{n'_\sigma n''_\sigma}\langle J'M'j'\ell'|\langle j'\nu'|V(r,R,\theta)|j''\nu''\rangle|J''M''j''\ell''\rangle \quad (52)$$

The matrix element of the radiation Hamiltonian is

$$\langle n_\sigma'\,|\langle J'M'j'\ell'|\langle j'\nu'|\hat{H}_{\mathrm{rad}}|j''\nu'\rangle|J'M'j'\ell'\rangle|\,n_\sigma'\rangle = \delta_{n'_\sigma n'_\sigma}\delta_{J'J''}\delta_{M'M''}\delta_{j'j''}\delta_{\ell'\ell''}\delta_{\nu'\nu''}\hbar\omega n_\sigma \quad (53)$$

The matrix elements of the interaction Hamiltonian can be written as

$$\langle n_\sigma'\,|\langle J'M'j'\ell'|\langle j'\nu'| - \vec{\mu}_{\mathrm{BC}}\cdot E|j''\nu''\rangle|J''M''j''\ell''\rangle|\,n_\sigma''\rangle = -E_0\sqrt{n_\sigma''}\,\delta_{n'_\sigma,n''_\sigma-1}\langle J'M'j'\ell'|\langle j'\nu'|\vec{\mu}_{\mathrm{BC}}\cdot\hat{e}_\sigma|j''\nu''\rangle|J''M''j''\ell''\rangle + E_0\sqrt{n_\sigma''+1}\,\delta_{n_\sigma',n''_\sigma+1}\langle J'M'j'\ell'|\langle j'\nu'|\vec{\mu}_{\mathrm{BC}}\cdot\hat{e}^*_\sigma|j''\nu''\rangle|J''M''j''\ell''\rangle \quad (54)$$

where $\vec{\mu}_{\mathrm{BC}}$ is the electric dipole moment of the diatom BC and $\vec{E}$ is the electric field strength.

Combining all the derivations about the matrix elements above, we obtain

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + k_{j'\nu'n'_\sigma}{}^2 - \frac{\ell(\ell+1)}{r^2}\right] G^{JMj\ell\nu n_\sigma}_{J'M'j'\ell'\nu'n'_\sigma}(r) = \frac{2\mu}{\hbar^2}\sum_{J''M''j''\ell''\nu''}\{\langle J'M'j'\ell'|\langle j'\nu'|V(r,R,\theta)|j''\nu''\rangle| J''M''j''\ell''\rangle G^{JMj\ell\nu n_\sigma}_{J''M''j''\ell''\nu''n'_\sigma}(r) - E_0\sqrt{n_\sigma'+1}\,[\langle J'M'j'\ell'| \langle j'\nu'|\vec{\mu}_{\mathrm{BC}}\cdot\hat{e}_\sigma|j''\nu''\rangle|J''M''j''\ell''\rangle]G^{JMj\ell\nu n_\sigma}_{J''M''j''\ell''\nu''n_\sigma p+1}(r) + E_0\sqrt{n_\sigma'}\,[\langle J'M'j'\ell'|\langle j'\nu'|\vec{\mu}_{\mathrm{BC}}\cdot\hat{e}^*_\sigma|j''\nu''\rangle| J''M''j''\ell''\rangle]G^{JMj\ell\nu n_\sigma}_{J''M''j''\ell''\nu''n'_\sigma-1}(r)\} \quad (55)$$

where

$$k_{j'\nu'n'_\sigma}{}^2 \equiv \frac{2\mu}{\hbar^2}(E - \epsilon_{j'\nu'} - \hbar\omega n_\sigma') \quad (56)$$

IV. Calculation Results

In this section, we consider an S-state, structureless argon (Ar) atom colliding with a Σ-state carbon monoxide (CO) molecule in the presence of an intense laser field. On the basis of the theory developed in previous sections, we are interested in the collision leading to the rotation−vibration transitions. The electronic transitions are not accessible and therefore not included. Note that the energy associated with rotational transitions is usually less than the energy associated with vibrational transitions which is usually less than the energy associated with electronic transitions. As a consequence, a vibrational transition is normally accompanied by rotation transitions. In this Ar + CO collision problem, we assume the relative kinetic energy is low (e.g., ≤500 cm^{-1}) so that no vibrational transition for CO can be observed in the absence of the laser field, that is, we can only excite the rotational energy levels but not the vibrational energy levels of CO in the absence of the laser field. When the collision system Ar + CO is in the laser field, the carbon monoxide may collide with the laser photon and absorb the photon energy. Therefore, we can adjust the laser frequency, that is, the photon energy, so that the vibrational transitions for CO will be accessible. We define the energy defect Δ as follows: by adjusting the laser frequency so that when the energy level for the $\nu = 0$, $j = 0$ state which has absorbed one photon ($N = n - 1$) has the same energy as the level $\nu = 1$, $j = 0$ with no photon absorbed ($N = n$), we say the energy defect is zero. If the energy level for the $\nu = 0$, $j = 0$ ($N = n - 1$) state is 4 cm^{-1} below the level $\nu = 1$, $j = 0$ ($N = n$), then the energy defect is −4 cm^{-1}. The calculated values of the rotation−vibration energy levels of carbon monoxide are given in Table 1. From Table 1, we know the energy defect will be zero if the photon energy is 2200.85966 cm^{-1}.

We shall apply the SF theory, which we developed in section IIIA, to compute the rotation−vibration transition probabilities as a function of the energy defect. The transition probability P_{if} between the initial state $|i\rangle$ and the final state $|f\rangle$ is related to the square of **S**-matrix element

$$P_{if} = |\langle i|S|f\rangle|^2 \quad (57)$$

The **S**-matrix is related to the **K**-matrix by

$$\mathbf{S} = (\mathbf{I} + i\mathbf{K})(\mathbf{I} - i\mathbf{K})^{-1} \quad (58)$$

TABLE 1: Rotation−Vibration Energy of CO

ν (vibration)	j (rotation)	energy (au)	energy (1/cm)
0	0	0.0049486339	1086.09955
0	1	0.0049661784	1089.95011
0	2	0.0050012667	1097.65110
0	3	0.0050538975	1109.20223
0	4	0.0051240690	1124.60310
1	0	0.0149764889	3286.95921
1	1	0.0149937781	3290.75374
1	2	0.0150283561	3298.34274
1	3	0.0150802222	3309.72605
1	4	0.0151493756	3324.90345

TABLE 2: Coefficients for the Dipole Moment Function of CO

$m_0 = -0.1212$
$B = 0.8628$
$C = -0.010087$
$a_1 = -1.2748$
$a_2 = 6.9394$
$a_3 = -8.2501$

TABLE 3: Molecular Constants for the Potential Energy of CO

$B_0 = 2.776904753$
$b_1 = -0.69730961$
$b_2 = -0.58547656$
$b_3 = -0.13627322$
$b_4 = 0.36833499$

where the **K**-matrix can be obtained by solving the coupled-channel equations using the log derivative method.[15]

To solve the coupled-channel equations, we shall introduce the dipole moment function of CO, the potential energy of CO, and the intermolecular potential energy of Ar + CO. The dipole moment function $\mu_{CO}(R)$ of carbon monoxide, which will be used in computing the interaction Hamiltonian matrix, is given as[16]

$$\mu_{CO}(R) = \mu_{CO}(y) = m_0 + a_1By/(1 - By) - a_2\ln(1 - By) + a_3(1 - By)\ln(1 - By)/By + a_3 + Cy(1 - y) \quad (59)$$

with

$$y = 1 - \exp[-a(R - R_e)] \quad (60)$$

where a (2.390439 Å^{-1}) is the parameter of the equivalent Morse oscillator and R_e is the equilibrium position of CO. The coefficients in eq 59 are listed in Table 2, and the units of R and μ_{CO} are angstroms and debye, respectively. Because atomic units are used in solving the coupled-channel equations, we provide the conversion factor used to convert angstrom and debye units into atomic units, that is, 1 D = 0.39354113 au and 1 Å = 1.88972688 au. In atomic units, the equilibrium position of CO is given as 2.132 au. The potential energy of CO can be written as the power series form[17]

$$V_{CO}(R) = V_{CO}(z) \approx B_0z^2(1 + b_1z + b_2z^2 + b_3z^2 + b_4z^2) \quad (61)$$

where $z = (R - R_e)/R$ and the potential energy is given in atomic units. The numerical values of B_0 and b_i are given in Table 3. A detailed discussion on the potential energy of CO can be found in the paper by Finlan and Simon.[17] The intermolecular potential energy $V(r,R,\theta)$ of Ar + CO has the form

$$V(r,R,\theta) = \sum_n V_n(r,R)P_n(\cos\theta) = \sum_{nm} \bar{V}_{nm}(r)(R - R_e)^m P_n(\cos\theta) \quad (62)$$

where $P_n(\cos\theta)$ values are the Legendre polynomials. The Ar + CO potential energy has been fully developed and discussed by Parker and Pack.[18]

TABLE 4: Transition Probability of CO with E = 0.01514 au and Δ = +4 (1/cm) at Different Laser Intensities

	10^5 (W/cm^2)	10^7 (W/cm^2)	10^9 (W/cm^2)
00 → 1	80.784×10^{-6}	80.693×10^{-4}	62.051×10^{-2}
01 → 1	8.180×10^{-6}	8.174×10^{-4}	7.262×10^{-2}
02 → 1	7.661×10^{-6}	7.658×10^{-4}	6.448×10^{-2}
03 → 1	4.809×10^{-6}	4.502×10^{-4}	4.283×10^{-2}

TABLE 5: Energy Defect (cm^{-1}) for the Exact Resonance of CO[a]

νj	00	01	02	03	04
10	0.0	*−3.85056*	−11.55155	−23.10268	−38.50355
11	*3.79453*	−0.05603	*−7.75702*	−19.30815	−34.70902
12	11.38353	*7.53297*	−0.16802	*−11.71915*	−27.12002
13	22.76684	18.91628	*11.21529*	−0.33584	*−15.73671*
14	37.94424	34.09368	26.39269	*14.84156*	−0.55931

[a] Dipole-allowed transitions are italicized.

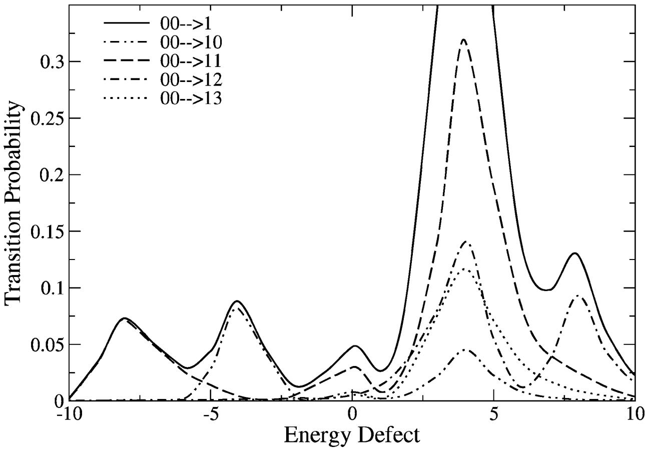

Figure 1. Ar + CO (00 → 1), E = 0.01514 au.

Given the atomic masses of Ar (39.96238 au), C (12.0 au), and O (15.99491 au), the laser intensity I, the energy defect Δ, the relative energy E, the field-free total angular momentum J = 0,1, the vibrational quantum number ν = 0,1, and the integration range from r_{min} = 0.65 au to r_{max} = 90.0 au, the coupled-channel equations are then solved until convergence of the transition probability is obtained within 1%. For the Ar + CO collision system, we also need all j values up to 10 to obtain convergence.

Our calculations show that the rotation−vibration transition probability of CO increases linearly with the laser intensity up to 1.0 × 10^9 watt/cm^2 (Table 4). We will use this laser intensity to calculate transition probabilities of CO from $\nu = 0$ and selected initial rotational states to $\nu = 1$ as a function of energy defect. Figure 1 shows the transition probabilities from $\nu = 0$, $j = 0$ to $\nu = 1$ for relative energy E = 0.01514 au. Note that the solid curve in Figure 1 represents the summation of the transition probabilities over the final rotational states. The transition probabilities from $\nu = 0$, $j = 0$ to all final rotational states are also shown in Figure 1 with different line types. As expected, the solid curve shows a large transition probability at Δ = +4 cm^{-1}. This corresponds to the dipole-allowed transition for CO from $\nu = 0$, $j = 0$ to $\nu = 1$, $j = 1$; the laser frequency is almost in resonance with this dipole-allowed transition. The energy defect for the exact resonance of CO is given in Table 5. Note that the $\nu = 1$, $j = 1$ level may have a rotational transition to $\nu = 1$, $j = 0$ or a rotational excitation to a higher rotational level (e.g., $\nu = 1$, $j = 2$), but these transition probabilities are smaller than that from $\nu = 0$, $j = 0$ to $\nu = 1$, $j = 1$ as shown in Figure 1. We also notice that there are

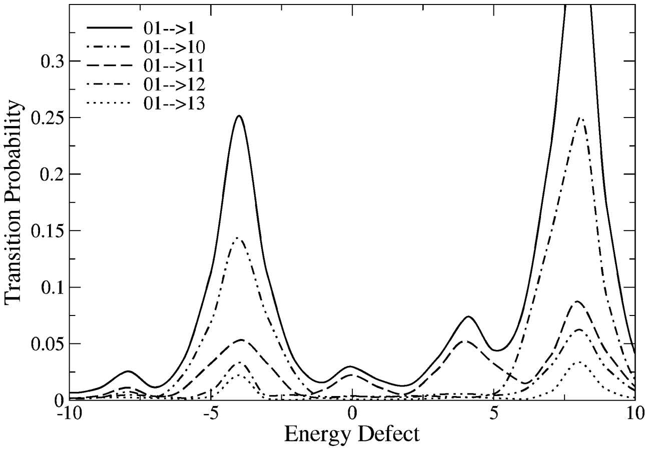

Figure 2. Ar + CO (01 → 1), $E = 0.01514$ au.

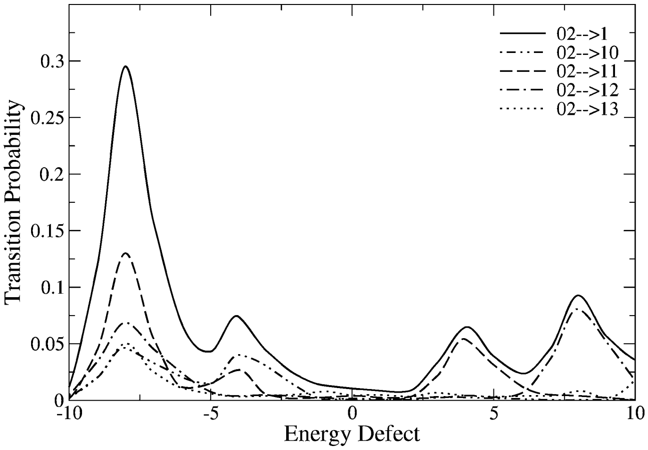

Figure 3. Ar + CO (02 → 1), $E = 0.01514$ au.

significant transition probabilities about $\Delta = -8$, -4, and $+8$ cm^{-1} in Figure 1, which is because the rotational states of CO can be excited by the collision partner Ar. For example, the transition probability at $\Delta = -4$ cm^{-1} can be thought of as a two-step process, a rotational excitation from $\nu = 0, j = 0$ to $\nu = 0, j = 1$ and then a photon absorption to energy defect $\Delta = -4$ cm^{-1}. This corresponds to the dipole-allowed transition from $\nu = 0, j = 1$ to $\nu = 1, j = 0$. Without the collision partner Ar, we cannot produce this transition and the transition probability should be zero. Likewise, without the laser field, this transition is impossible.

Figure 2 shows the transition probabilities from $\nu = 0, j = 1$ to $\nu = 1$. Again, the solid curve represents the summation of the transition probability over the final rotational states. The transition probabilities from $\nu = 0, j = 1$ to all final rotational states are also shown in Figure 2 with different line types. We notice that there are two peaks (large transition probabilities) of the solid curve in Figure 2. The first peak is at $\Delta = +8$ cm^{-1}, which corresponds to the dipole-allowed transition from $\nu = 0, j = 1$ to $\nu = 1, j = 2$. The second peak is at $\Delta = -4$ cm^{-1}, which corresponds to the dipole-allowed transition from $\nu = 0, j = 1$ to $\nu = 1, j = 0$. We notice that there is a significant transition probability about $\Delta = +4$ cm^{-1}. This corresponds to a two-step process, first a rotational transition from $\nu = 0, j = 1$ to $\nu = 0, j = 0$, then a photon absorption to energy defect $\Delta = +4$ cm^{-1}. Again, without the collision partner Ar and the laser field, this two-step process cannot be generated and its transition probability should be zero.

For the transition probabilities from $\nu = 0, j = 2$ to $\nu = 1$, there is a large transition probability at $\Delta = -8$ cm^{-1} as shown in Figure 3. This corresponds to the dipole-allowed transition from $\nu = 0, j = 2$ to $\nu = 1, j = 1$. Note that though the $\nu = 1, j = 1$ level may have a rotational transition to $\nu = 1, j = 0$ or a rotational excitation to higher rotational level, these transition probabilities are smaller than that from $\nu = 0, j = 2$ to $\nu = 1, j = 1$. We also notice that there are significant transition probabilities about $\Delta = -4$, $+4$, and $+8$ cm^{-1} in Figure 3, which represent multistep processes to final states $\nu = 1, j = 0$; $\nu = 1, j = 1$; and $\nu = 1, j = 2$, respectively. Note that the transition probabilities from $\nu = 0, j = 2$ to the specific rotational states are also shown in Figure 3 with different line types.

In Figure 4, the solid curve is the transition probability from $\nu = 0, j = 3$ to $\nu = 1$. Examining the solid curve, we would expect a large transition probability at $\Delta = -12$ cm^{-1}, which corresponds to the dipole-allowed transition from $\nu = 0, j = 3$ to $\nu = 1, j = 2$. There are also significant transition probabilities at $\Delta = -4$, $+4$, and $+8$ cm^{-1}, which represent multistep processes to final states $\nu = 1, j = 0$; $\nu = 1, j = 1$; and $\nu = 1, j = 2$ as shown in Figure 4.

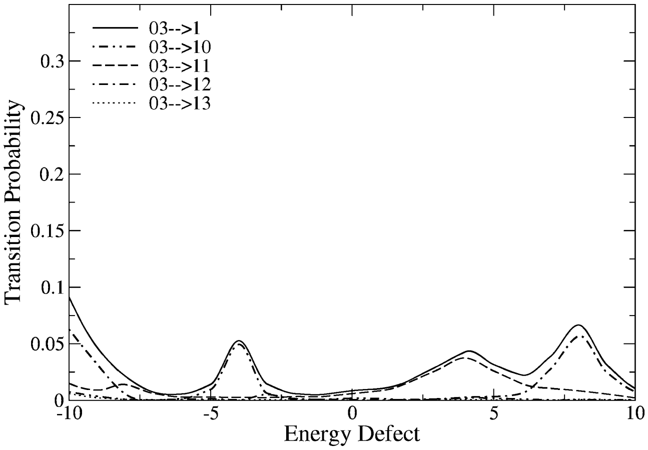

Figure 4. Ar + CO (03 → 1), $E = 0.01514$ au.

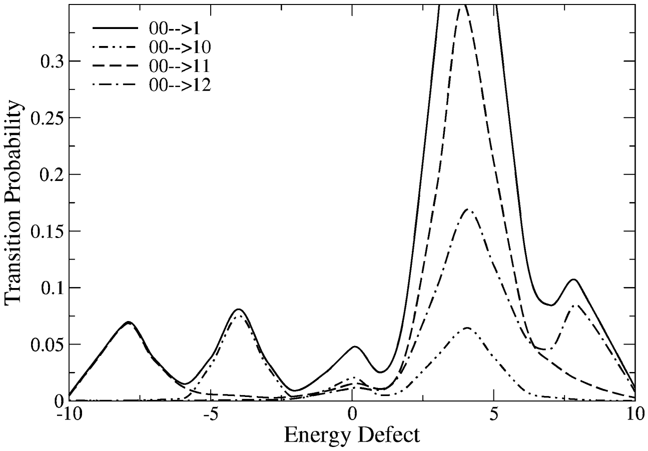

Figure 5. Ar + CO (00 → 1), $E = 0.01508$ au.

If we keep the same laser intensity (1.0×10^9 watt/cm^2) but lower the relative energy E to 0.01508 au, which only opens the final rotational states up to $j = 2$, we can observe the transition probability from $\nu = 0$ with some initial rotational states to the $\nu = 1$ states as we did in the $E = 0.01514$ au case. Figure 5 shows the transition probabilities from $\nu = 0, j = 0$ to $\nu = 1$. Here, the solid curve is the summation of the transition probabilities over the final rotational states. The transition probabilities to the specific rotational states are also shown in Figure 5 with different line types. As for the solid curve, there

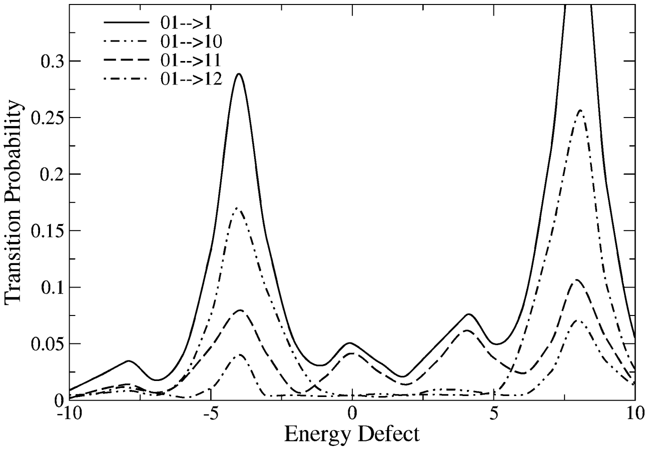

Figure 6. Ar + CO (01 → 1), $E = 0.01508$ au.

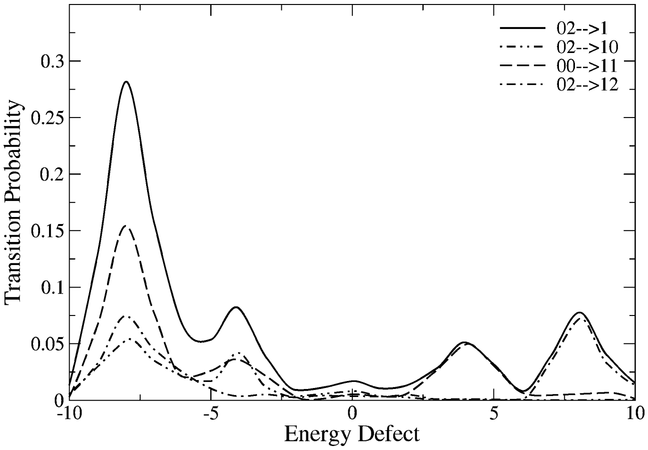

Figure 7. Ar + CO (02 → 1), $E = 0.01508$ au.

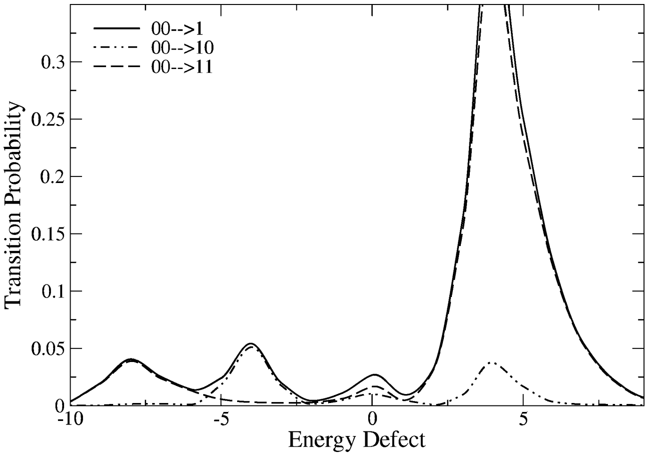

Figure 8. Ar + CO (00 → 1), $E = 0.01502$ au.

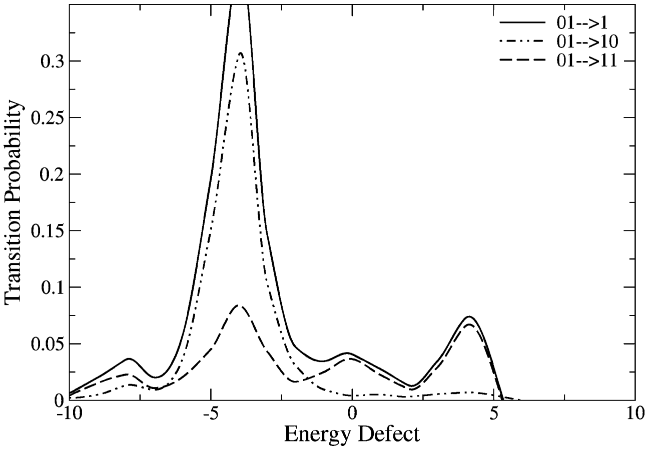

Figure 9. Ar + CO (01 → 1), $E = 0.01502$ au.

is a large transition probability at $\Delta = +4$ cm^{-1} as expected. This corresponds to the dipole-allowed transition from $\nu = 0$, $j = 0$ to $\nu = 1$, $j = 1$. With the collision partner Ar and the laser field, we also obtain significant transition probabilities about $\Delta = -8$, -4, and $+8$ cm^{-1}. These transition probabilities correspond to the multistep processes from $\nu = 0$, $j = 0$ to $\nu = 1$, $j = 1$; $\nu = 1$, $j = 0$; and $\nu = 1$, $j = 2$. Figure 6 shows the transition probabilities from $\nu = 0$, $j = 1$ to $\nu = 1$. As we look at the solid curve in the figure, we find two large transition probabilities as we found in $E = 0.01514$ au. The first one is at $\Delta = +8$ cm^{-1}, which corresponds to the dipole-allowed transition from $\nu = 0$, $j = 1$ to $\nu = 1$, $j = 2$. The second one is at $\Delta = -4$ cm^{-1}, which corresponds to the dipole-allowed transition from $\nu = 0$, $j = 1$ to $\nu = 1$, $j = 0$. Note that the transition probabilities from $\nu = 0$, $j = 1$ to the specific rotational states are shown in Figure 6 with different line types. For the transition probabilities from $\nu = 0$, $j = 2$ to $\nu = 1$, we would expect a large transition probability at $\Delta = -8$ cm^{-1} as shown in Figure 7. This corresponds to the dipole-allowed transition from $\nu = 0$, $j = 2$ to $\nu = 1$, $j = 1$. Figure 7 includes the transition probabilities to the specific rotational states out of $\nu = 0$, $j = 2$.

We now reduce the relative energy to 0.01502 au, which will only open the final rotational states up to $j = 1$. Therefore, we would not expect the dipole-allowed transition from $\nu = 0$, $j = 1$ to $\nu = 1$, $j = 2$. Let's first look at the transition probabilities from $\nu = 0$, $j = 0$ to $\nu = 1$ as shown in Figure 8. The solid curve again represents a summation of the transition probabilities over the final rotational states. Again, we obtain a large transition probability at energy defect $\Delta = +4$ cm^{-1}, which corresponds to the dipole-allowed transition from $\nu = 0$, $j = 0$ to $\nu = 1$, $j = 1$. Note that the level $\nu = 1$, $j = 1$ may have a rotational transition to $\nu = 1$, $j = 0$, but this transition probability is much smaller than that from $\nu = 0$, $j = 0$ to $\nu = 1$, $j = 1$ as shown in Figure 8. Figure 9 shows the transition probabilities from $\nu = 0$, $j = 1$ to $\nu = 1$. The large transition probability at $\Delta = -4$ cm^{-1} of the solid curve corresponds to the dipole-allowed transition from $\nu = 0$, $j = 1$ to $\nu = 1$, $j = 0$. The level $\nu = 1$, $j = 0$ may then have a rotational excitation to $\nu = 1$, $j = 1$. This transition is much smaller than that from $\nu = 0$, $j = 1$ to $\nu = 1$, $j = 0$ as shown in Figure 9.

V. Conclusion

In this paper, we have developed the general theory for an atom−diatom system interacting with a laser field. The multipolar gauge is applied in order to obtain gauge invariance. This theory is valid for both strong laser fields and weak laser fields and can be directly applied to the weak laser field case, where we use the long wavelength approximation to simplify the Hamiltonian. In the future, this theory will be used to study weak laser field coherent control of an atom−diatom system. For the strong laser field, we quantized the laser field and combined the laser Hamiltonian with the field-free Hamiltonian. A general theory was developed for both adiabatic and nonadiabatic interactions.

Our computer code has been examined with the theory for the strong laser field case. As an example, we studied the collisions of Ar with CO in the presence of an intense laser field. We presented rotation−vibration transition probabilities as a function of the energy defect. In the presence of a laser field, our results indicate that there are significant transition probabilities between certain initial and final rovibrational energy levels of CO, which have zero transition probabilities in the absence of a laser field. Presently, our theory is restricted to a Σ-state diatomic molecule, that is, there is no electronic angular momentum about its internuclear axis and dipole-allowed transitions do not include the so-called Q-branch transitions ($\Delta j = 0$). However, the theory can be easily generalized to include non-Σ-state diatomic molecules. Finally, we point out that although the extra couplings increase the complexity of the collision, they provide a much richer range of phenomena than that in the absence of the laser field. The results turned out to be sound and reasonable. It ensures us that the scattering codes and the theory are working well. The theory we have developed shall help us in understanding the dynamics of atom−diatom collisions in the presence of a laser field.

This paper is the first in a series studying the atom−diatom system with a laser field. The theory developed herein will be used to perform coherent control studies of an atom−diatom system. Both of the adiabatic and the nonadiabatic cases will be studied to test the effect of conical intersections in collision dynamics.

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