4-1-1988

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PHYSICAL REVIEW A VOLUME 37, NUMBER 7 APRIL 1, 1988

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(Received 9 November 1987)

A theoretical study is presented of the process of photodetachment of a negative ion by subthreshold-frequency radiation in the presence of a simultaneous collision. Calculations are carried out for the H^--He case and the resulting cross section is compared with other competing processes, such as two-photon photodetachment and nonradiative collisional detachment.

I. INTRODUCTION

Laser-induced collisional processes have been studied experimentally and theoretically for many years.[1] All nonradiative inelastic processes such as energy and charge transfer, Penning ionization, as well as associative and dissociative versions of these, will also occur when suitably tuned radiation is present to provide overall energy conservation.

In this note we would like to present a study of the laser-induced collisional-detachment process (LICD), in which an electron is detached from a negative ion by means of the combined effects of the laser field and a collision with a gas atom, $A^- + B + \hbar\omega \rightarrow A + B$. An alternate description of this process would be collisionally induced photodetachment. Such a process is of interest only if the laser photon energy is below the threshold for single-photon photodetachment. Then the interesting question, which we are presently addressing, is — how large is the LICD rate compared with the two-photon photodetachment rate? These rates will be proportional to NI and to I^2, respectively, where N is the atom density and I the laser intensity. Thus it is clear that there must be regions of N and I where one or the other detachment process predominates. Another critical process competing with LICD is that of nonradiative collisional detachment, for which the rate is proportional to N alone.

We will study in detail the system of H^- impacting on He atoms. A simple estimate of the magnitude of the cross section for the process can be obtained if we assume that during the collision the proximity of the atom B causes a temporary lowering of the A^- photodetachment threshold, such that the electron may be detached by one-photon absorption. Based on this picture the LICD cross section estimate would be

$$\sigma_L \sim \bar{\kappa} F \tau_c \pi R_c^2 , \tag{1}$$

where $\bar{\kappa}$ is a mean photodetachment cross section, F is the laser photon flux density, τ_c is an effective collision time, and R_c is a mean effective impact parameter. The first two factors, the photodetachment cross section times the photon flux density, give the rate of detachment. When these are multiplied by the time duration of a collision between A^- and B they give an estimate of the probability that detachment takes place during that collision. That probability times the A^--B collision cross section gives the LICD cross section. Letting $\tau_c = R_c / v$, and taking $\bar{\kappa} \sim 2\times 10^{-17}$ cm^2 (Ref. 2) and $R_c \sim 3a_0$ (this choice will be justified in a later section), we find

$$\sigma_L \sim (1.3\times 10^{-27}) \frac{I\,(\mathrm{W/cm^2})}{[E\,(\mathrm{eV})]^{1/2}}\ \mathrm{cm}^2 . \tag{2}$$

In Sec. II we present a somewhat more detailed theory and calculations. The purpose is to obtain, not high-precision results, but simple estimates, which may be helpful to experimenters who wish to examine this process.

II. THEORY AND CALCULATIONS

Potential energy curves for the HeH^- system were calculated by Olson and Liu[3] using self-consistent-field-configuration-interaction (SCF-CI) methods (Fig. 1). These curves represent the lowest bound-state energies for the quasimolecular states $^1\Sigma(HeH^-)$ and $^2\Sigma(HeH)$. We see that the HeH^- curve is more strongly repulsive than the HeH curve, so the proximity of He does indeed reduce the binding energy of the electron and the photodetachment threshold. In fact, at $R = R_c = 2.70a_0$ the curves cross, and electron detachment occurs rapidly even in the absence of a laser.

A complete theory of LICD must include the effect of the laser on a system that is already undergoing direct collisional electron detachment. The theory of collisional detachment is complicated, however (and still controversial besides), so we shall not attempt such a complete theory. We will treat the system as if the electronic energy of HeH^- were a well-defined function of R, denoted $E_i(R)$.

With this approximation, one can still ask whether $E_i(R)$ should be the HeH^- energy calculated by Olson and Liu. The presence of the crossing between bound and free states suggests that Olson and Liu have obtained a partially "diabatic" representation, since the completely "adiabatic" representation is one in which the HeH and HeH curves avoid crossing. In such a completely adiabatic representation, the HeH^- curve would merge into the $HeH + e^-$ continuum from below; therefore the energy gap would be zero inside some radius close to R_c.

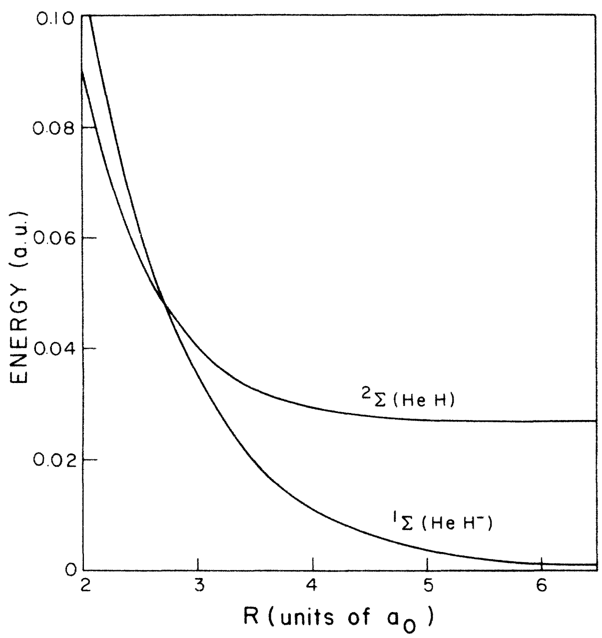

FIG. 1. Potential curves for the lowest states of HeH^- and HeH as evaluated by Olson and Liu.

It is not clear which representation would provide the better starting point for a first-order calculation of LICD. We chose an adiabatic representation. However, we note that the issue is academic, since we will show below that at the energies for which collisional detachment is allowed, it swamps the LICD cross section. Therefore LICD can only be seen at those collision energies such that the atoms do not enter the region of crossing or avoided crossing of the curves so the problem of "diabatic" or "adiabatic" representation does not arise.

The transition amplitude between the discrete and continuum states of HeH^- caused by the radiation field can be calculated using first-order perturbation theory and the rotating-wave approximation. The result (in atomic units) is

$$a_{ik}=\frac{E_0}{2}\int_{-\infty}^{\infty}dt\left[\int d\mathbf{r}\,\Phi_k^*(\mathbf{r},R)\Sigma z_j\Phi_i(\mathbf{r},R)\right]\times\exp\left[-i\int_{-\infty}^{t}dt'[E_k(R)-E_i(R)+\omega]\right]. \tag{3}$$

Here a_{ik} is the probability amplitude for finding the electron in the free state with energy $E_k=E_f+(k^2/2)$ after the collision. $\Phi_{i,k}$ are the electronic wave functions, E_i and E_f are the $^1\Sigma(\mathrm{HeH}^-)$ and $^2\Sigma(\mathrm{HeH})$ curves in Fig. 1, and $E_k(R)=E_f(R)+(k^2/2)$. Also, the rotating-wave approximation is used in (3) and E_0 is the laser electric field strength amplitude. The dipole moment operator

$$\mu(R)=\int d\mathbf{r}\,\Phi_k^*(\mathbf{r},R)\sum_j z_j\Phi_i(\mathbf{r},R) \tag{4}$$

is a complicated function of R when evaluated with the full CI forms for Φ_i and Φ_f, even with the simplifying assumption that the ejected electron will not appreciably distort Φ_f, i.e.,

$$\Phi_k(\mathbf{r},R)\cong\Phi_f(\mathbf{r}_1,\mathbf{r}_2,R)\psi_k(\mathbf{r}_3)\ . \tag{5}$$

The asymptotic form of $\mu(R)$ is the atomic negative ion bound-free matrix element, which is very well known from many theoretical studies[4] on the photodetachment of H^-, and which is in good agreement with experiment.[2] The departure of $\mu(R)$ at smaller R from its asymptotic value would arise from an effective decrease in the binding energy of an electron to an H atom in the presence of a He atom as reflected in the energy curves in Fig. 1. We make the initial simplification that $\mu(R)\cong\mu(\infty)$. The extreme values of $\mu(R)$ are $\mu(\infty)$ corresponding to H^- and the united ion $\mu(0)$ corresponding to Li^-. The calculation of Ref. 5 showed that the maximum value of the photodetachment cross section of Li^- is about twice that of H^-. Thus we can be reasonably confident that our approximation $\mu(R)\cong\mu(\infty)$ will at worst lead to LICD cross sections which are low by $\lesssim 50\%$. Further, we evaluate $\mu(\infty)$ in the negative ion model[5] where the radial bound-free matrix element for H^- is expressed as

$$D(k)=\int_0^{\infty}dr\,r^2\phi_0\chi_{1k}\ , \tag{6}$$

where ϕ_0 and χ_{1k} are the radial wave functions as defined in Ref. 5, and we neglect any inner-shell contributions to the bound-free process. The resulting LICD probability at the end of a classical collision is

$$P(\rho)=\frac{2E_0^2}{3\pi}\int_0^{\infty}dk\,D^2(k)\left|\int_{-\infty}^{\infty}dt\exp[-i\int_0^t dt'\left[\omega-\frac{k^2}{2}-(E_f-E_i)\right]\right|^2 . \tag{7}$$

The forms we use for $E_i(R)$ and $E_f(R)$ are the curves given in Fig. 1 for $R>R_c$, but with $E_i(R)=E_f(R)$ for $R\le R_c$. We have carried out the t' integral in (7) analytically after fitting $E_f(R)-E_i(R)$ for $R>R_c$ to the form

$$\frac{C_4}{R^4}+\frac{C_6}{R^6}+\frac{C_8}{R^8}+0.0271\ .$$

In Fig. 2 we show $D^2(k)$ corresponding to $R=\infty$. It should be noted that for $\omega<E_f(\infty)-E_i(\infty)$, i.e., ω below the photodetachment threshold, there is no $\delta(k^2-k_0^2)$ part present, and all of the Fourier transforms in (7) are well defined. They have been evaluated numerically.

We have evaluated the cross-section differential in ejected electron energy and the total cross section for the two relative kinetic energies, 0.7 and 10 eV, and for a laser photon energy of 0.55 eV. The lower kinetic energy corresponds to an energy below the free negative ion de-

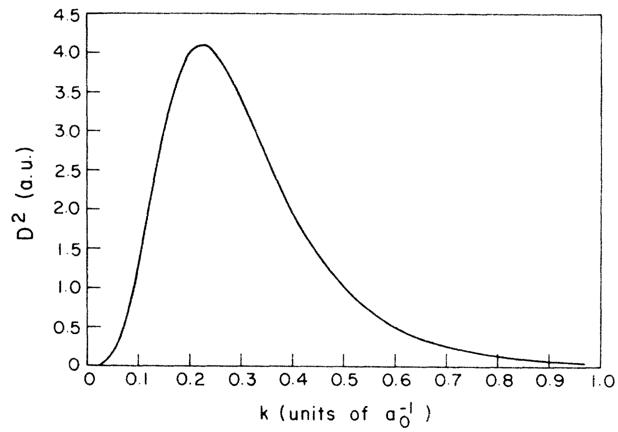

FIG. 2. Variation of the square of the bound-free radial matrix element with ejected electron momentum.

tachment threshold of 0.75 eV and hence radiationless collisional detachment may not occur. The latter process becomes very probable for energies where the curve crossing between E_i and E_f can be reached (this occurs at >1.3 eV). Since the two atomic bodies may not approach one another more closely than $3.2a_0$ at 0.7 eV kinetic energy, we assume specular reflection from a hard sphere of this radius to describe the trajectories of smaller impact parameters. For the higher energy (10 eV) all impact parameters are treated by straight-line paths. Figure 3 shows $P(\rho)$ (integrated over all electron momenta) and Fig. 4 shows the differential cross section in k (integrated over the impact parameter).

The total LICD cross sections are 1.18×10^{-28} I (W/cm^2) cm^2 for 10 eV and 1.28×10^{-28} I (W/cm^2) cm^2 for 0.7 eV. Our simple estimate in (2) comes fortuitously close to these values in giving 4.1×10^{-28} I (W/cm^2) cm^2 at 10 eV and 1.6×10^{-28} I (W/cm^2) cm^2 at 0.7 eV. The full calculated values do not follow the $E^{-1/2}$ dependence in (2) because the use of a hard sphere for the lower-energy trajectories reduces the cross section (see Fig. 3).

III. COMPARISON WITH OTHER PROCESSES

As mentioned briefly in Sec. I, any attempt to experimentally measure LICD cross sections would have to sort them our from the competing processes of two-photon photodetachment

$$H^- + 2\hbar\omega \rightarrow H + e \tag{8}$$

and nonradiative collisional detachment

$$H^- + He \rightarrow H + He + e \ . \tag{9}$$

The latter process has been studied theoretically[6] and experimentally[7] with good quantitative agreement. This theoretical work was also based on the potential curves of Olson and Liu,[3] and requires the conversion of kinetic energy of relative motion into electronic energy in attaining the transition from initial to final state. This means that it has zero cross section for kinetic energies below the 0.75-eV threshold, and hence this process will not compete with LICD at 0.7 eV, but will do so at 10 eV. A more decisive threshold for this process will be at the merging or apparent crossing of the curves, and to reach this point requires about 1.3 eV. The calculated and measured cross sections at 10 eV are

$$\sigma_N \cong 11a_0^2 = 3.1\times10^{-16}\ \text{cm}^2 \ .$$

We may make a reasonable estimate of the two-photon photodetachment cross section on the basis of several theoretical evaluations.[8] The values found by these authors at $\hbar\omega=0.55$ eV for this generalized cross section $\hat{\sigma}^{(2)}$ are

$$0.7\times10^{-48}\ \text{cm}^4\,\text{s}$$

from Crance and Aymar;

$$0.9\times10^{-48}\ \text{cm}^4\,\text{s}$$

from Fink and Zoller; and

$$1.0\times10^{-48}\ \text{cm}^4\,\text{s}$$

from Arrighini *et al.* We take the average value of

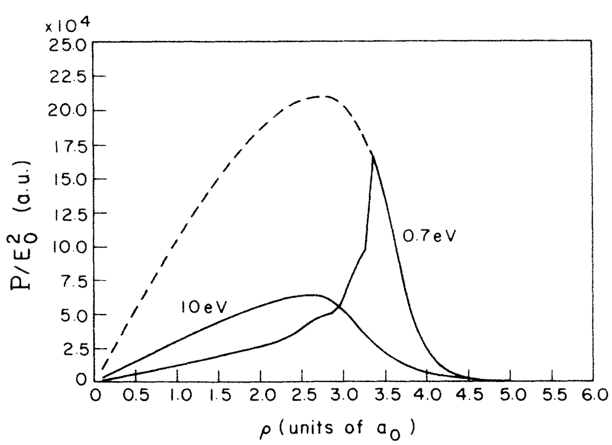

FIG. 3. Variation of total LICD probability (P/E_0^2) with impact parameter. The dashed curve shows the 0.7-eV result for uninterrupted straight-line paths.

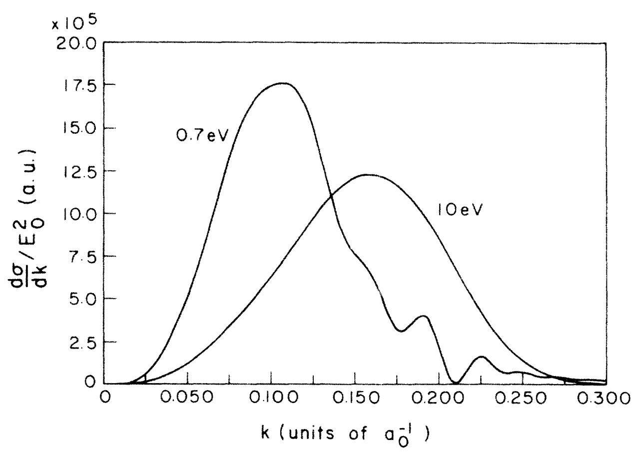

FIG. 4. Variation of LICD differential cross section $[(d\sigma/dk)/E_0^2)]$ with ejected electron momentum.

0.9×10^{-48} $\mathrm{cm}^4\,\mathrm{s}$ for use in estimating the magnitude of the detachment rate due to this mechanism.

We combine the above cross sections to obtain the following rates for electron detachment. For LICD

$$W_L(\mathrm{s}^{-1}) = \begin{bmatrix} 0.59\ (\text{at } 0.7\ \text{eV}) \\ 2.1\ (\text{at } 10\ \text{eV}) \end{bmatrix} \times 10^{-5} \times I\,(\mathrm{W/cm}^2) N\,(\mathrm{Torr})\ ,$$

for nonradiative collisional detachment

$$W_N(\mathrm{s}^{-1}) = \begin{bmatrix} 0\ (\text{at } 0.7\ \text{eV}) \\ 5.4\ (\text{at } 10\ \text{eV}) \end{bmatrix} \times 10^{7}\, N\,(\mathrm{Torr})\ ,$$

and for two-photon photodetachment

$$W_2(\mathrm{s}^{-1}) = (1\times 10^{-10})[I\,(\mathrm{W/cm}^2)]^2\ .$$

From these rates it is clear that for 10-eV collisions W_L and W_N will be comparable in magnitude only at the very high laser intensity of $\sim 10^{12}$ $\mathrm{W/cm}^2$. At such an intensity and reasonable gas densities W_2 will be much larger than either of these collisional rates. This means there is no chance in practice of observing LICD as isolated from nonradiative collisional detachment for any kinetic energies above the detachment threshold.

On the other hand, for collisional energies below threshold, only W_L and W_2 need be compared, and we see that for $N(\mathrm{Torr})=100$ the LICD process will dominate at $I\,(\mathrm{W/cm}^2) < 4.0\times 10^7$, which is a reasonable range of intensities to work with. It is hoped that such measurements with slow negative ions may be performed as a demonstration of laser-induced collisional detachment.

ACKNOWLEDGMENTS

D. L. has received support from National Science Foundation (NSF) Grant No. AST82-16481. J. B. D. acknowledges support from the Joint Institute for Laboratory Astrophysics. All computations have been carried out on the JILA VAX/8600, and have been supported by NSF Grant No. PHY86-04504 to the University of Colorado.

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