Comments

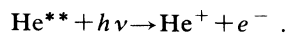## Laser-assisted ionization as the only process consistent with experiment

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In this Reply, it is shown how our experimental results lead us to the conclusion that the two-step process proposed in the recent Comment by Gillen [Phys. Rev. A **39**, 2248 (1989)] cannot explain the ion signals observed for $E_{c.m.} \leq 50$ eV, whereas laser-assisted ionization is the only mechanism consistent with our observations in this energy range. The measured amplitude of the signals can be interpreted in terms of a transition-dipole enhancement induced by the collision. Such an enhancement has been ignored in the estimates of Gillen.

The experimental evidence of laser-assisted processes has always been based on a careful check of other competing channels. This actual fact applies obviously to the present case, where the two-step process involving collisional excitation of $He^*(2^{1,3}S)$ to higher excited levels, followed by atomic photoionization, is a process able to compete with laser-assisted ionization:

$$He^*(2^{1,3}S) + He \rightarrow He^{**} + He,$$

$$He^{**} + h\nu \rightarrow He^+ + e^-.$$

This process, labeled process (3) in the Comment by Gillen,[1] is clearly identified in our experiments for kinetic energies $E_{c.m.} > 50$ eV, since the ion signal increases with increasing $E_{c.m.}$, in agreement with the expected behavior of the first step, inelastic process.[2] However, for $E_{c.m.} \leq 50$ eV, the measured ion signal exhibits a very different dependence versus $E_{c.m.}$, and follows the characteristic variation law of an assisted process, with a cross section $\sigma_a \propto E_{c.m.}^{-1/2} \propto$ collision time. This is this important feature which leads us to conclude that laser-assisted ionization is the only process consistent with our observations for $E_{c.m.} \leq 50$ eV.[2]

However, the estimations of the Comment assert that the two-step process may account for our measurements for all energies. As a consequence, we feel it is necessary to recall in this Reply the series of experimental results which lead us to eliminate the contribution of the two-step process *for all excited levels of* He. These experimental evidences have been already published[2−4] and lead sometimes to redundant conclusions in what follows.

(i) The $2\,^1P$ level is the most serious candidate, since it is the nearest neighbor of the initial $2\,^1S$ level (the energy defect is 0.6 eV): it can efficiently be populated collisionally, and afterwards ionized by a photon of energy $\hbar\omega = 3.5$ eV (the photoionization threshold is 3.37 eV). However, the collisional excitation cross section from the

$2\,^1S$ is obviously an increasing function of kinetic energy.[5] Therefore the variation of the laser-induced signal as a function of kinetic energy $E_{c.m.}$ represents an efficient probe for this channel. This has been performed experimentally:[4] when $E_{c.m.}$ increases from 25 to 50 eV, the observed ion signal decreases as $E_{c.m.}^{-1/2}$, that is, as the laser-assisted process, but not as an inelastic process. It is concluded that the laser-assisted process is the main ionization process in this energy range. Above 50 eV, the ion signal begins to increase rapidly with $E_{c.m.}$. It is then concluded that the increasing inelastic channel becomes dominant over the decreasing laser-assisted process above 50 eV. This conclusion is based on the kinetic energy dependence of the laser-induced process only (Fig. 8 of Ref. 2). It is not based, as asserted in the Comment, on the kinetic energy dependence of the contrast C between the laser-induced signal and the field-free diabatic signal, that is, the ratio between two very different energy dependent signals.

These experimental features show that *the* $2\,^1P$ *level does not contribute significantly for* $E_{c.m.} \leq 50$ *eV.* Unquestionable proof could be obtained by using a photon energy lower than the photoionization threshold of the $2\,^1P$ level and observing the persistence of the laser-induced signal.

(ii) The $2\,^3P$ level is obviously not involved, owing to the value of its ionization threshold.

(iii) The whole singlet series of He^* starting from the $2\,^1P$ level was eliminated by observing[2] the persistence of the assisted signal with a pure $2\,^3S$ beam (Fig. 10 of Ref. 2).

(iv) The $3\,^3P$ level might be a viable candidate, according to Gillen's Comment. However, two distinct experimental features show that this level cannot explain the observed signals.

(a) Collisional excitation of this level from the $2\,^3S$ involves an energy defect $E = 3.2$ eV. This energy has to be taken from the kinetic energy of the collision system.

Therefore the photoions produced during the laser pulse from this $3\,^3P$ level would have a time-of-flight (TOF) longer than that of the metastable beam. The corresponding TOF increase would be ~ 90 nsec for $E_{c.m.} = 35$ eV and 150 nsec for $E_{c.m.} = 25$ eV. These delays, which were easily detectable in our TOF analysis (Sec. V C [reaction (iii)] of Ref. 2), have never been observed.

(b) The very long lifetime of the $3\,^3P$ level ($\tau = 100$ nsec) is such that ion production during the laser pulse would control and significantly deplete the $3\,^3P$ population. Hence ion production through this level would not be the linear function of laser intensity which has been measured.[3] This argument can be checked from the rate equation of the $3\,^3P$ population density n^{**}

$$\frac{dn^{**}}{dt} = \sigma_{in}nn^*v - n^{**}/\tau - \sigma_\varphi \mathscr{J}n^{**} \, , \tag{1}$$

where the first term is the inelastic production rate (with cross section σ_{in}) from the $2\,^3S$ (with density n^*) colliding with He (with density n); v is the relative velocity. The second term is the radiative loss, and the third is the photoionization loss (with cross section σ_φ) occurring during the laser pulse (with intensity $\mathscr{J}$ in photons/cm^2 s). The ion production rate via the two-step process is

$$\frac{dn^+}{dt} = \sigma_\varphi \mathscr{J}n^{**} \, . \tag{2}$$

During the laser pulse, the solution of (1) and (2), corresponding to the case $1/\tau \ll \sigma_\varphi \mathscr{J}$, can be written

$$n^{**}(t) = n_0^{**} \exp(-\sigma_\varphi \mathscr{J}t) \, ,$$

$$n^+(t) = n_0^{**}[1 - \exp(-\sigma_\varphi \mathscr{J}t)] \, ,$$

where $n_0^{**} = \sigma_{in}nn^*v\tau$ is the $3\,^3P$ population density before laser firing. Varying[3] the laser energy between 6 and 36 mJ, i.e., $2\times10^{24} \lesssim \mathscr{J} \lesssim 1.2\times10^{25}$ cm^{-2}s^{-1} would give for the exponential factor $\sigma_\varphi \mathscr{J}t$ a variation range between 0.3 and 1.8, since $t=20$ nsec and $\sigma_\varphi \sim 7\times10^{-18}$ cm^2 (Refs. 6 and 7). Therefore, the ion signal n^+ from the $3\,^3P$ level would considerably deviate from a linear dependence on laser intensity (250% deviation at the highest intensity). This is in contradiction with the linearity already reported.[2,3] Therefore, both a and b arguments show that the $3\,^3P$ level does not contribute to the observed ion signal.

(v) The $n \geq 3$ levels, both singlet and triplet, involve an energy defect larger than 3.2 eV for the collisional step. Hence the argument (iv) (a) holds for these levels. The $n \geq 3$ levels are therefore not concerned.

(vi) The $n \geq 4$ (singlet and triplet) levels lie within 1 eV below the $(He^+ + e^-)$ continuum. They can therefore be ionized by a photon of energy $\hbar\omega = 1.16$ eV. However, we have observed[2] (Sec. V A [argument (ii)] of Ref. 2) that the laser-induced signal disappears when the interaction region is irradiated with the fundamental frequency of the laser ($\hbar\omega = 1.16$ eV). This shows that the $n \geq 4$ levels do not contribute.

(vii) All the long-lived excited states of He ($n > 2$) do not either contribute, owing to argument (iv) (b). Therefore a two-step process involving the excited states of He

is in contradiction with the experimental data. Other possible competing mechanisms[2-4] cannot explain the measurements either. This is why we still claim that the laser-assisted process is the only process consistent with our observations for $E_{c.m.} \leq 50$ eV.

The discrepancy between the measured signals and the "reasonable cross-section estimates" performed in the Gillen's Comment can be explained as follows: The estimates assume that the photoionization cross section of the transient $He^* + He$ collisional complex should be equal to that of the atomic metastable He^*. However, there is no reason for supporting this assumption, since photon absorption occurs only during the collision, at very short internuclear distances $R < 2$ Å. In this range of R, the above assumption does not describe the system under study, since the collisional perturbation, dominated by short-range exchange interaction, strongly modifies the orbital of the optical electron of He^*, which becomes very different from the initial atomic one. Reliable calculations[8,9] demonstrate that Pauli repulsion from the filled $1s$ core of the He colliding partner strongly distorts the $He^*(2s)$ orbital of the optical electron and pushes it away from its nuclear center along the internuclear axis, by several atomic units. As a consequence, a substantial enhancement of the bound-free dipole transition moment is expected, as compared with the optically induced atomic value corresponding to atomic photoionization. A crude estimate of this dipole moment starting from such a collision-perturbed $2s$ initial state and taking the final continuum state as a free-electron state leads to an enhancement of roughly 10 to 30. This corresponds to an enhancement in the ionization probability of 100 to 900. There is an additional enhancement effect arising in the collisional system under study. This effect is due to the nonstationary character of the electron wave function, which changes, for $R \lesssim 2$ Å, in a lapse of time $t \sim 10^{-8}$ cm/6×10^6 cm s$^{-1} = 1.3\times10^{-15}$ s, that is of the same order as the Bohr frequency (which is modified, by the way). This nonadiabatic effect is met also under field-free conditions and accounts for the field-free "diabatic" background signal observed.[2-4] Obviously, under field-assisted conditions, the response of the collisionally accelerated electron to the laser field is not that induced by the field alone. A substantial enhancement occurs since the frequency spectrum of the collisional perturbation is close to the optical frequency.

In conclusion, the two-step process proposed in the Comment is clearly in contradiction with our experimental observations. The assisted process seems to be the only one consistent with these observations. The estimation of the assisted signals performed in the Comment assumes that the photoionization cross section of the transient collisional complex is the same as for the atomic metastable. This assumption amounts to neglect the effect of the collision on photon absorption, to show that photon absorption is negligible during the collision. This "self-consistent demonstration" omits the collisional enhancement of the transition dipole,[10] however. Instead, in the assisted process under study, one has to consider the effect of the collision as twofold: (1) it allows photoionization by lowering the ionization potential, (2)

it enhances the ionization probability as compared to the atomic metastable (for the same kinetic energy of the ejected electron).

It is precisely this enhancement effect[8,9] which led us to expect that the assisted process could be measured, even when considering the very short lifetime of the transient molecule and the very small number of collisions, which both lead to very small signals, such as presented in Refs. 2–4.

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