

Halide–Metal Complexes at Plasmonic Interfaces Create New Decay Pathways for Plasmons and Excited Molecules

Andrei Stefancu, Oana M. Biro, Otto Todor-Boer, Ioan Botiz, Emiliano Cortés,* and Nicolae Leopold*

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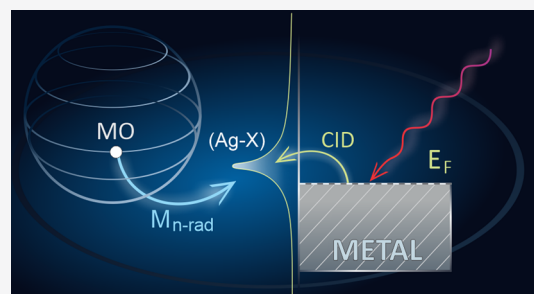
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ABSTRACT: We show that by modifying the chemical interface of silver nanoparticles (AgNPs) with halide ions, it is possible to tune the total decay rate of adsorbed excited molecules and the plasmon damping rate. Through single-molecule surface-enhanced Raman scattering and surface-enhanced fluorescence enhancement factors of crystal violet (CV) and rhodamine 6G (R6G), we show that I^- -modified AgNPs (AgNPs@I) and Br^- -modified AgNPs (AgNPs@Br) lead to an increase in the total decay rate of excited CV and R6G by a factor between ~ 1.6 – 2.6 , compared to Cl^- -modified AgNPs (AgNPs@Cl). In addition, we found that the chemical interface damping, which characterizes the plasmon resonance decay into surface states, is stronger on AgNPs@I and AgNPs@Br when compared to AgNPs@Cl. These results point toward the formation of metal–halide surface complexes. These new interfacial states can accept electrons from both excited molecular orbitals and surface plasmon excitations, completely altering the electronic dynamics and reactivity of plasmonic interfaces.

KEYWORDS: SERS, SEF, halide ions, decay rate, chemical interface damping, plasmonic interfaces



the formation of a surface complex (halide– Ag^+ –dye complex).^{17,18}

Furthermore, differences among the halide ions themselves (i.e., Cl^- , Br^- , and I^-) were often reported in terms of enhancing the Raman signal of adsorbed molecules or their absorbance. More specifically, the effects of halide ions in surface science seem to follow the sequence: Cl^- – Br^- – I^- , in increasing or decreasing order. For example, the affinity of adsorption to the metal surface of the three halide ions increases in the sequence $Cl^- < Br^- < I^-$, which leads to the same sequence for the halide–metal (partial) charge transfer upon adsorption. Because of this, the Fermi level of metal NPs increases in the same sequence, influencing their interaction with adsorbed molecules.¹⁹ In terms of Raman enhancement, the effect of the three halide ions seems to depend on the specific target analyte. In some cases, the Raman enhancement was found to increase in the sequence:^{20,21} $Cl^- < Br^- < I^-$, whereas in some cases, I^- quenched the SERS signal.^{21,22} Although these differences in Raman enhancement are usually attributed to the displacement of target analytes from the NP surface^{22,23} by I^- , we show here for R6G and crystal violet

INTRODUCTION

The optical properties of molecules change drastically when they are adsorbed on metal nanoparticles (NPs). The radiative emission (Raman or fluorescence) of adsorbed molecules can be enhanced, with typical enhancement factors of Raman scattering of the order of 10^8 , or quenched due to de-excitation of molecules to non-radiative states in the metal NPs. Physically, the changes in the radiative and non-radiative decay rates are due to the coupling of molecular transitions to the various plasmon modes of the metal NPs.^{1–7}

A persistent mystery in the realm of surface-enhanced Raman scattering (SERS) and nanoparticle–molecule interaction is the role of halide ions, which goes beyond the simple aggregation of the colloidal solution.^{8–13} Doering and Nie showed that even on fixed, single AgNPs, halide ions turn on the SERS signal of rhodamine 6G (R6G).¹⁴ In fact, single-molecule SERS (SM-SERS) of cationic dyes has only rarely been achieved¹³ without the use of halide ions (most commonly Cl^-). More recently, the optical absorption of molecules directly adsorbed on AgNPs was measured, for under-monolayer coverages.^{15,16} Although the physical interpretation differs, the measurements clearly show that the optical absorbance of the dyes shifts significantly only in the presence of halide ions; in the absence of halide ions, no change in the molecular absorption is being observed. This suggests that halide ions determine a stronger interaction of molecules with the AgNP surface, leading either to a shift of molecular electronic levels and change of polarizability or to

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