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Optical spectroscopy for single-molecules near a microstructure at varying substrate temperatures

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Abstract

The spectroscopic characteristics for a single-molecule in the vicinity of a metallic structure are studied as a function of the substrate temperature via a phenomenological model. Emphasis is put on the role of the surface plasmon excitation of the structure and its variation with the change of temperature. From the emission characteristics such as the decay rates and frequency-shifts of the molecule, it is concluded that such effects should be accounted for in certain recent experiments in single-molecule imaging using metallic tips. In addition, from the photoabsorption line-shape of the molecule, it is speculated that certain surface-enhanced photochemical reactions under realistic catalytic conditions may indeed be feasible, provided that other complications to the surface processes can be put under control during the variation of the substrate temperature. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

It has been well-known for over 50 years that the emission characteristics of free molecules can be modified drastically in the vicinity of a surface or microstructure [1]. For example, the lifetimes, emission frequencies, and absorption line-shapes for a molecule in the vicinity of a metallic surface are all very different from those for one in the gas phase. In particular, the recent success in the imaging of single-molecules using metallic or metal-coated tips such as that in SNOM, has confirmed the strong dependence of these emission characteristics on the relative position between the molecule and the tip [2].

Since the 1970s, there has been many theoretical works devoted to the understanding of the above phenomena. One of the simpler and effective approaches is the classical phenomenological model using electromagnetic theory to account for the energy transfer between the molecule and the surface or a microstructure [3]. This has been applied successfully in a previous investigation of these effects at a SNOM tip to account for apparently conflicting observations between different

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experimental groups [2]. However, in all these previous modeling works [2,3], the metallic substrate or tip is assumed to remain at constant (ambient) temperature so that the excitation of the surface plasmons is characterized completely by the dispersion and geometry of the structure. On the other hand, it is an established fact that these tips many times get heated up during the imaging process, due to the dissipation of the light source in the metallic structure [4]. Hence it would be of interest to study how these "tip-induced" effects will vary with the change of temperature of the environment [5]. In addition, it has also been proposed in the literature to use this single-molecule imaging technique as a probe of the environment in the immediate vicinity of the molecule [6]. Our following study will also shed some light on this issue, as regard to the possibility of using this technique as a probe for local temperature variations.

Besides tip-induced fluorescence from single-molecules, our present work is also motivated by the exploration of the feasibility of achieving surface-enhanced photochemistry under realistic catalytic conditions such as elevated surface temperatures. Since the discovery of the surface-enhanced Raman scattering (SERS) from rough noble metal substrates, it has been known that the same mechanism based on resonant excitation of the surface plasmon (SP) at the metallic structure can lead to enhancement of other optical processes such as photochemical reactions [7]. Moreover, to our knowledge, all these previous studies so far have been limited to reactions taking place at room temperature on the substrate surface. Since it has been mentioned that in some cases certain surface catalytic reactions may be facilitated at elevated temperatures [8], it is thus intriguing to study what will happen to these processes as the temperature of the substrate surface varies. In particular, due to the damping of the SP excitation at high temperatures, one would like to investigate whether such enhanced photochemistry can still be sustained as the substrate temperature rises. To this end, we will follow the previous works in the literature [9] to model the photoabsorption of the admolecule near a microstructure and study the variation of it with the substrate temperature.

2. Model

Let us consider a fluorescing molecule (modeled as a point dipole in free space) in the vicinity of a microstructure (modeled as a sphere), and for simplicity, we assume the dipole to be oriented along a radial direction and at a distance d from the center of the sphere. Then according to the phenomenological model using classical electrodynamics, the modified decay rate (inverse lifetime) and the shift in emission frequency of the admolecule can be expressed as [1,3,9]:

$$\gamma = \gamma_{\mathrm{M}}^{0} + \alpha_{\mathrm{M}} \frac{(\omega_{\mathrm{M}})^2}{\omega} \sum_{n=1}^{\infty} \left[\mathrm{Im}\alpha_n \frac{(n+1)^2}{d^{2(n+2)}} \right], \tag{1}$$

and

$$\Delta\omega = \omega_{\mathrm{M}} \left(1 - \alpha_{\mathrm{M}} \sum_{n=1}^{\infty} \left[\mathrm{Re}\alpha_n \frac{(n+1)^2}{d^{2(n+2)}} \right] \right)^{1/2} - \omega_{\mathrm{M}}, \tag{2}$$

where α_n is the nth-pole polarizability of the sphere given by

$$\alpha_n = \frac{n(\varepsilon - 1)}{n(\varepsilon + 1) + 1} a^{2n+1}. \tag{3}$$

In the above equations, γ_{M}^{0}, ω_{M} and α_{M} are the decay rate, emission frequency, and molecular polarizability of the free molecule; a is the radius and $\varepsilon = \varepsilon(\omega)$ is the dielectric function of the metal sphere, respectively; and ω is the driving frequency of the external light source. Note that for a free classical oscillating dipole and for molecules with a quantum yield equal to q, we have $\gamma_{\mathrm{M}}^{0} = \gamma_0/q$, where the free radiative decay rate is given in terms of the polarizability as $\gamma_0 = \frac{2}{3}(\omega_{\mathrm{M}}^4/c^3)\alpha_{\mathrm{M}}$ and $\alpha_{\mathrm{M}} = e^2/m\omega_{\mathrm{M}}^2$. In the above expressions, e and m are the electronic charge and mass, respectively, and c is the speed of light. In the case when the tip-induced lifetimes are measured via a pulsed-excitation of the molecule, one simply sets $\omega = \omega_{\mathrm{M}}$ in the above equations. Note that both the long wavelength limit and the dipole approximation for the response of the sphere have been assumed in the above equations. We have therefore assumed that both a and d are small compared to the excitation wavelength of the source.

To model the photoabsorption of the molecule at the surface structure, we follow a simple phenomenological model due first to Nitzan and collaborators [9]. This model empolys a Lorentzian lineshape to simulate the photoabsorption or fast (direct) photodissociation of a molecule, with the surface effects on the admolecule entering via the Lorentzian parameters (level width and resonance frequency) and the field enhancement factor. Aside from the fact that photoabsorption is the most fundamental process involved in any photochemical reactions for physisorbed molecules, our choice of the study of this process is also motivated from the very recent confirmation of the SP-enhanced optical absorption of various molecules adsorbed on a silver film [10]. Thus, in the absence of the surface, the photoabsorption cross-section can be expressed as [9]:

$$\sigma_0 = 2\pi\alpha_{\mathrm{M}}(\omega_{\mathrm{M}}^2/c)\frac{\gamma_{\mathrm{M}}^0}{(\omega-\omega_{\mathrm{M}})^2+(\gamma_{\mathrm{M}}^0/2)^2}. \tag{4}$$

In the presence of the surface structure, Eq. (4) is modified to take the form

$$\sigma = 2\pi\alpha_{\mathrm{M}}(\omega_{\mathrm{M}}^2/c)\frac{\gamma}{(\omega-\omega_{\mathrm{M}}-\Delta\omega)^2+(\gamma/2)^2}S(E), \tag{5}$$

where $S(E)$ is the surface field enhancement factor, $\Delta\omega$ and γ are the structure-induced frequency-shift and decay rate for the molecule given in Eqs. (1) and (2), respectively. Note that (5) is no longer Lorentzian in form since all the factors $S(E)$, $\Delta\omega$ and γ are functions of the driving frequency in general [9]. For the above radial dipole, $S(E)$ can be obtained in the long wavelength limit in the following form [9]:

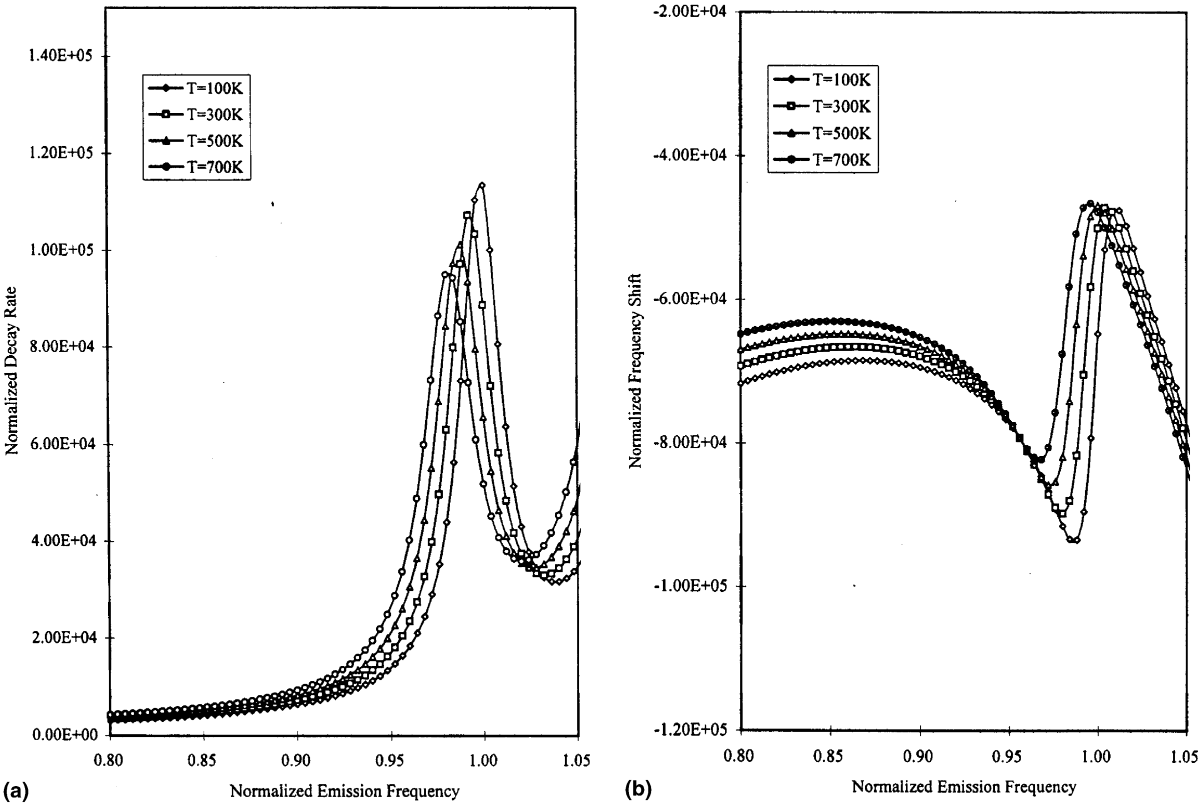

Fig. 1. Emission characteristics of a molecule at a silver sphere as a function of normalized emission frequency and temperature of the sphere: (a) molecular decay rates and (b) shifts in emission frequency, both normalized to the free decay rate of the molecule. The molecule-sphere distance is fixed at 5 nm.

$$S(E) = \left| 1 + \frac{2}{d^3} \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right) a^3 \right|^2. \tag{6}$$

As has been pointed out in previous works, the SP enhancement of σ in (5) originates from the resonance condition $\varepsilon + 2 = 0$ in Eq. (6) above. Hence, in order to study the effect of the substrate temperature on the emission characteristics [Eqs. (1) and (2)] and on the SP enhancement of the photoabsorption [Eq. (5)] for the molecule, we have to introduce a temperature-dependent model for the dielectric function ε. To this end, we have followed our previous approach to use the simple Drude model for the substrate metal [11]. Hence we have

$$\varepsilon(\omega, T) = 1 - \frac{\omega_p^2(T)}{\omega[\omega + i\omega_c(T)]}, \tag{7}$$

where both the plasmon and collision frequencies are modeled as temperature-dependent: with the dependence for the former coming mainly from volumetric effect through the free electron density, and that for the later from electron–phonon and electron–electron collision mechanisms. Details for the modeling of these frequencies can be referred to our previous works [11]. We have to remark that besides the application of this model to the study of SP sensors as was done in [11], we have also applied the same model to SERS previously [12] in which the enhancement ratio was calculated as a function of substrate temperature. Subsequent experiments have been carried out on silver island films and qualitative accuracy of our model has been established in the literature [13].

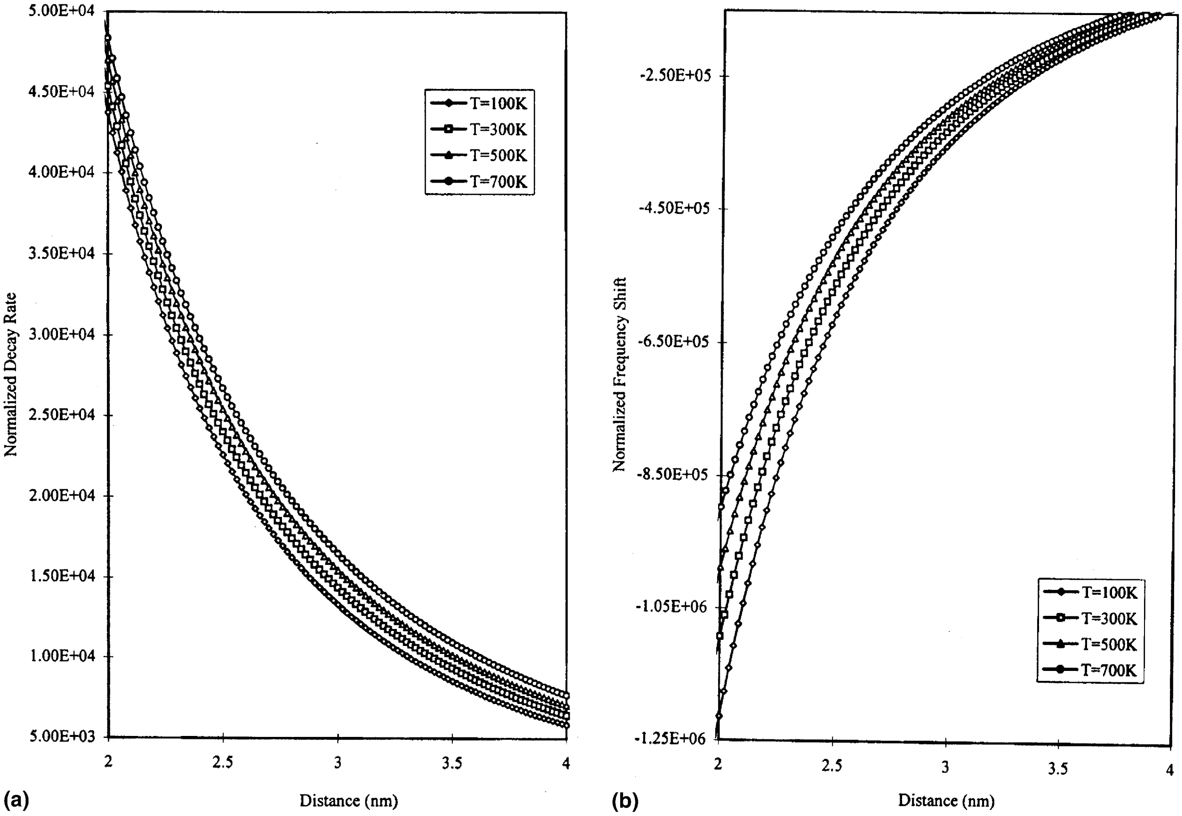

Fig. 2. Similar to Fig. 1, with the quantities plotted against the molecule-sphere distance for different temperatures at fixed emission frequency $\omega_M = 0.8\omega_{SP}^0$.

3. Numerical results and discussion

To illustrate the possible effects from our model, we have considered a two-level molecular system interacting with a silver sphere. For fluorescence modeling, we assume the quantum yield is unity ($q = 1$) and for modeling of photoabsorption, we will assume a very small value for the quantum yield in the decay rate expression in Eq. (1). For the sphere, we have ω_{SP}^0 as the surface plasmon resonance frequency and $a = 20$ nm the radius, both at room temperature ($T = 300$ K). All the parameters for the modeling of the temperature dependence of the Drude model can be found in our previous works [11,12], and ω_{SP}^0 obtained from the Drude model turns out to be somewhat higher than realistic values ($\omega_{\mathrm{SP}}^0 \sim 5.2$ eV for Ag from the Drude model). We have also accounted for the expansion of the sphere.

Fig. 1 shows the spectral variation (at fixed distance $d - a = 5$ nm) of the decay rates and frequency-shifts as a function of the emission frequency of the molecule which is normalized to ω_{SP}^0. The rates and shifts are also normalized with respect to γ_{M}^0 ($= \gamma_0$ for $q = 1$). The results in Fig. 1(a) show that the structure-induced decay peaks at the surface plasmon resonance frequency of the sphere, with peak values decreased and slightly red-shifted as the temperature increases. The latter is due to the fact that the surface plasmon frequency decreases as the electronic density decreases at high temperatures. Fig. 1(b) shows the frequency-shifts of the molecule (normalized to γ_{M}^0) as a function of normalized emission frequency. These typical "anomalous dispersion curves" are seen to be also slightly red-shifted, but with their "peak values" staying relatively constant, as the temperature of the structure increases.

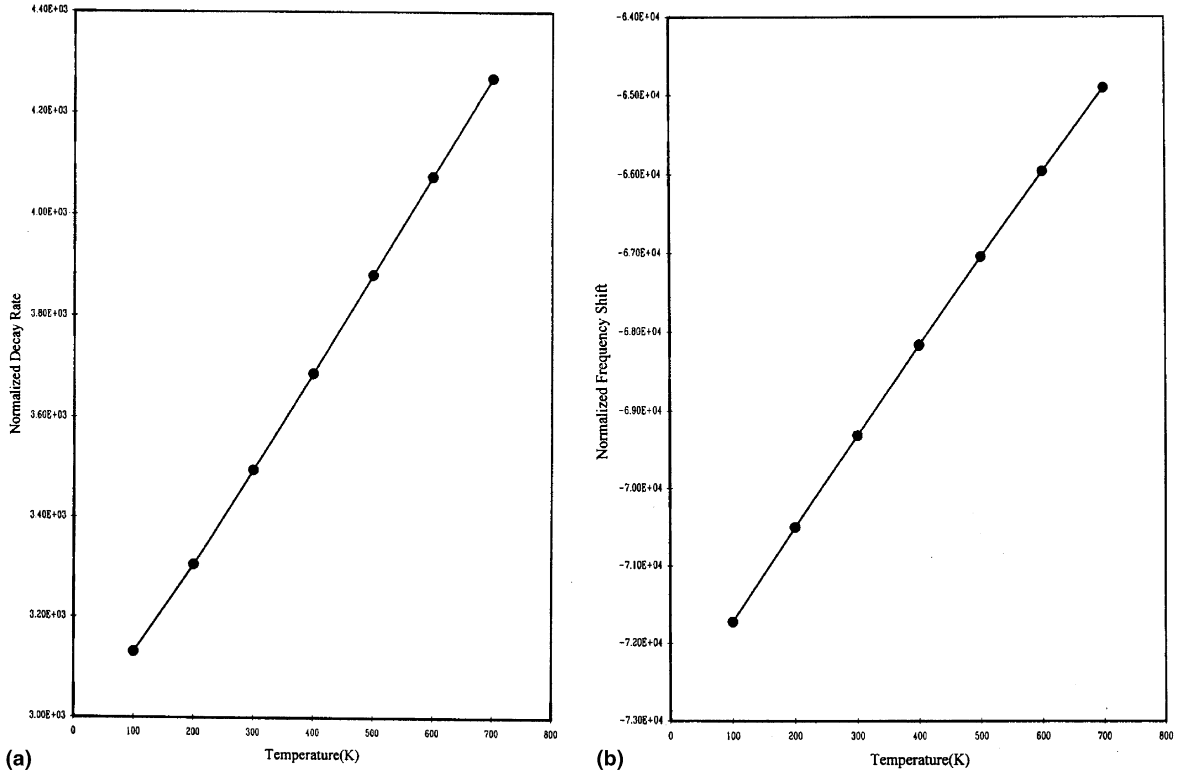

Fig. 3. Variation of the emission characteristics with temperature of the sphere at fixed distance (5 nm) and emission frequency (at 0.8 ω_{SP}^0).

Fig. 2 shows the variation of the same rates and shifts as a function of molecule-structure distance at a fixed emission frequency of $\omega_M = 0.8\omega^0_{SP}$. As expected, the structure-induced effects become less pronounced as the molecule is moved farther away from the sphere. As the temperature increases, the decay rate increases and the emission frequency becomes less red-shifted, while both assume a slightly slower rate of change with the increase of the molecule-sphere distance. Fig. 3 shows these results more explicitly for a fixed distance $(d - a)$ at 5 nm and ω_M at $0.8\omega^0_{SP}$, and the resulting changes are almost linear in temperature. Note that these behaviors can change completely in an opposite way if one looks at an emission frequency above the surface plasmon resonance frequency of the metal as can be observed from Fig. 1. However, for most electronic spectroscopy of molecules, the transition frequencies are well below the plasmon frequencies of the metal so that our results in Figs. 2 and 3 will be of relevance to recent experiments involved in tip-imaging of molecules [2,14]. In particular, one sees from Fig. 3 that a change of molecule lifetime by about 3% and the emission frequency shift by about 2% can take place for a modest change of temperature from 300 to 400 K. As reported in the literature, such temperature change of the tip is not uncommon in the SNOM experiments [4].

Fig. 4 shows the photoabsorption spectrum at a distance $(d - a)$ fixed at 5 nm and a very small value for the quantum yield $(q = 5 \times 10^{-8})$. As it is clear, the previously well-known "double-peak" feature showing, respectively, the molecular and surface plasmon resonance [9], is reproduced with the sensitivity to temperature changes clearly shown. It is also seen that the same red shifts in the resonance of the cross-section at the surface plasmon frequency occurs as occurred in Fig. 1.

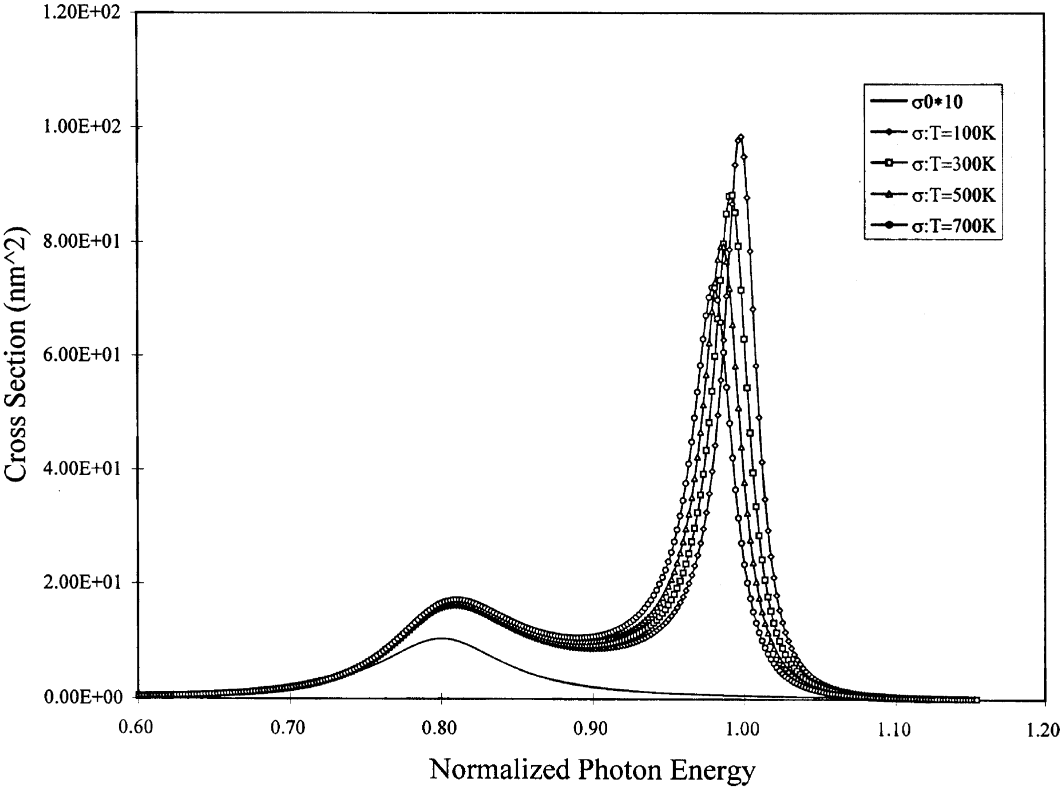

Fig. 4. Photoabsorption cross-section line-shapes for the molecule both without (σ_0) and with (σ) the presence of the metal sphere, at varying temperatures of the sphere.

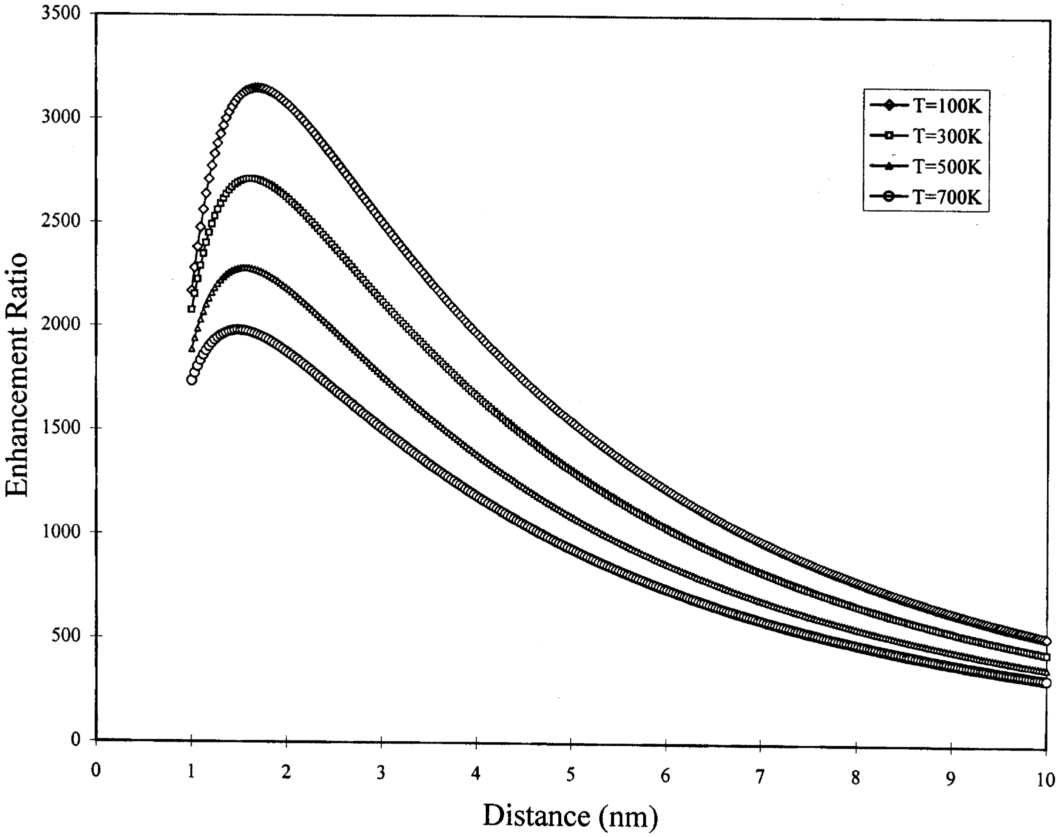

Fig. 5. Enhancement ratio as a function of molecule-surface distance at various substrate temperatures. The photon frequency is set at the resonant SP frequency for each particular temperature (see Fig. 4).

Fig. 5 plots the enhancement ratio ($R \equiv \sigma/\sigma_0$) as a function of molecule-surface distance ($d - a$) at various substrate temperatures. The photon frequency is set at the value for surface plasmon resonance at that particular temperature (see Fig. 4). It is seen that while enhanced photoabsorption is achieved for all the conditions explored, in spite of the fact that the SP is strongly damped at high temperatures, there exists an optimal distance (of about 2 nm) at which the absorption rate becomes maximum. This latter feature has been well-known since the early days of studies in surface photochemistry. As was understood then, this optimal molecule-surface distance arises from the competition between the two mechanisms: surface-enhanced field and surface-induced decay for the admolecule [9]. We have thus shown here that these two competing factors prevail at high temperatures, giving rise to a roughly constant optimal distance. In addition, the modeling seems to indicate also that such SP-enhanced photoabsorption may be made more efficient by cooling the surface to lower temperatures (e.g., $T = 100$ K). We believe this last result should have some validity since it was established that the Drude model should be valid for temperatures down to about $T = 100$ K [15].

4. Conclusion

We have hence demonstrated, through a simple phenomenological modeling, the possible effects of temperature variation on the tip-induced emission characteristics from single-molecules as probed in some of the recent SNOM experiments. Although our numerical results are limited by the limitations of the Drude model [16], we believe that these effects should be accounted for in these imaging experiments using metallic tips.

In addition, we have also demonstrated the feasibility of achieving SP enhanced photoabsorption at high substrate temperatures. This opens up the possibility of performing certain surface-enhanced photochemical reactions under realistic catalytic conditions [8]. In reality, of course, this possibility is limited to systems with desorption rate not much affected by the increase of the substrate temperature. In any case, we believe that a systematic experimental study on the effects revealed in our present model can be of interest, just as the previous ones which studied such effects on SERS at substrate temperatures both above [8] and below [13] that at $T = 300$ K.

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