Persson, Zhao, and Zhang Reply: In Ref. [1] we presented a new mechanism of chemical contribution to surface enhanced Raman scattering and estimated that it may give an enhancement of 10^2 for adsorbates on small metal particles and even higher enhancement (up to $\sim 10^4$) for adsorbates on flat metallic surfaces. Le Ru and Etchegoin [2] argue that these enhancement factors are misleading and claim that the mechanism we consider "is not expected to play a role in most SERS experiments".

Le Ru and Etchegoin point out that more than 20 years ago it was suggested by various authors (see Ref. [3] for a summary including references) that charge transfer between the adsorbed molecule and the substrate (metal particle or flat surface) would modulate the (dynamical) polarizability of the system and contribute to the enhanced Raman scattering. For example, charge oscillations between an adsorbate and a small metallic particle during adsorbate vibration will modulate the carrier concentration in the metal particle, leading to a fluctuating plasmon frequency and hence a fluctuating polarizability of the metal particle. However, the mechanism we considered in Ref. [1] is very different from that emphasized in Ref. [2] and in fact much more important: the adsorbate vibrations will modulate the cross section for diffusive scattering of the metal electrons from the adsorbate and such a modulation has a much stronger influence on the polarizability of the metal particle than the fluctuations in the plasmon frequency. In fact, the situation considered in Ref. [1] is very similar to the influence of adsorbates on the resistivity of thin metallic films, studied in detail about 15 years ago. For example, Tobin *et al.* have shown that the (static) charge transfer between the metal film and the adsorbate induces a much smaller change in the film resistivity (by roughly a factor of 10–100) than the contribution from diffusive scattering of the metal film conduction electrons from the adsorbate [4]. This situation is very similar to the present case and we expect a similar difference in the magnitude of the charge transfer and diffusive scattering effects on the chemical contribution to SERS as observed by Tobin *et al.* for the resistivity of thin metallic films.

In Ref. [2] it is stated that "there is a fundamental difference between the usual SERS enhancements (chemical and EM) and VIPM", and "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." We disagree with this statement. Raman scattering is a coherent quantum mechanical scattering process, where the probability for a particular outcome is the absolute square of a sum of probability amplitudes. As such, it in general cannot be decomposed into a sum of independent processes. For the same reason, we disagree about the statement "there is no real enhancement, but simply an additive contribution to the Raman signal." Such statements are inconsistent with the basic superposition principle of quantum mechanics.

Furthermore, in our estimate of the enhancement of the Raman scattering intensity we assumed that $\alpha'(0)$ (the derivative of the electronic polarizability of the molecule with respect to the vibrational normal mode coordinate) for small typical molecules such as CO is of order 1 Å^2 as expected from dimensional arguments. In Ref. [2] it is instead stated that for CO, $\alpha'(0) \approx 4$ Å^2, which the authors claim has been obtained using density functional theory. However, it is well known from experiment (see, e.g., Ref. [5]) that for CO (and other similar small molecules) $\alpha'(0) \approx 1.5$ Å^2, i.e., of order 1 Å^2 as assumed in our estimation of the SERS enhancement.

Le Ru and Etchegoin state that SERS relies on large values of $|M|$ (electric field enhancement) and argue that the mechanism we consider does not exhibit the same strong field enhancement. However, as shown in Ref. [1], the same field enhancement occurs for the process we consider, and the ratio between the Raman scattering cross section we calculate and that due to the direct coupling to the adsorbed molecule does not depend on $|M|$ [see Eq. (12) in [1]].

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Received 2 October 2006; published 10 November 2006
DOI: 10.1103/PhysRevLett.97.199702
PACS numbers: 78.30.−j, 78.68.+m

[1] B. N. J. Persson, K. Zhao, and Z. Y. Zhang, Phys. Rev. Lett. **96**, 207401 (2006).
[2] E. C. Le Ru and P. G. Etchegoin, preceding Comment, Phys. Rev. Lett. **97**, 199701 (2006).
[3] M. Moskovits, Rev. Mod. Phys. **57**, 783 (1985).
[4] K. C. Lin, R. G. Tobin, P. Dumas, C. J. Hirschmugl, and G. P. Williams, Phys. Rev. B **48**, 2791 (1993); E. F. McCullen, Ching-Ling Hsu, and R. G. Tobin, Surf. Sci. **481**, 198 (2001).
[5] J. E. Hesser, J. Chem. Phys. **48**, 2518 (1968); Y. Tanaka, J. Chem. Phys. **26**, 862 (1957); Kuei-Chiao, Chin. J. Phys. (Taipei) **8**, 58 (1970).

