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# Controlling Plasmonic Chemistry Pathways through Specific Ion Effects

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Dedicated to Professor Jochen Feldmann on the occasion of his 60th birthday

**Plasmon-driven dehalogenation of brominated purines has been recently explored as a model system to understand fundamental aspects of plasmon-assisted chemical reactions. Here, it is shown that divalent $Ca^{2+}$ ions strongly bridge the adsorption of bromoadenine (Br-Ade) to Ag surfaces. Such ion-mediated binding increases the molecule's adsorption energy leading to an overlap of the metal energy states and the molecular states, enabling the chemical interface damping (CID) of the plasmon modes of the Ag nanostructures (i.e., direct electron transfer from the metal to Br-Ade). Consequently, the conversion of Br-Ade to adenine almost doubles following the addition of $Ca^{2+}$. These experimental results, supported by theoretical calculations of the local density of states of the Ag/Br-Ade complex, indicate a change of the charge transfer pathway driving the dehalogenation reaction, from Landau damping (in the lack of $Ca^{2+}$ ions) to CID (after the addition of $Ca^{2+}$). The results show that the surface dynamics of chemical species (including water molecules) play an essential role in charge transfer at plasmonic interfaces and cannot be ignored. It is envisioned that these results will help in designing more efficient nanoreactors, harnessing the full potential of plasmon-assisted chemistry.**

## 1. Introduction

Until recently, the plasmonic chemistry community focused mainly on Landau damping as the primary electron/energy transfer from plasmonic nanostructures to adsorbed molecules.[1–4] In the context of surface plasmon resonance, Landau damping represents the scattering of hot electrons (electrons with energy greater than the thermal energy) at the surface of nanostructures[5] (thus, it scales with $1/R$ for spherical nanostructures, where $R$ is the radius[6,7]). Nonetheless, despite the enormous efforts and advances to increase the efficiency of chemical reactions through Landau damping, the efficiency of such reactions remains low. The low efficiency is mainly due to the unavoidable losses in the metals (provided by bulk scattering, electron-electron scattering, and thermalization of hot electrons), which often surpass the energy gain provided by the plasmon resonance modes.[8–10]

Therefore, the plasmonic community started slowly to shift focus from Landau damping to chemical interface damping (CID) as the primary pathway for electron/energy transfer from plasmonic nanostructures to adsorbates.[11–13] Contrary to Landau damping, which is a multistep effect (first, the electrons are excited above the Fermi level, then they are scattered at the surface of the nanostructures, where

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