ENHANCED ELECTRON ATTACHMENT TO RYDBERG STATES IN MOLECULAR HYDROGEN DISCHARGES

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Generation of H^- ions using H_2 discharges is actively being pursued due to the need for intense H^- ion beams for particle accelerators and for magnetic fusion energy research. Since the late 1970's, an exhaustive experimental and theoretical effort has been devoted to understanding the experimental observations in H_2 discharge sources [1]; electron attachment to the high-vibrational states (HV states) of the ground electronic state of H_2 has been considered as the major H^- formation mechanism. However, recent studies [2-4] show that the experimentally measured H^- number densities can not be completely accounted for by electron attachment to HV states. Based on our observations on enhanced electron attachment to laser-excited H_2, in 1994 we pointed out [5] that electron attachment to highly-excited electronic states of H_2 [which are high-Rydberg (HR) states], that are populated in H_2 discharges may account for the difference.

In a recent paper, Hiskes [6] estimated the number density of HR states in a H_2 discharge and concluded that the contribution of such HR states to the H^- formation is negligible compared to H^- formation via electron attachment to HV states. In this calculation, it was assumed [6] that a vibrational level v of a HR state with principal quantum number n, H_2*(n,v), would decay via autoionization if its energy was above the lowest ionization threshold: The low angular momentum (l = 0,1) states that were populated via electron impact were assumed to undergo rapid autoionization before they had time to undergo l- and m-mixing to higher l- and m-states with long lifetimes (m is the magnetic quantum number). In the following we will present evidence to show that this assumption is not valid and therefore the contribution from the H_2*(n,v) states with total energies above the lowest ionization threshold (which are superexcited HR states) need to be taken into account.

Our experimental evidence is two-fold: we have conducted experiments where molecular excitation was achieved via laser irradiation and also via excitation transfer in a gas discharge. Within the past several years we have shown that molecules laser-excited to energies above their ionization thresholds attach electrons efficiently to form negative ions via dissociative electron attachment, see [7] and references therein; in one of these studies, we observed H^- formation in

H_2 laser-excited to an energy above its ionization threshold [5, 8]. Subsequently, we showed that such excitations lead to the population of long-lived superexcited HR states with lifetimes up to several microseconds [9]. In addition, the zero electron kinetic energy (ZEKE) photoelectron spectroscopy [10] that has been developed over the past fifteen years is based on the population of long-lived HR states where the initial laser-excited HR states with low-l values are believed to be rapidly converted to long-lived states with high-l and high-m values due to inhomogeneous stray fields [11].

We recently developed a plasma mixing scheme [12] to produce highly-excited states of molecules using excitation transfer from the long-lived metastable states of rare gases that are efficiently produced in glow discharges, see Fig. 1. The rare gas metastable states produced in a glow discharge were extracted to an adjoining discharge-free region (target region) using a gas flow scheme. A molecular gas was introduced to the target region where excitation transfer from the rare- gas metastables led to the formation of highly-excited states of the molecular gas. Low-energy electrons were also extracted to the target region using an axial magnetic field, and efficient capture of electrons by the excited molecules was observed for rare gas/molecular gas combinations where the ionization threshold of the molecular gas was higher than the energy of the metastable states of the rare gas [12, 13], i.e., excited states of the molecules lying below their ionization thresholds were populated.

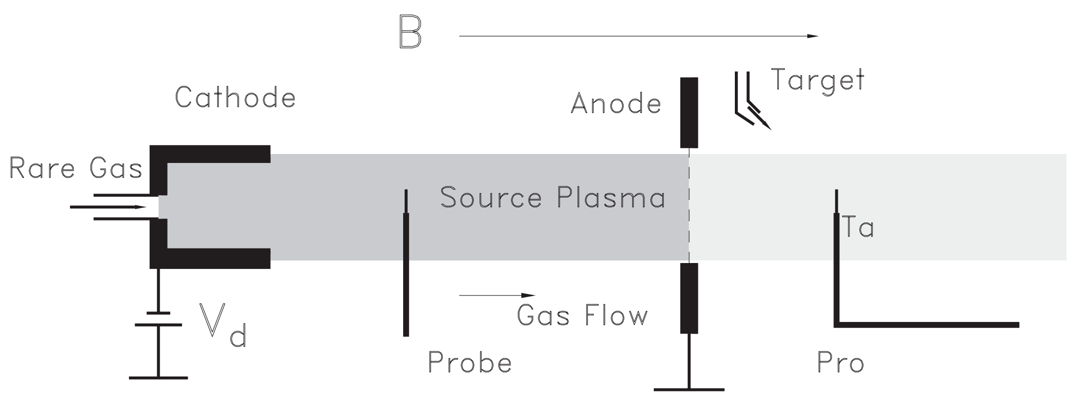

Figure 1. A schematic diagram of the plasma mixing apparatus. It is important to note that the molecular gas (target gas) was not subjected to the discharge.

Using the above apparatus, we have observed efficient negative ion formation for rare gas/molecular gas combinations where the ionization threshold of the molecular gas was smaller than the energy of the metastable states of the rare gas, i.e., the total energy of the excited states of the molecules populated via excitation transfer exceeded the ionization threshold. A significant fraction of molecules turned out to be in long-lived highly-excited states while the majority of them ionized; electron attachment to these highly-excited states resulted in negative ion formation. As an example, we will discuss the Ar/NO combination. In this case Penning ionization of NO (ionization threshold ≈ 9.3 eV) can be expected, since the energy of the metastable Ar is ≈ 11.5 eV. Using a Langmuir probe, the change in electron density in the target region was monitored; with the introduction of NO to the target region the electron density in the target region increased indicating significant Penning ionization, see Fig. 2(a). However, even

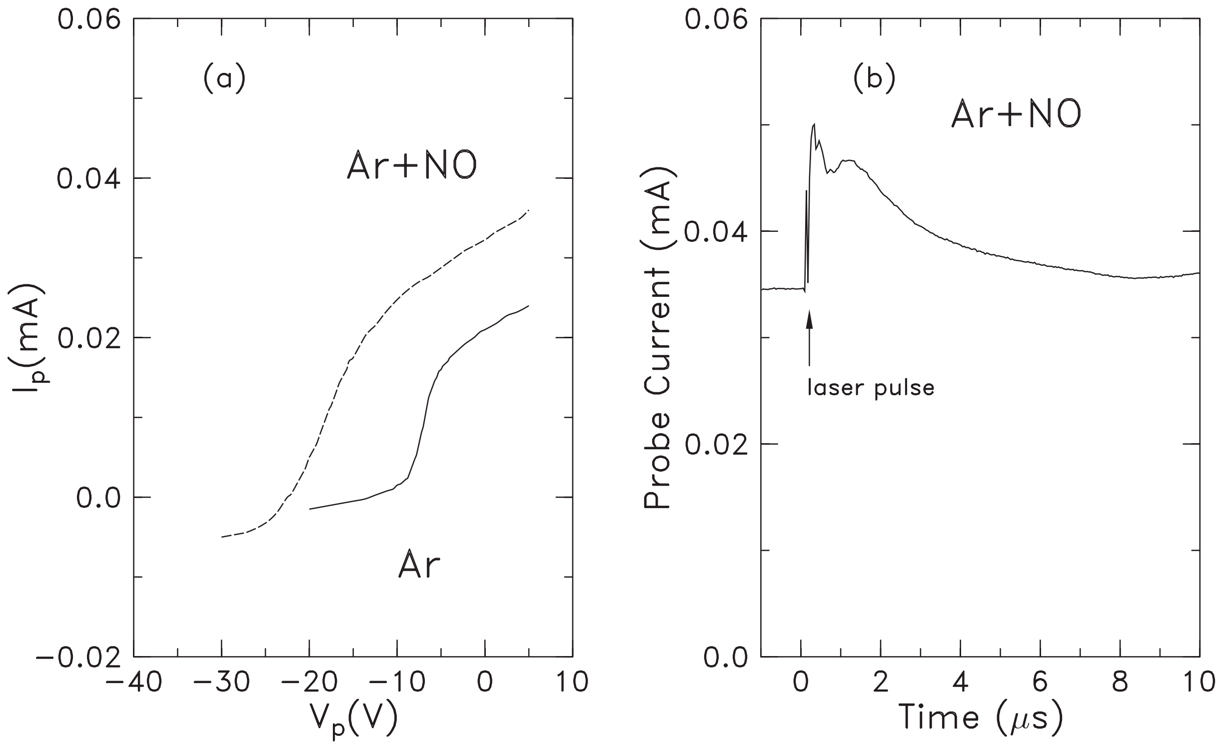

Figure 2. (a) Langmuir probe characteristics for pure Ar and Ar/NO mixture in the target region. The increase in electron density due to Pennning ionization of NO is clear. (b) Photodetachment signal observed for Ar/NO mixture.

in this case a significant density of O^- ions was produced in the target region, as was verified by a photodetachment experiment [13]: The O^- ions were photodetached using a frequency-tripled Nd-Yag laser. A sample photodetachment signal is shown in Fig. 2(b). This O^- formation cannot be due to electron attachment to ground state of NO: Dissociative electron attachment to the ground electronic state of NO occurs for electron energies between ≈ 7 and ≈ 11 eV with a maximum cross section of $\approx 10^{-18} cm^2$, see [14] and references therein. Therefore, in addition to Penning ionization of Eq (1), HR states of NO must be produced via excitation transfer, viz.,

$$Ar_m^* + NO \longrightarrow NO^* + Ar \tag{1}$$

where the "excess energy" above the ionization threshold must have been converted to the ro-vibrational modes [9]. Now, the attachment of a free electron to a HR state of NO leads to the efficient formation of O^- ions,

$$NO^{**} + e^-_{\text{slow}} \longrightarrow N + O^- \tag{2}$$

This is also consistent with our previous observation of enhanced O^- formation when NO molecules were laser excited to energies above its ionization threshold [15].

From the above mentioned laser and plasma experiments it is clear that when molecules are excited to energies above (and within a few electron volts) of their ionization thresholds, long-lived core-excited HR states are populated in significant densities; also, dissociative electron attachment to such excited molecules leads to efficient negative ion formation.

It is quite likely that long-lived HR states of H_2 with total energies exceeding its lowest ionization threshold are populated with significant number densities by electron impact in the H_2 discharge sources. Therefore, their contribution, together with that due to HR states lying below the lowest ionization threshold, should be taken into account for H^- formation in H_2 discharges.

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