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Use of Dusty Plasmas for Surface-Enhanced Vibrational Spectroscopy Studies

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Dusty plasmas are low-temperature, weakly ionized gases containing micron- to submicron-sized solid particles that are charged by plasma collection currents. In this theoretical note, we propose the possible use of dusty plasmas as substrates for surface-enhanced vibrational spectroscopy studies, because of several possible advantages over some traditional substrates. Surface-enhanced Raman scattering, or surface-enhanced infrared (IR) absorption spectroscopy, has used metal colloids as substrates on which the analyte molecules are adsorbed. As compared with colloids, dust in plasmas have much faster charging times, are immersed in background plasma that is generally transparent to IR, can be composed of a wide variety of materials, are free of solvents, and allow a range of temperatures. Plasma properties also may lead to reduced aggregation as compared with colloids and may allow the use of different dust materials that have electromagnetic resonances in the IR as well as in the visible. Possible complications associated with the use of plasmas are also discussed.

1. Introduction

There is currently much interest in surface-enhanced vibrational spectroscopy techniques which analyze the vibrational spectra of molecules, because of their high sensitivity. Surface-enhanced Raman scattering (SERS) or surface-enhanced infrared absorption (SEIRA) spectroscopy studies have used various metal materials with particle-like properties, such as metal colloids, roughened metal surfaces, or metal island films, as substrates on which the analyte molecules are adsorbed. It is thought that an electromagnetic (EM) mechanism involving the interaction between an adsorbate and a surface mode (e.g., a surface plasmon) in the underlying metal substrate often plays a major role in the enhanced scattering or absorption (see reviews in refs 1−4). This EM mechanism involves the optical properties of small particles (see, e.g., ref 5).

In this note, we consider theoretically the potential use of dusty plasmas as substrates for surface-enhanced vibrational spectroscopy studies, in analogy with the use of metal colloids. Dusty plasmas are low-temperature, weakly ionized gases containing micron- to submicron-sized solid particles (dust) that are charged by electron and ion collection currents. Since the electrons are more mobile, the dust charges negatively, much like a small probe in the plasma. The charge on an isolated spherical dust grain can be estimated using $Q_d = -Z_d e = a\phi$, where Z_d, a, and ϕ are the charge state, radius, and surface potential of the grains, respectively, where generally $|e\phi| \sim$ few times the electron temperature T_e [e.g., 6]. Generally, in laboratory dusty plasma experiments, T_e has ranged between a few eV to a fraction of an eV (see, e.g., reviews in refs 7−10). For example, in an argon plasma with $T_e \sim 0.1$ eV, a dust particle of radius $a = 0.1\ \mu$m can acquire a charge state of about $Z_d \sim 20$, assuming $\phi \sim -3T_e$. Owing to their charge, dust can be levitated and confined by electric fields in the plasma. The presence of a high-pressure neutral background gas at room temperature can “cool” the kinetic motion of the dust grains.[8,9]

Dusty plasmas may offer several potential advantages over aqueous colloids as substrates for SERS and SEIRA. These include (a) faster particle charging times and better particle dispersal, (b) superior IR transparency, (c) an expanded repertoire of dispersible particles, (d) freedom from solvent effects, and (e) larger viable temperature range. Even if complications associated with the use of plasmas limit the practical use of dusty plasmas, such systems may be useful as models with which to study EM enhancement mechanisms for surface-enhanced spectroscopy. It is hoped that the discussion in this note may spur future spectroscopic studies or experiments.

The rest of the paper is organized as follows. Section 2 discusses the use of dusty plasmas as substrates for surface-enhanced spectroscopy, as well as possible complications associated with the use of plasmas. Section 3 gives a brief summary.

2. Use of Dusty Plasma as Substrate

For background purposes, we first review the EM enhancement mechanism of surface-enhanced Raman spectroscopy for isolated metal particles, which involves the optical properties of small particles (e.g., ref 2). For a spherical particle with dielectric constant ϵ_s, embedded in a medium with dielectric constant ϵ_0, the sphere polarizability is given by (e.g., ref 5)

$$\alpha_s = \left(\frac{\epsilon_s - \epsilon_0}{\epsilon_s + 2\epsilon_0}\right)a^3 \tag{1}$$

where a is the radius of the sphere. Consider a particle with radius a much smaller than the wavelength of an incident electromagnetic wave. When the real part of $\epsilon_s = -2\epsilon_0$ and the imaginary part of ϵ_s is small, α_s can become large, and thus the induced dipole electric field that results from the polarization of the sphere can become large. If this induced field is stronger than the field of the incident EM wave, it can strongly excite Raman scattering of adsorbed molecules, resulting in SERS.[2] Basically, the dipolar-plasmon resonance of the metal particle

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acts like an antenna that amplifies both the incident field at the location of the adsorbed molecule and also the Raman-shifted radiated wave.[11] A similar EM mechanism may also play a role in SEIRA,[4] but since metals absorb in the IR, the change in optical properties of the metal substrate, at the vibrational frequencies of the adsorbed molecules, can be a more important EM effect.[4,12]

The plasmon resonance condition discussed above dictates the use of coinage metals (Ag, Au, Cu) as substrates in SERS where visible light is used.[13,14] For example, for a Ag colloidal dispersion in which the real part of the dielectric function of the background aqueous solution is ∼1.33, the plasmon resonance condition can be satisfied for wavelength $\lambda \sim 400$ nm, where the real part of $\epsilon_s \sim -3.6$ and the imaginary part of $\epsilon_s \sim .3$ (e.g., ref 15). In addition, the condition $a \ll \lambda$ implies that the colloidal particle sizes should be on the order of tens of nanometers.[1]

We propose the possible use of dusty plasmas as substrates for SERS or SEIRA studies, in analogy with the use of metal colloids. There are similarities between dusty plasmas and charged colloidal dispersions; for example, the mutual Coulomb repulsion between the like-charged particles inhibits aggregation. However, the dynamics of dusty plasmas occurs on a time scale which is about a million times faster than in colloidal systems.[16]

This points to the first of several potential advantages of dusty plasmas as regards the deactivation properties of metal colloid substrates. The SERS activity of metal colloids suffers from irreversible deactivation once the particles become aggregated due, for example, to replacement of charged ions on the colloids by neutral adsorbates or to the presence of extraneous products, resulting from colloid preparation, in the suspension that can interfere with surface reactions and cause aggregation.[17,18] In a dusty plasma, the time scale for a grain to charge to its equilibrium value is very fast, about $\tau_{ch} \sim (\lambda_D/a)\omega_{pi}{}^{-1}$, where λ_D is the Debye screening length in the plasma, and ω_{pi} is the ion plasma frequency (e.g., ref 6). For example, for an argon plasma with $T_e \sim 0.1$ eV and ion density $n_i \sim 10^9$ cm^{-3}, the charging time for a dust grain of size $a \sim 0.1$ μm would be about 100 μs. Thus, assuming the total dust charge density is less than n_i, it may be expected that there would be sufficient charge from the background plasma to keep the grains charged to their equilibrium value on sub-ms time scales, which should play a role in inhibiting aggregation.

A second potential advantage of dusty plasmas is related to the background plasma being generally transparent to IR, in contrast to the colloidal dispersion in an aqueous solution. The plasma is transparent to EM waves with angular frequency ω when its dielectric function

$$\epsilon = 1 - \frac{\omega_{pe}{}^2}{\omega(\omega + i\nu_e)} \qquad (2)$$

is ≈1. This would occur for waves with $\omega \gg \omega_{pe}$ and $\omega \gg \nu_e$ (here ω_{pe} and ν_e are the electron plasma and collision frequencies, respectively). For a plasma with electron density $n_e \sim 10^9$ cm^{-3}, $T_e \sim 0.1$ eV, and neutral inert gas density $n_n \sim 10^{16}$ cm^{-3}, the plasma would be transparent to EM waves with wavelengths smaller than a few cm. Thus, it seems possible that SEIRA studies could be done in a volume of dusty plasma containing charged metal particles.

Different dust grain materials could be used that may have surface plasmon resonances in the IR, in contrast to metals that can absorb in the IR. The resultant SEIRA spectrum would then be indicative of the spectrum of the adsorbed molecules, without the complications of the underlying absorption properties of the substrate (see, e.g., refs 4, 19, 20). The plasmon resonance for semiconductors would be expected to be in the infrared, rather than in the UV or visible part of the spectrum as for metals, since the free electron density in semiconductors is orders of magnitude lower than in metals.[21] Using values from ref 15, the dielectric function of the semiconductor materials gallium phosphide (GaP) and indium phosphide (InP) can satisfy the plasmon resonance condition, with $\epsilon_0 = 1$, at a wavelength about 25 μm (for GaP) and 30 μm (for InP), where the imaginary parts of ϵ_s are also small. Another example is SiC, which satisfies the plasmon resonance condition at about 11 μm.[5] Furthermore, larger particles in the micron-size range could be used, since they would satisfy the requirement that $a \ll \lambda$, when λ is in the mid-IR range.

As an example of dusty plasma parameters, consider an Ar plasma with $n_i \sim 10^9$ cm^{-3} and $T_e \sim 0.1$ eV, containing semiconductor material grains of size $a = 0.1$ μm, with number density $n_d \sim 5 \times 10^7$ cm^{-3}. A region of length $L \sim 3$ cm would be optically thin, since the optical depth $\tau \sim \pi a^2 n_d L \sim 0.05 \ll 1$. The number of dust grains in a volume of size L^3 would be $\sim 10^9$, so the cumulative dust surface area in this volume would be about 0.3 cm^2. (The dust grain charge state would be about $Z_d \sim 20$, so that the electrostatic energy between neighboring dust grains would be about room temperature; this would inhibit aggregation if the dust kinetic energy was also near room temperature.) Assuming a trace amount of analyte in the range of picograms, a low range analyzed using SEIRA,[4] and assuming each molecule has a mass about 100 proton masses, this would imply about 6×10^9 molecules in the sample, or about 6 molecules adsorbed on average per dust grain.

Another potential advantage of using dusty plasmas would be to do SERS studies using IR light and micron-sized semiconductor material particles. Advantages, compared to the use of visible light and metal colloids for SERS measurements, are that (i) there would be a larger relative change in frequency in the Raman scattering process, perhaps making measurement easier, and (ii) the charging time for dust in a plasma, which is very fast, decreases as the dust size increases, which may further help inhibit aggregation upon adsorption of molecules, as mentioned above. We note that approximately 1−100 femtomole limits of detection using various SERS substrates have recently been reported.[22] A dusty plasma with parameters such as those in the previous paragraph might be adequate for dust surface adsorption of the lower range of such molecular concentrations in the gaseous phase.

This brings up a third potential advantage of using dusty plasmas, which is the possibility of having an expanded repertoire of dispersible particles. In principle, submicron-sized particles of any material can be charged negatively and become suspended in a plasma. The charge state could even be changed by using additional charging mechanisms such as, for example, photoemission under UV radiation that would tend to reduce the magnitude of the grain charge (e.g., ref 23).

As another potential advantage, the use of dusty plasmas, especially with inert buffer gases such as He, Ar, and Xe, might free SERS and SEIRA from confounding effects of solvents, and thus lay bare for study the molecule−substrate interactions. Solvents are known to alter dissolved molecules significantly and to electrochemically change surfaces. Since solvents can be a determinant of chemical activity, dusty plasmas may offer a means by which their importance can be assessed.

Finally, the use of dusty plasma may offer the potential advantage of allowing a larger viable temperature range. By employing the various modes of dusty plasma production, one should be able to vary the substrate temperature between roughly 300−2000 K, and thereby investigate temperature dependencies of molecule−substrate interactions. For the low end of the temperature scale, one can use low pressure (<1 Torr) inert gases (e.g., He, Ar, Xe) for the plasma. For higher temperatures, one could employ various means, such as laser heating of the grains,[24,25] or a "solenoidal barbecue",[24] wherein the dust and gas are heated in a current-heated, solenoidal blackbody cavity. These should allow temperatures 300−2000 K.

Although there may be advantages associated with the use of dusty plasmas as substrates for SERS or SEIRA, there may also be complications, and we briefly mention two. First, a plasma may excite the vibrational molecular levels due to electron impact. Since vibrational energies of reasonably sized molecules can be about 100 s of cm^{-1} (500 cm^{-1} corresponds to an energy of about 0.06 eV), electrons may have enough energy to excite such levels even in a plasma with low $T_e \sim 0.1$ eV. However, the mean free path for collisions of electrons with molecules adsorbed on the dust would generally be orders of magnitude larger than that for electron−neutral or electron−dust grain collisions, owing to relatively small excitation cross sections ($\sim 10^{-16}$ cm^2, see e.g., refs 26, 27) and the small number density of analyte molecules. Of course, if molecular vibrational levels were excited, this would be expected to result in enhanced anti-Stokes lines (rather than Stokes lines) in Raman scattering. A way to mitigate such electron excitation effects, if they are significant, is to limit studies to molecular vibrational excitation levels with energies larger than the plasma electron energies. In a plasma with $T_e \sim 0.1$ eV, this would imply energy levels with wavenumbers on the order $\gtrsim 800$ cm^{-1}. Another complication, involving interaction of analyte molecules with reactive gases, could in principle be mitigated by using inert background gas.

3. Summary

We have discussed the possible use of dusty plasmas as substrates for surface-enhanced vibrational spectroscopy studies, in analogy with the use of metal colloids. There may be advantages associated with the use of dusty plasmas as substrates. As compared with colloids, dust in plasmas have much faster charging times, are immersed in background plasma that is generally transparent to IR, and can be composed of a wide variety of materials. These properties may lead to reduced aggregation as compared with colloids and may allow the use of different dust materials that have electromagnetic resonances in the IR as well as in the visible. Advantages may include (1) reduced deactivation of the substrate in SERS studies and (2) application of the EM enhancement mechanism, thought to occur in SERS, directly to SEIRA through the use of substrate dust particles that have surface modes in the IR. Dusty plasmas may also be useful as a research tool for systematically studying EM enhancement mechanisms for surface-enhanced vibrational spectroscopy. This is due to the wide range of dust materials with surface modes in frequency regimes ranging from the visible to the IR, that could in principle be used.

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