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Charge transfer in helium in a laser field

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With use of a diabatic molecular representation in two states, resonant charge transfer in helium in the presence of a laser field has been studied within the semiclassical impact-parameter approximation. The laser-frequency dependence of the charge transfer cross section shows an anomalous-looking feature quite distinct from cases studied earlier involving excitation. An effect of the laser field on the angular distribution of the charge transfer ions is also indicated.

Seely[1] carried out a study of the charge transfer reactions (i) $\mathrm{He}^{2+}+\mathrm{H}(1s)\rightarrow\mathrm{He}^{+}(n=2)+\mathrm{H}^{+}$ and (ii) $\mathrm{H}^{+}+\mathrm{H}(1s)\rightarrow\mathrm{H}(2s)+\mathrm{H}^{+}$ in a laser field. The first reaction has recently also been studied by Mendez, Errea, and Riera,[2] using, as Seely had, the formalism of Copeland and Tang.[3] Basically the approach is to expand the total wave function in a molecular basis set, and then to solve, within the semiclassical approximation, the coupled equations obtained from the time-dependent Schrödinger equation in the presence of a strong radiation field. This approach was first used by Gudzenko and Yakovlenko[4] who suggested that presence of a laser field could lead to an appreciable increase in the excitation transfer in atomic collisions. Mittleman[5] has used the same approach to study H^{+}-H symmetric resonant charge transfer in a laser field, although he did not give any numerical results.

As Kroll and Watson[6] pointed out, the variation of level spacing with changing internuclear separation can permit resonance absorption and/or emission of one or more photons in atomic collisions in a laser field. Except for reaction (i) above, all the reactions in Refs. 1–3 involve an energy defect, the potential curves running parallel to each other at large internuclear separations; reaction (i) is accidentally resonant (no energy defect) but, owing to the Coulomb repulsion within the exit channel, the approach of the curves towards each other is extremely slow.[1,7] Thus, in all these cases, the laser photon can be in resonance or near resonance with the level spacing over a fairly extended period of time. One can characterize this feature by the term "extended-duration photon resonance" (EDPR). In contrast, in a symmetric resonant case the energy gap decays nearly exponentially, and a condition of sharply localized photon resonance (SLPR) obtains except at low photon energies.

Excitation in atom (ion) -atom (molecule) collisions in a laser field has been treated by various authors,[8] using both time-dependent and time-independent approaches. In an interesting work, de Vries and George[9] extracted a time-dependent description of atomic collisions from the time-independent, stationary-state description. However, except in Ref. 8(d), all the authors have used *adiabatic* molecular eigenfunction basis to expand the system wave function.

In the present work we use the time-dependent approach to study He^{+}-He resonant charge transfer in a laser field, using a *diabatic* molecular representation[10] developed some time ago for this system as an approximation to Smith's[11] definition of diabatic states. Numerical results obtained within a two-state approximation in a linearly polarized monochromatic laser field are presented for two ion energies over a wide range of laser frequency. Variation of laser frequency shifts the photon resonance region, and is found to result in an anomalous-looking feature in the frequency dependence of the charge transfer cross section.

We restrict ourselves to a single radiation mode. In the weak-field limit, the wave function of the system (atom + ion + radiation) would have the form

$$\psi(t)=\sum_{j} c_j(t)\phi_j(\vec{r},R)\,|n\rangle\ , \tag{1}$$

ϕ's being molecular wave functions. Mittleman[5] chose an adiabatic basis and, following Kroll and Watson,[6] further modified it for strong fields by diagonalizing $(\mathrm{H}_{\mathrm{el}}+\mathrm{H}_{\mathrm{rad}})$—a procedure which, within the two-state approximation, is limited to not too intense fields. For the diabatic basis expansion we find the following approach more useful. Let us allow the system to evolve in time in the presence of electron-radiation interaction; then we would have

$$\begin{aligned}&\psi(t)=U(t)\psi(0),\quad U(t)\propto\exp(-iH_{\mathrm{int}}t)\ ,\\&H_{\mathrm{int}}=\sqrt{2\pi/V\omega}\,(a+a^{\dagger})\hat{e}\cdot\vec{p}\ ,\end{aligned} \tag{2}$$

$\hat{e}$ being the linear polarization vector and $\vec{p}$ the electron momentum. We are using atomic units except where otherwise stated.

Since H_{int} is linear in a and $a^{\dagger}$, it is obvious that the effect of the evolution operator is to introduce, in the linear combination, basis functions of the form $\phi_j|n\pm1\rangle$, $\phi_j|n\pm2\rangle$, ... Thus, in general we would have

$$\psi=\sum_{j}\sum_{k}\left(c_j^{(-k)}\phi_j|n+k\rangle+c_j^{(k)}\phi_j|n-k\rangle\right)\ . \tag{3}$$

We are ignoring any possible level broadenings and/or shifts due to coupling with the radiation field. For a bound molecule this cannot be done,[12] but for diabatic molecular functions the following argument provides a rough upper limit of the field strength up to which this *can* be done. The diabatic basis[10] is formed of atomic orbitals "frozen" throughout the collision where, in the region of closest approach, electric fields of order 10^{9} V/cm or higher due to the nuclei are encountered by the electrons. Thus, so long as the electric field of the radiation is within this limit—the corresponding intensity being of order $10^{16}\ \mathrm{W\,cm^{-2}}$—the diabatic states are not affected, and Eq. (3) for the wave function is justified.

Substituting ψ in the time-dependent Schrödinger equation and projecting out the individual components $\phi_j|n \pm k\rangle$, we obtain the coupled equations for the c's. To extract some qualitative idea of the extent of the laser field effect, we solved the equations for a two-state expansion. The adequacy of the two-state diabatic representation in this system when inelastic channels can be ignored has already been demonstrated.[13,14] Choosing the two diabatic states (see Fig. 1) to be the lowest ${}^2\Sigma_u$ and ${}^2\Sigma_g$ states in Ref. 10 and restricting ourselves to the emission and/or absorption of a single photon, the coupled equations assume the form

$$\begin{aligned}\frac{da_1}{dt} &= -a_2^+\frac{\Delta H}{\hbar\omega}D_{12}\exp\left[-i\int_{-\infty}^{t}(\Delta H-\hbar\omega)\,dt'\right] ,\\ \frac{da_2^+}{dt} &= a_1\frac{\Delta H}{\hbar\omega}D_{12}\exp\left[i\int_{-\infty}^{t}(\Delta H-\hbar\omega)\,dt'\right] ,\end{aligned} \tag{4}$$

with a similar pair of equations for a_2 and a_1^-. Here,

$$a_k(t)=c_k(t)\exp\left[i\int_{-\infty}^{t}(H_{kk}+E_R)\,dt'\right] ,$$

$$a_k^{\pm}(t)=c_k^{\pm}(t)\exp\left[i\int_{-\infty}^{t}(H_{kk}+E_R\mp\hbar\omega)\,dt'\right] ,$$

$$\Delta H=H_{22}-H_{11} ,$$

H_{kk}'s being the respective diabatic state energies. Also, $E_R=(n+\frac{1}{2})\hbar\omega$, radiation field energy, and

$$D_{12}=\sqrt{2\pi I/c}\;\hat{e}\cdot\langle\phi_1|\vec{r}|\phi_2\rangle ,$$

I being the intensity of radiation.

We have made use of the rotating-wave approximation, in that terms involving phase factors $\exp(\pm i\int(\Delta H+\hbar\omega)\,dt)$ have been ignored. It is evident from the equations that the more slowly ΔH changes with time, i.e., the longer the two potential curves run parallel to each other, the stronger is the coupling. The equations were solved in the straight-line impact parameter approximation, with $\hat{e}$ chosen parallel to the relative velocity; for convenience we used in our calculations the semiclassical equivalence between the impact parameter b and the orbital angular momentum l as done in an earlier work.[15]

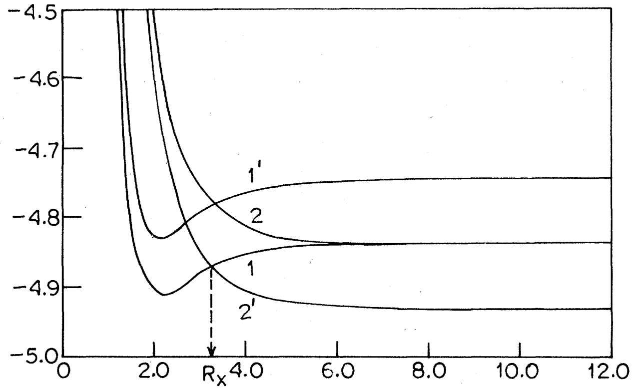

FIG. 1. "Dressed" diabatic states $\phi_1\{|n\rangle,|n+1\rangle\}$ and $\phi_2\{|n\rangle,|n-1\rangle\}$ at 5000-Å radiation. At $R=R_x$ either of two transitions becomes possible: (i) $\phi_1|n\rangle$ can absorb a photon and be excited to $\phi_2|n-1\rangle$; (ii) $\phi_2|n\rangle$ can emit a photon and go down to $\phi_1|n+1\rangle$. So long as $b<R_x$, transitions are possible both during incoming as well as outgoing trajectory.

Calculations were carried out at a laboratory ion energy of 300 eV and, in somewhat less detail, at 1000 eV. Figures 2(a) and 2(b) show a sample plot of P_x and P_0, charge transfer probabilities with and without laser field, respectively, at an intensity of 1×10^{14} W/cm^2 for two different wavelengths. Two effects of the laser field are immediately obvious: (i) overall shift of the upper/lower envelopes of the curves, and (ii) dephasing. The plateaulike behavior of P_x as in Fig. 2(b), 10 000 Å has also been obtained by Copeland and Tang.[3]

In an experiment, the dephasing would result in a shift in the angular distribution of charge-exchange ions, whereas the effect (i) would lead to changes in the total charge transfer cross section Q_x. Figure 3 shows the relative change $(Q_x-Q_0)/Q_0$ for several photon energies at an intensity of 1×10^{14} W/cm^2. An examination of Eqs. (4) helps us understand the nature of the photon energy dependence of Q_x. At resonance $(\Delta H=\hbar\omega)$ Eqs. (4) go through a stationary phase, which lasts much longer in the cases of

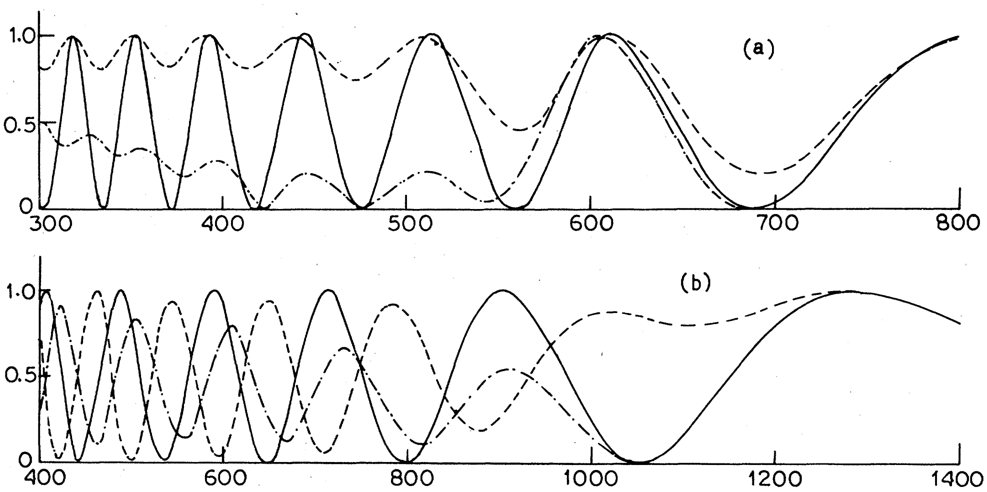

FIG. 2. Charge transfer probability with and without laser field at intensity $I=1\times10^{14}$ W/cm^2. (a) 300-eV, (b) 1000-eV laboratory ion energy. Full line, P_0; chain line, P_x (5000 Å); broken line, P_x (10 000 Å).

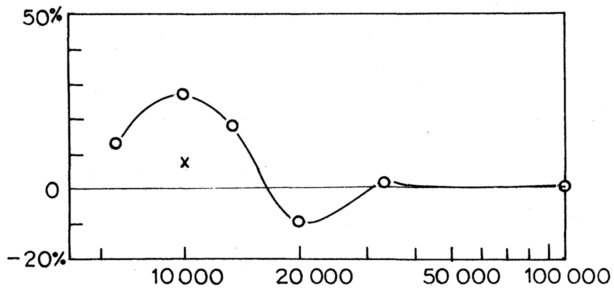

FIG. 3. Relative change in charge transfer cross section $(Q_x - Q_0)/Q_0$ at 300 eV vs photon energy (cm^{-1}), Q_x and Q_0 being the cross section with and without field, respectively. The circles refer to $I = 1\times10^{14}$ W/cm^2; the cross is a sample calculation at $I = 1\times10^{13}$ W/cm^2. The line joining the circles is only meant to guide the eye.

EDPR than in the (present) case of SLPR. An off-resonance shift in $\hbar\omega$ leads to oscillations in the phase integral, leading to effective decoupling of the equations; again, this effect is more pronounced in the case of EDPR than SLPR. This effect, combined with the fact that decrease in $\hbar\omega$ increases the coupling coefficient, gives rise to the anomalous-looking structure in Fig. 3. In Seely's[1] work where EDPR obtains, a maximum in Q occurs in the higher (photon) energy side for the accidentally resonant case of $\text{He}^{++} + \text{H} \rightarrow \text{He}^{+}(n=2) + \text{H}^{+}$—no structure appears towards the lower-energy side, where the cross section falls monotonically with decreasing $\hbar\omega$. On the other hand, the intensity dependence is straightforward, being determined by the term D_{12} alone. Extensive results showing the intensity dependence of Q_x have been given in Refs. 1–3, and here we give only a sample result in Fig. 3 at 1×10^{13} W/cm^2.

A question that must be faced at these high intensities is whether or not this effect will be masked by multiphoton ionization (MPI). The measurements made by Lompre *et al.*[16] of MPI of rare gases offer a direct means of comparison between the two phenomena at $\lambda = 10\,000$ Å, where for $I = 10^{14}$ W/cm^2, $\Delta Q/Q \sim 30\%$ (cf. Fig. 3). Using a pulsed Nd-YAG laser operating at 10 643.5 Å, with a bandwidth of 0.8 Å and pulse duration of 28 psec, nonresonant MPI of helium at 10^{-4} Torr was found to obey the power law $\propto I^n$, with $n = 22$; at $I = 0.7\text{–}1.5\times10^{15}$ W/cm^2, Lompre *et al.* obtained an ionization rate of $10^{10\pm1}$ sec^{-1} within a focal volume of diameter 25 μm. Thus, at 10^{14} W/cm^2, we would expect an ionization rate/volume of order $10^{\pm1}$ sec^{-1} cm^{-3}. On the other hand, with a 300-eV He$^+$ beam incident on neutral He, both at the same density as above, the laser-induced change in the rate of production of charge transfer ions/volume turns out to be of order $\sim10^{16}$ sec^{-1}cm^{-3}; MPI could occur at a comparable rate only at intensities $\gtrsim 6\times10^{14}$ W/cm^2. Thus under such experimental conditions[17] where instrumental saturation effects are avoided by using short pulses (of order psec) and resonances or near resonances with Stark-broadened intermediate (atomic) levels are avoided by using narrow bandwidth, there is no reason why this laser-induced change in charge transfer cross section should be masked by MPI.

Throughout this work we have tacitly assumed that the laser field acts for a time longer than the collision time, typically of order 10^{-15} to 10^{-16} sec. This assumption is justified for all currently available lasers.

In conclusion, the practical consequence of the work seems to lie in the possibility of fairly extensive control of the charge transfer reaction by variation of laser frequency and intensity. On the other hand, these results are not meant to be quantitative; dipole-allowed transitions between ground and excited states open up new inelastic channels, and within the close-coupled treatment a fuller picture can only be obtained by including higher-lying molecular states to allow for loss of flux in the inelastic channels. Moreover, if a series of dipole-connected states run parallel to each other over a length of time, resonant multiphoton transitions are apt to be of significance at these high intensities, with a consequential gain in importance of field correlation effects as recently shown by Daniele, Faisal, and Ferrante.[18] More detailed work incorporating these aspects is in progress.

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[1] J. F. Seely, J. Chem. Phys. **75**, 3321 (1981).

[2] L. Mendez, L. F. Errea, and A. Riera, in *Proceedings of the Thirteenth International Conference on the Physics of Electronic and Atomic Collisions, Berlin, 1983. Abstracts of Contributed Papers,* edited by J. Eichler *et al.* (ICPEAC, Berlin, 1983), p. 691.

[3] D. A. Copeland and C. J. Tang, J. Chem. Phys. **65**, 3161 (1976); **66**, 5126 (1977).

[4] L. I. Gudzenko and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. **62**, 1686 (1972) [Sov. Phys. JETP **35**, 877 (1972)].

[5] M. H. Mittleman, Phys. Rev. A **14**, 586 (1976).

[6] N. M. Kroll and K. M. Watson, Phys. Rev. A **13**, 1018 (1976).

[7] D. R. Bates and T. R. Carson, Proc. R. Soc. London Ser. A **234**, 207 (1956).

[8] The literature in this field is expanding fast, and the following is only a representative list: (a) R. Z. Vitlina, A. V. Chaplik, and M. V. Entin, Zh. Eksp. Teor. Fiz. **67**, 1667 (1974) [Sov. Phys. JETP **40**, 829 (1974)]; (b) J. M. Yuan, J. R. Laing, and T. F. George, J. Chem. Phys. **66**, 1107 (1977); (c) J. C. Light and A. Szöke, Phys. Rev. A **18**, 1363 (1978); (d) P. L. DeVries and T. F. George, Mol. Phys. **36**, 151 (1978); (e) M. G. Payne, V. E. Anderson, and J. E. Turner, Phys. Rev. A **20**, 1032 (1979); (f) M. Hutchinson and T. F. George, Mol. Phys. **46**, 81 (1982); (g) L. F. Errea, L. Mendez, and A. Riera, Chem. Phys. Lett. **104**, 401 (1984).

[9] P. L. DeVries and T. F. George, Phys. Rev. A **26**, 1419 (1982).

[10] T. K Rai Dastidar and K. Rai Dastidar, Chem. Phys. Lett. **85**, 229 (1982).

[11] F. T. Smith, Phys. Rev. **179**, 111 (1969).

[12] See, e.g., C. A. S. Lima and L. C. M. Miranda, J. Chem. Phys. **78**, 6102 (1983).

[13] W. Lichten, Phys. Rev. **131**, 229 (1963).

[14] S. S. Bhattacharya and T. K. Rai Dastidar, J. Phys. B **8**, 1522 (1975); T. K. Rai Dastidar and S. S. Bhattacharya, Ind. J. Phys. **50**, 731 (1976).

[15] T. K. Rai Dastidar, K. Rai Dastidar, and R. Sen Gupta, Chem. Phys. Lett. **96**, 85 (1983).

[16] L. A. Lompre, G. Mainfray, C. Manus, S. Repoux, and J. Thebault, Phys. Rev. Lett. **36**, 949 (1976).

[17] P. Lambropoulos, Adv. At. Mol. Phys. **12**, 87 (1976); see postscript to the article for a discussion of this point.

[18] R. Daniele, F. H. M. Faisal, and G. Ferrante, J. Phys. B **16**, 3831 (1983).