Optical Properties of Admolecules near a Phase-Conjugate Mirror

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위상 공액 거울에 흡착된 분자의 광학적 성질

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Abstract – The induced linewidth, frequency shift and absorption spectrum for a molecular dipole in the vicinity of a phase-conjugate mirror have been investigated within a classical phenomenological model, with particular reference to the technique of optical phase conjugation by a surface. While the shifts and the widths show similar characteristics as those obtained recently by Bochove who considered the problem within the context of four-wave mixing, the results obtained in the present model can be defined uniquely with the possibility of an infinite lifetime for the excited admolecule. Furthermore, the absorption lineshape obtained here some interesting features which depend on both the magnitude and the phase of the complex reflectivity of the mirror.

요   약 – 위상 공액 거울에 흡착된 분자 쌍극자의 흡수 스펙트럼에서 선폭 변형과 주파수 이동들에 대하여 위상 공액 기술을 이용하여 고전적인 현상학적 모델로 연구하였다. 본 연구 결과, 선폭 변형과 주파수 이동들은 최근 네가지 파의 혼합으로 이 문제를 다룬 Bochove의 결과와 유사한 성질들을 보여주는 동시에 공액 위상 거울에 흡착된 흥분된 분자가 무한대의 lifetime을 가질수 있는 가능성을 보여주었다. 또한 여기서 얻어진 흡수 스펙트럼의 모양은 거울의 복소수 반사계수의 크기와 위상 모두에 의존한다는 것을 알았다.

1. Introduction

In the past two decays, there has been a large amount of effort in the study of molecular spectroscopy in the vicinity of an ordinary surface with linear optical properties. Both experimental and theoretical investigations have been devoted to various possible substrate materials including metallic and semiconducting surfaces of various morphologies, which can be flat or rough[1]. Among these investigations, the spectroscopic properties of prime interest are the decay rate, frequency shift and absorption lineshape for the admolecules. The following general conclusions have been reached; (1) the frequency shifts induced by the presence of the surface are generally negligible; (2) the decay rate is in general enhanced with large dependencies on the orientation and location of the molecule with respect to the surface; and (3) the absorption lineshape is very sensitive to the interaction between the admolecule and the surface[1-4]. The recently discovered generation of phase-conjugate fields has attracted much attention for the past ten years[5,6]. The mechanisms of production and possible applications of such fields have been widly investigated[7]. It appears that molecular spectroscopy on top of such a phase-conjugate mirror (PCM) has yet to be explored. This will serve as one interesting example of how the spectroscopic properties of the admolecules can be affected due

to the nonlinear optical properties of the substrate surface.

The first attempt in this direction seems to be the communication published by Agarwal[8] in 1982, in which he calculated the decay rate of a molecule near a PCM using a classical model and concluded that the induced decay rate (γ) does not depend on the orientation and distance of the molecule with respect to the PCM. However, the results are very sensitive to both the magnitude and the phase of the complex reflectivity (η) of the PCM. In particular, γ can become negative for $|\eta| > 1$, which is feasible due to nonlinear interaction[6]. Very recently, Bochove[9] reanalyzed the problem by both the classical and quantum approaches by taking into account both induced decay rate and the frequency shift ($\triangle\omega$) of the molecule, while a-dopting four-wave mixing (FWM) as the phase conjugate mechanism for such spectroscopic studies. The results for γ obtained in his work are essentially consistent with those of Agarwal, except that there is not dependence on the phase of η.

One main problem in making this kind of PCM-molecular spectroscopy practical is the fact that the intensities from molecular emissions are usually too weak to excite nonlinear interactions which are essential in producing a phase-conjugated (PC) field. Hence a class of PC methods, such as simulated Brillouin scattering, which requires an intense probe field cannot be applied. Fortunately, there are at least two PC mechanisms, namely, FWM and OPCS (optical phase conjugation by a surface), which do not require a strong incident field since η in these two mechanisms depend on the pump fields, which of course can be made as intense as desired irrespect to the molecular emissions[6]. Furthermore, these two mechanisms can provide a backward-going conjugated wave which is necessary for the study of the induced spectroscopic quantities. Since the FWM technique has already been explored by Bochove in the context of this problem[9], we shall

pay particular attention to the OPCS technique in our present work. We shall present our model in Sec. II, where we shall calculate both the induced γ and $\triangle\omega$ as well as the absorption spectrum. Some numerical studies and conclusions will then be presented in Sec. III and IV, respectively. For the reason of simplicity, we shall adopt the classical phenomenological approach throughout the work[8,9].

2. Theoretical Model

The OPCS technique, first proposed by Zel'dovich et al[10] and then verified experimentally [11], involves the interference of a strong pump field (E_0) and a probe field (E_d) (which may be of weak intensity) on a nonlinear surface whose reflectivity ρ is a function of the field intensity (I). With the two fields coherent with each other, it can then be shown that aside from the ordinary Fresnel fields, a backward-going conjugated field (with respect to E_d) is produced which may be expressed in the form[12]

$$E_c(r,t) = E_d(r,-t), \qquad (1)$$

where η is the complex reflectivity of the PCM and is given by[6]

$$\eta^* = (\partial\rho / \partial I)_{I_0} E_0^2 \qquad (2)$$

In the following, we shall apply these results to study our problem of PCM-molecular spectroscopy via the OPCS technique. For simplicity, let us model our molecule as a point dipole (located at r_0) satisfying the driven-damped oscillator model[2,4]

$$\ddot{\mu}(t) + \gamma_0\dot{\mu}(t) + \omega_0^2(t) = \alpha [E_c(r_0, t-\tau) + E_{ext}(r_0,t)] \qquad (3)$$

where ω_0 and γ_0 are the natural frequency and width of the molecule, τ is the retardation time for the molecular emission to return to its own site

upon reflection from the PCM, and $E_{ext}(r, t)$ is the continuously driving external field. Furthermore, γ_0 can be written as

$$\gamma_0 = \gamma_R/q \tag{4}$$

with γ_R being the radiative decay rate and q the intrinsic quantum yield of the molecular system. α in Eq. (3) is given by e^2/m, where e is the electronic charge and m the effective mass of the dipole. Hence from Eq. (1), Eq. (3) becomes

$$\ddot{\mu}(t) + \gamma_0\dot{\mu}(t) + \omega_0^2\mu(t) = \alpha\ [\eta\ E_d(r_0,\ -t+\tau) + E_{ext}(r_0,\ t)] \tag{5}$$

Now if we let E_d be the dipole field, as usually done for cases with ordinary surface[2, 4], it is not difficult to see that an infinity arises since we are looking at the dipole field at the location of its own source. This infinity (due to the self-field) is of course erroreous, since in the classical modeling γ_0 is an input finite parameter whose origin is also connected to the self-field. Hence, to treat γ_0 and E_d on the same footing, we adopt Bochove's ansatz to express $E_d(t)$ in the form[6]

$$E_d(t) = -\gamma_R\dot{\mu}(t) \tag{6}$$

Equations (5) and (6) then lead to the final expression for our model in the form

$$\ddot{\mu}(t) + \gamma_0\dot{\mu}(t) + \omega_0^2\mu(t) + \alpha\eta\ \gamma_R\dot{\mu}(-t+\tau) = \alpha\ E_{ext}(t) \tag{7}$$

From now on, we shall assume τ to be negligible[6], which is justifiable if the induced decay (γ) we find satisfies $\gamma\tau << 1$[2, 4]

In the following, we shall analyze the spectroscopic properties implied by the model in Eq. (7) and shall further divide into two cases:

Case (i): $E_{ext} = 0$

This corresponds to the situation of a fluorescence experiment in which the molecules are excited by a short pulse laser at $t = 0$ and the de-caying intensity is monitored to obtain the information on the induced level-shift and broadening[13]. We solve the equation by assuming a form for $\mu(t)$ as

$$\mu(t) = A\ exp(i\omega t) + B\ exp(-i\omega t) \tag{8}$$

where A and B are constants and $\omega = \omega_0 + \triangle\omega + i\gamma/2$ with $\triangle\omega$ and γ being the PCM-induced level shift and broadening, respectively. Substituting Eq. (8) into (7) (with $E_{ext} = 0$), we obtain a secular equation of the form

$$(\omega^2 - \omega_0^2) + \omega^2\gamma_0 - \omega^2\eta^2\gamma_R^2 = 0 \tag{9}$$

Solving Eq. (9), we finally obtain

$$\triangle\omega = [(ReQ + |Q|)/2]^{1/2} - \omega_0 \tag{10}$$

$$\gamma = 2\ ImQ/[2(ReQ + |Q|)]^{1/2} \tag{11}$$

where

$$Q = \omega_0^2 + (\eta^2\gamma_R^2 - \gamma_0^2)/2 \pm [(\eta^2\gamma_R^2 - \gamma_0^2)\ \ (\eta^2\gamma_R^2 - \gamma_0^2 + 4\omega_0^2)]^{1/2}/2 \tag{12}$$

Case (ii): $E_{ext} \neq 0$

Here we assume that an external field is continuously driving the molecules upon a PCM, and we want to study the absorption spectrum of thses molecules. For simplicity, we assume grazing incident (i.e., E_{ext} is traveling parallel to the surface of the PCM), so that the problem will not be complicated by other reflected fileds produced by E_{ext} on the PCM. Assuming

$$xt = E_0\ exp(i\omega t) \tag{13}$$

and

$$\mu(t) = \mu_1(\omega)\ exp(i\omega t) + \mu_2(\omega)\ exp(-i\omega t) \tag{14}$$

we finally obtain (for $\mu_1\ ||\ \mu_2\ ||\ E_{ext}$)

$$\mu_1(\omega) = \alpha\ E_0(\omega_0^2 - \omega^2 - i\omega\gamma_0)\ /\ [((\omega_0^2 - \omega^2)^2 + \omega^2(\gamma_0^2 - \eta^2\gamma_R^2)] \tag{15}$$

$$\mu_2(\omega) = -i\omega\eta\gamma_R\alpha\ E_0\ /\ [((\omega_0^2 - \omega^2)^2 + \omega^2(\gamma_0^2 - \eta^2\gamma_R^2)] \tag{16}$$

To calculate the absorption profile $I(\omega)$, we have to calculate the time-averaged energy absorbed per unit time by the molecule and then divide it by the incident flux of the external field[21]. This then yields

$$I(\omega) = 8\pi < \mathrm{Re}\dot{\mu}(t) \; \mathrm{Re}E_{ext}(t) >_{time} / c \, | \, E_{ext} |^2 = 4\pi(\omega / c) \, [f_2(\omega) - f_1(\omega)] \tag{17}$$

where c is the speed of light and the function f_1, f_2 are given by

$$f_1(\omega) = \mathrm{Im}[\mu_1(\omega) / E_0] \tag{18}$$

$$f_2(\omega) = \mathrm{Im}[\mu_2(\omega) / E_0] \tag{19}$$

For the case where η is real and $\eta \leq 1$, it is not difficult to show that $I(\omega)$ reduces the usual Lorentzian form with the width modified by the factor $\eta\gamma_R$. For other cases where η is complex, I(ω) is in general distorted from the Lorentzian profile depending on the phase of η, as we shall see below.

3. Numerical Results

We have performed numerical studies for the two cases by assuming a Lorentzian lineshape for the free molecule (in absence of a PCM) with almost unity intrinsic quantum yield, so that $\gamma_R \cong \gamma_0$. Figure 1 shows the results for $\triangle\omega$ and γ (Eqs. (10) and (11)) for the case where η is real, where we have chosen $\gamma_0 = 0.01 \; \omega_0$. We observe that there are two branches of solution for both $\triangle\omega$ and γ which arise from the two sign ($\pm$) in the expression for Q (Eq. (12)). A similar situation accurs in Bochove's FWM model[9]. However, in our present model we can make the physical solution unique by imposing the condition $\gamma \to \gamma_0$ as $\eta \to 0$. In doing so, we find that only the positive-branch solution is acceptable, and hence we conclude that only broadened and blue-shifted lines can occur in this model, in contrast to the case with Bochove's model. Another interesting feature is that for real
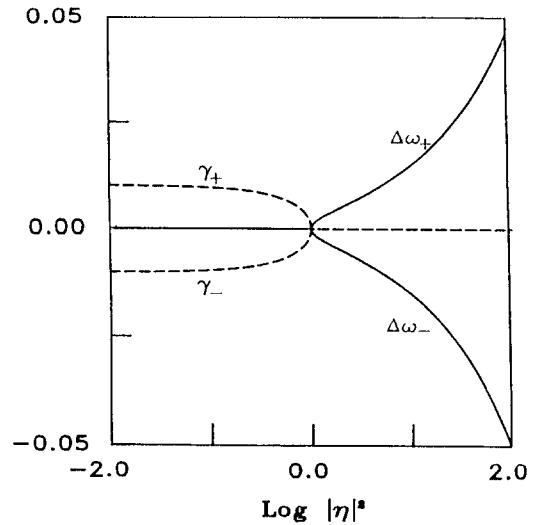

Fig. 1. Frequency shifts ($\triangle\omega+$ and $\triangle\omega-$) and decay rates ($\gamma+$ and $\gamma-$) as a function of the common logarithm of PCM reflectivity $|\eta|^2$, where $\eta = |\eta|$, $\gamma_0 = 0.01 \; \omega_0$ and q $= 1$. The unit of y-axis is ω_0.

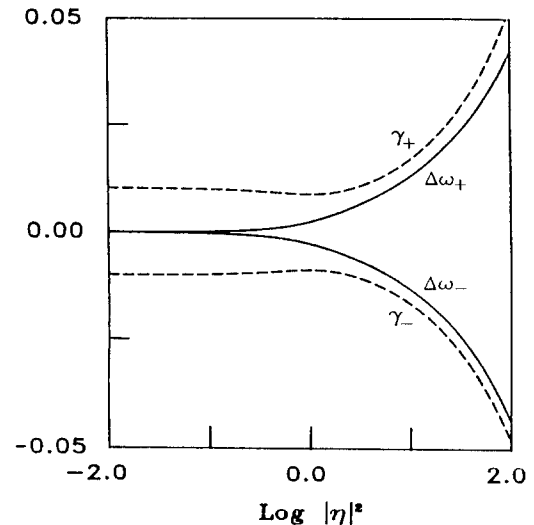**Fig. 2.** Same as Fig. 1, except $\eta = |\eta| \exp(i\theta)$ and $= \pi/6$.

$\eta \geq 1$, the lifetime of the excited molecule in the vicinity of a PCM is infinitely long. Furthermore, we want to remark that apparent symmetry (about zero) of the two branches of solution is merely due to the fact that $\gamma_0 / \omega_0 << 1$, and they start to be asymmetric for larger values of γ_0 / ω_0. In Fig. 2, we show a similar calculation as in Fig. 1 except
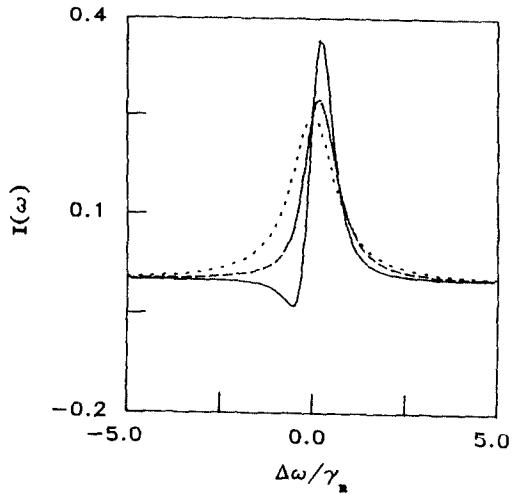
Fig. 3. Absorption profile $I(\omega)$ as a function of the detuning $\triangle\omega$ for the complex PCM reflectivity $\eta = |\eta|\exp(i\theta)$ with $|\eta| = 1.0$. The solid, dashed and dotted curves denote $\theta = \pi/6$, $\pi/3$ and $\pi/2$, respectivrly.
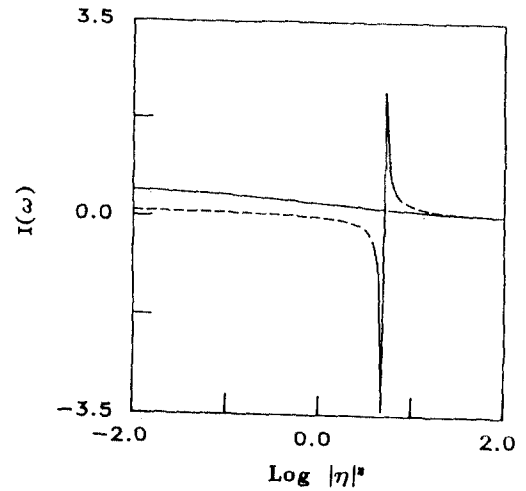

Fig. 5. Absorption profile $I(\omega)$ as a function of the common ligarithm of PCM reflectivity $|\eta|^2$, where $\eta = |\eta|$. The solid and dotted curves denote the on-resonance ($\omega_0/\omega = 1$) and off-resonance ($\omega_0/\omega = 1.01$), respectively.
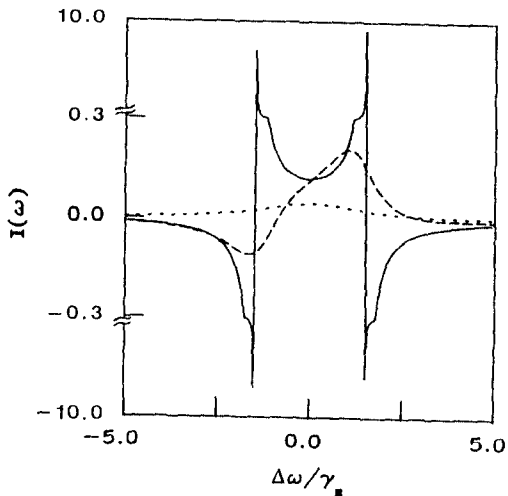

Fig. 4. Same as Fig. 3, except $|\eta| = 10^{0.5}$. The solid, dashed and dotted curves denote $\theta = 0$, $\pi/6$ and $\pi/2$, respectively. Note that the scale of the y-axis is not uniform.
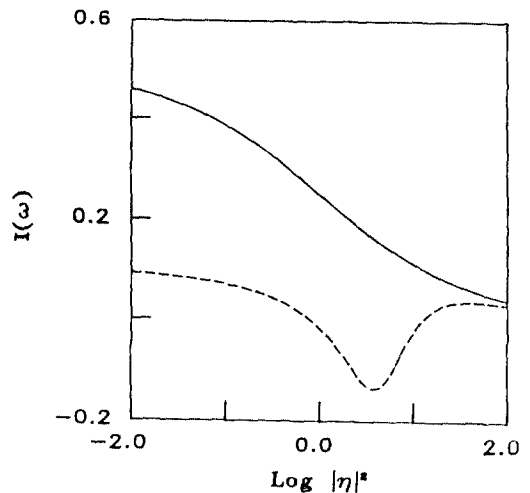

Fig. 6. Same as Fig. 5, except $\eta = |\eta|\exp(i\theta)$ and $\theta = \pi/6$.

that η is taken to be complext with its phase equal to $\pi/6$. Again, only the positive branches of solution are physical, and in addition, we can appreciate the effect of the phase of η in this model. Figure 3 shoes the absorption profile $I(\omega)$ as a funtion of the detuning $\triangle\omega$ for complex PCM reflectivity $|\eta|\exp(i\theta)$ with $|\eta| = 1.0$. We observe that the limeshape starts as a δ-function shape for real

$\eta(\theta = 0)$, becoming asymmetric as θ goes through the values $\pi/6$, $\pi/3$, ...ect., and finally restores its symmetric Lorentzian form for $\theta = \pi/2$. We would like to remark that an asymmetric lineshape occurs only for $|\eta| \geq 1$. For the case where $|\eta| < 1$, it has been observed that $I(\omega)$ always stays as a Lorentzian disregard the value of θ. For $|\eta| > 1$, we have shown in Fig. 4 the lineshapes for different values of θ, from which we see that the Lorentzian na-

ture is completely distored. Furthermore, we observe that for cases where $|\eta| \geq 1$, $I(\omega)$ can become negative. We interpret this as stimulated emission from the molecular dipole, which is possible since for large $|\eta|$, the PCM can transfer more energy to the dipole than it radiates and hence creates a certain kind of population inversion in the molecular system. This is the same origin for the infinite lifetime observed in Fig. 1. Finally, in Fig. 5 and 6 we show the variation of $I(\omega)$ with $|\eta|$ for both real ($\theta = 0$) and complex ($\theta = \pi/6$) values of η, respectively. Both the on-resonance ($\omega_b/\omega = 1$) and off-resonance ($\omega_b/\omega = 1.01$) cases are shown. It is interesting to observe that for the off-resonance case, there is some sort of singular behavior for about the same value of $|\eta|$ in both figures.

4. Conclusions

In this paper, we have investigated some novel spectroscopic features for molecules located in the vicinity of a PCM, based on a theoretical model which is developed through the application of the OPCS technique. In particular, the results obtained here for the induced decay rate, frequency shift and absorption lineshape are found to be independent fo the orientation and distance of the molecule with respect to the PCM, consistent with previous findings of Agarwal[8] and Bochove[9]. Moreover, we are able to determine within our model uniquely the physical solutions for $\triangle \omega$ and γ by imposing the asymptotic condition $\gamma \rightarrow \gamma_b$ as $\eta \rightarrow 0$, in contrast to the results obtained in Bochove's FWM model[9]. Furthermore, our results are quite sensitive to the phase (θ) of the PCM reflectivity, a phenomenon which does not appear in Bochove's work. While Bochove is consistent within his FWM model according to his definition of the conjugated field, we feel that such de-

pendences on θ are not completely unjustified, if one recalls that the phase of reflectivity for ordinary surfaces plays a very important role in the radiative and nonradiative energy transfers between admolecule and the substrate[4, 14].

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