Surface Distortions of Asymmetric Line Profiles

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Fano line profiles for a molecular system above a metallic grating surface are investigated within a simple model. A double-peak feature as well as a shift of the profile window are observed due to the surface plasmon mode.
SURFACE DISTORTIONS OF ASYMMETRIC LINE PROFILES

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Abstract

Distortions of asymmetric Fano profiles for a molecular system above a metallic grating surface are investigated within a simple model. A double-peak feature as well as a shift of the profile window are observed due to the surface plasmon mode.
I. Introduction

Recently, there has been great interest in the study of surface effects on photoabsorption and photodesorption line shapes for an adspecies on a surface. This includes the treatment of vibration and vibration-rotation spectra of chemisorbed and physisorbed molecules. In addition, line profiles involving electronic transitions leading to direct photodissociation of a molecule physisorbed on a rough metallic surface have also been studied for the cases of a metallic spheroid and a shallow sinusoidal grating as the substrate. Furthermore, the distortions of the spectra of a dipole on a randomly rough metallic surface have been studied in a fully quantum mechanical approach. Aside from adsorption spectra, the line shape of the photodesorption yield has also been examined for physisorbed molecules. However, in most of the previous investigations, the line profile for the free molecule (i.e., in the absence of the surface) has almost always been assumed to be symmetric, often of a Lorentzian type, so that asymmetric distortions are brought about by the presence of the surface. One very interesting example is the Langreth line shape which describes the distortion of a vibrational Lorentzian towards a Fano profile, due to energy transfer between the molecule and the surface via the electron-hole-pair mechanism. Nevertheless, among these surface distortion phenomena there remains one case uninvestigated, which is that when the line profile for the free molecule case is already asymmetric in nature. This would include, for example, processes like autoionization or predissociation in molecular systems. It is the purpose of the present letter to present a model study of the surface distortions of such "intrinsic" asymmetric profiles. Specifically, we shall study the dipole
photoabsorption spectra on top of a metallic grating, which is considered as a prototype of rough surfaces.

II. Theory

Instead of calculating exactly the line shape function in a quantum mechanical manner, we shall simulate the absorption process by a classical mechanical model and then look for relative profile distortions due to surface effects. This is in the same spirit of the previous work by our group\textsuperscript{7} and others\textsuperscript{6} in which the free Lorentzian profile for direct photodissociation processes is simulated in the context of the "driven damped oscillator model", and then profile distortions are found by introducing the surface effects into the process via terms including the external driving field and the damping constant.

To describe a "free asymmetric profile", we adopt the mechanical model recently proposed by Sorbello\textsuperscript{4} to describe the Fano effect in atomic physics.\textsuperscript{11} The model consists of the coupling of a normal mode ($\omega_o$) to a lossy broad-band system such as a viscous bath, with both the oscillator and the bath being described by one degree of freedom. The line shape function obtained in this model can be reexpressed\textsuperscript{12} in the form

$$I_o(\omega) = \frac{(q + \epsilon_o)^2}{1 + \epsilon_o^2} \sigma_o(\omega),$$

where $q$ is the asymmetric profile index depending on the ratio of the driving force on the oscillator to that on the bath, and $\sigma_o(\omega)$ is the background intensity due to direct excitation of the bath. In case of actual molecular processes, $q$ is defined as the ratio of the transition matrix elements from the initial state to two states whose linear combination gives the final state of the system,\textsuperscript{11,13} and $\sigma_o(\omega)$ corresponds
to the cross section for direct excitation of the continuum. The reduced
ergy variable $\varepsilon_o$ in Eq. (1) is expressed as

$$
\varepsilon_o = \frac{2(\omega - \omega_o - \Delta \omega_o)}{\gamma_o},
$$

(2)

where $\Delta \omega_o$ and $\gamma_o$ are the level shift and decay rate of the system,
respectively. In general, $\Delta \omega_o << \omega_o$, and hence

$$
\varepsilon_o \approx \frac{2\Delta \omega}{\gamma_o}
$$

(3)

with $\Delta \omega \equiv \omega - \omega_o$.

To investigate the distortions of $I_o(\omega)$ due to the presence of a rough
metallic surface, we shall consider the oscillator as a point dipole
oriented perpendicularly on top of a shallow sinusoidal grating, a case
which we have formulated before for a Lorentzian $I_o(\omega)$.\textsuperscript{7} Analogously, we
have the surface line shape function expressed as

$$
I(\omega) = \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} |\hat{n}_\mu \cdot [1 + A] \cdot \hat{n}|^2 \sigma(\omega),
$$

(4)

where quantities without the subscript 'o' refers to those at the surface,
and $\varepsilon$ is now defined as

$$
\varepsilon = \frac{2\Delta \omega}{\gamma}.
$$

(5)

We have in this approach neglected the surface effects on $q$ and $\omega_o$; this is
justified since, for the former, the effects enter into the ratio of two
transition matrix elements which may be regarded as approximately cancelling
each other, and for the latter such effects have been found to be small.\textsuperscript{14}
In this way, surface effects will only enter via the decay rate $\gamma$ in Eq. (5)
and the field enhancement factor $A$ in Eq. (4), the latter including both of the Fresnel reflected and the surface plasmon fields. $\hat{n}_\mu$ and $\hat{n}$ in Eq. (4) are the unit vectors of the molecular dipole and the incident field, respectively. For a dipole located at $(0,0,d)$, it has been found that

$$|\hat{n}_\mu \cdot [1 + A] \cdot \hat{n}|^2 = |1 + \Re e^{-k_z d} + \Se - k_z \Gamma g |^2 \sin^2 \theta,$$

(6)

where $\theta$ is the angle of incidence of the laser light, and the quantities $R$, $S$, $k_z$ and $\Gamma$ are defined as in Ref. 7. Furthermore, the surface-induced molecular decay rate can be expressed as

$$\gamma = 1 + \frac{3}{2} \frac{\alpha}{k^3} \Im G^R (1 + \frac{\Im G^R}{\Im G^F}),$$

(7)

where again all symbols are the same as in Ref. 7.

With the results in Eqs. (6) and (7) substituted into Eqs. (4) and (5), we can calculate the line profile for a molecule on top of a metallic grating by assuming some reasonable form for $\sigma_0(\omega)$. Within the present model study, we have considered the following three different cases with the surface always taken to be a sinusoidal silver grating whose dielectric constant as a function of photon energy is available in a numerically-fitted form.

Case (i) $\sigma_0(\omega) = \sigma(\omega) = \text{constant}$.

In this case, $I_0(\omega)$ may simulate certain atomic autoionization processes (e.g., the photoabsorption line shape of helium in the neighborhood of the first $^1P^0$ resonance). $^{11,15}$ In Fig. 1, we show both the line shapes $I_0(\omega)$ and $I(\omega)$ for some hypothetical profile constants (see the figure caption). We see that the frequency corresponding to the zero of the
absorption cross section shifts towards a larger value. This is because \( q < 0 \) in this case and \( \gamma > \gamma_o \) as in Eq. (7).

**Case (ii)** \( \sigma_o(\omega) = \sigma(\omega) = 1/\omega^2 \).

In this case, \( I_o(\omega) \) simulates a molecular predissociation process (e.g., the predissociation of the \( D^1\Pi_u^+ \) levels by the \( B^1\Sigma_u^+ \) continuum in the photodissociation experiment of hydrogen molecules\(^16\)). The result is shown in Fig. 2, where we see that the 'window' at the steep edge at the low frequency end of the original profile is broadened due to the enhancement effect by the surface plasmon field. At the high frequency end of the distorted profile, the surface plasmon resonance leads to a new window.

**Case (iii)** \( \sigma_o(\omega) = \frac{\gamma_o}{(\omega - \omega_o)^2 + \gamma_o^2/4} \).

For the above Lorentzian, \( \sigma(\omega) \neq \sigma_o(\omega) \) since \( \gamma_o \) is replaced by \( \gamma \) in Eq. (7). The effects of the surface distortion of the profile \( I_o(\omega) \) are similar to case (ii) (Fig. 3), except that the original window is not broadened as much.

**III. Results and Discussion**

In all cases (i) to (iii), the dipole is fixed at a distance of 500 Å from the grating, which has a spatial period of 8000 Å and an amplitude-to-period ratio of approximately \( 10^{-2} \). In addition, the angle of incidence is fixed at 0.6 rad and the surface plasmon resonance occurs at about 2.9 eV photon energy. We observe that the "double peak" feature\(^6\) appears in all cases, corresponding to the resonance of the molecular system and that of the surface plasmon, respectively. Furthermore, a surface enhancement effect is in general observed, implying that enhanced molecular photopredissociation may also be possible, provided the molecule is not located
too close to the surface and the resonant plasmon field decays very slowly in the direction perpendicular to the surface. 7, 17

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References

12. We have changed some of Sorbello's original notations from Ref. 4. Here we denote every quantity which refers to the free molecule case in the absence of the surface with the subscript 'o'.
Figure Captions

1. Distortion of the Fano profile with \( \sigma_0(\omega) = \text{constant} \). The profile
   constants are: \( \gamma_0 = 5 \times 10^2, \omega_0 = 1.6 \times 10^4 \) and \( q = -2.65 \). Note that
   the scales for \( I_0(\omega) \) and \( I(\omega) \) are different. The y-axis quantities are
   in arbitrary units for all three figures.

2. Distortion of the Fano profile with \( \sigma_0(\omega) = 1/\omega^2 \). The profile constants
   are: \( \gamma_0 = 4 \times 10^3, \omega_0 = 1.17 \times 10^4 \) and \( q = +3.0 \).

3. Distortion of the Fano profile with a Lorentzian \( \sigma_0(\omega) \). The profile
   constants are the same as in Fig. 2.
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