URSI GASS 2021, Rome, Italy, 28 August - 4 September 2021

The associative detachment reaction of nitrogen molecules with the anion of atomic oxygen revisited in the context of sprite streamer initiation

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Although molecular oxygen, O_2, is an attaching gas, current growth measurements in air demonstrate negligible electron attachment, see for example [1]. This observation is interpreted in terms of an electron detachment mechanism involving O^- ions and excited molecular nitrogen, N_2, since detachment of electrons from O^- ions by collision with unexcited O_2 and N_2 molecules practically does not occur at low gas temperatures [2, 3, 4]. It has been demonstrated that for the associative detachment reaction to proceed, N_2 must be excited to at least the first vibrational level [5]. Contrary to studies above and based on a unique flow-drift tube setup, Rayment and Moruzzi [6] argued that ground state N_2 is in fact responsible for the associative detachment reaction. We note that Doussot et al. [7] also arrive at the same conclusion with rates in qualitative agreement with those presented in [6], though the O_2/N_2 ratio is significantly different in the two works. Also, it is not obvious how excited species are identified or removed from the drift region to limit the study to O^- reacting with ground state N_2. Here, we review the unique flow-drift tube setup in [6] as it's the only work which provides values for the detachment rate coefficient in a considerable range of reduced electric fields, and is the basis of recent studies devoted to initiation of sprite streamers, for example [8]. In particular, we (1) demonstrate that excited N_2 species in fact do contaminate the experimental setup in [6], (2) model the experimental setup in [6] using a Green's function method and provide corrections to the theoretical approach outlined in that work, (3) demonstrate that using values of the detachment coefficient per unit pressure $\beta_{\rm d} = \alpha_{\rm d}/p$ [Torr^{-1} cm^{-1}] provided in [6] neither theoretical models obtain results in agreement with figure 3 of [6], (4) $\beta_{\rm d}$ values in [6] are inconsistent with the detachment rate coefficient $\kappa_{\rm d}$ [cm^3 s^{-1}] depicted in figure 4 of [6], (5) propose an alternative detachment mechanism which includes only vibrationally excited N_2 and calculate the rate of this reaction under conditions similar to those outlined in [6], and (6) underscore that reaction rates in majority of flow-drift tube setups mentioned above are obtained under steady state conditions which are not reflective of the transient nature of gas discharge dynamics [9].

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