# Comment on "Chemical Contribution to Surface-Enhanced Raman Scattering"

Persson *et al.* [1] proposed a new "chemical" mechanism for surface-enhanced Raman scattering (SERS); the vibrations of an adsorbed molecule result in a modulation of the polarizability of a metallic substrate, and hence in a Raman signal at the vibrational frequency. We call this effect vibrationally induced polarizability modulation (VIPM) for short. Reference [1] claims the effect could result in an increased SERS signal by a factor $\approx 10^2$ for a spherical particle as compared to the SERS signal expected from the electromagnetic (EM) enhancement only. Hereby we argue that this figure is misleading and that VIPM is not expected to play a role in most SERS experiments.

We first remark that other chemical contributions to SERS involving polarizability modulation of the substrate have already been studied, with theories such as the modulated reflectivity (MR) or inelastic Mie scattering (IMS) models (see Ref. [2], pp. 819–821), but were then thought to be irrelevant to most SERS experiments.

In SERS, the local field $E_{\mathrm{Loc}}$ is modified compared to the incident field $E_{\mathrm{ext}}$ by a factor $M$, which depends on the dielectric function $\epsilon(\omega)$ of the substrate. The SERS enhancement is approximated by $|M|^4$, and for Ag $|M|^4$ can be $\sim 10^4$–$10^{10}$. In a first approximation, the substrate can be considered as a polarizable unit with polarizability $\alpha_p$. Reference [1] argues that $\alpha_p$ is affected by the presence of vibrational motions ($Q$) of an adsorbed molecule. For this, $\epsilon(\omega)$ is taken from a Drude model with a damping $\gamma$ depending on $Q$. The $Q$ dependence of $\gamma$ (coupled through the parallel field) is the main difference with other variants of polarizability modulation models like MR or IMS [2]. $\alpha_p$ then gains a $Q$ dependence, exactly as the polarizability $\alpha_m$ of a molecule exhibits a $Q$ dependence. By expanding $\alpha_p(Q) \approx \alpha_p(0) + \alpha'_p(0)Q$, this results in an induced Raman dipole $p_p = \alpha'_p(0)QE$ in the substrate, which produces a VIPM Raman signal [1].

Our main criticisms are as follows. (i) There is a fundamental difference between the usual SERS enhancements (chemical and EM) and VIPM. This was already emphasized in the context of IMS [2], but is not clearly stated in Ref. [1]. In SERS the signal from the molecule itself is amplified. VIPM is an entirely independent process whereby another (coherent) signal at the molecule's vibrational frequencies is emitted by the metallic substrate. There is no real enhancement, but simply an additive contribution to the Raman signal. Because this effect is additive rather than multiplicative, it is misleading to characterize VIPM by an enhancement factor with respect to SERS or normal Raman. Reference [1] argues that VIPM is $\sim 10^2$ larger than SERS for a molecule with a (non-SERS) Raman tensor $\alpha'_m(0) \approx 1$ Å$^2$. Such a molecule would be a very poor Raman (and SERS) scatterer and this is the cause of the apparent strength of VIPM compared to SERS. For CO, for example, the Raman tensor amplitude is $\alpha'_m(0) \approx 4$ Å$^2$ (computed from density-functional theory ), corresponding to a (total) Raman cross section of $\approx 1.4 \times 10^{-30}$ cm$^2$ at 633 nm. The VIPM contribution is therefore only about 6 times (and not $10^2$) that of the standard EM enhancement. Moreover, when comparing VIPM to the SERS signal of a resonant dye with a typical non-SERS cross section of $\approx 10^{-26}$ cm$^2$ (this is, for example, the value for rhodamine 6 G at 633 nm in preresonance conditions), the signal is, in fact, $\approx 10^3$ smaller than SERS. A more appropriate way to characterize VIPM is its absolute cross section, as was done for MR or IMS [2], which is then of the order of $\approx 10^{-25}$ cm$^2$ (for an Ag sphere). This is much smaller than SERS cross sections in most circumstances. (ii) One could argue that, in a similar fashion as SERS, VIPM might be more important in situations of large field enhancements. This typically occurs for aggregates of metallic particles, where the SERS enhancement factor can be as large as $10^{10}$ at junctions between particles (hot spots). A simple argument can be put forward against this possibility: SERS relies on large values of $|M|$, which is a local field property. Contrariwise, VIPM relies on a large $\alpha'_p(0)$, which can be expected when $\alpha_p$ is also large. But $\alpha_p$ is essentially a far-field property (it characterizes the substrate's scattering properties). Although it is expected that $|M|$ and $\alpha_p$ show qualitatively the same resonances (which have the same EM origin), $|M|^4$ can exhibit quantitative variations much larger that $|\alpha_p|^2$. This has been emphasized recently [3], and is particularly pronounced for large $|M|$'s. The VIPM signal should therefore be even smaller compared to SERS in high-enhancement substrates.

In closing, the new mechanism for SERS in Ref. [1] is mostly ineffective because (i) like MR and IMS [2], it is an additive (rather than multiplicative) effect and could only be observed if it is larger than SERS itself; (ii) in the proposed example of a silver sphere [1], it is not stronger than SERS for most molecules except the poorest Raman scatterers; and (iii) for substrates with larger SERS enhancements, its relative intensity with respect to SERS is expected to be even smaller.

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