

Anomalous increase of the cross section of spontaneous Raman processes near an absorbing particle

V. R. Blok

Research Institute for Organic Intermediate Products and Dyes

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The nonlinear susceptibility of a complex consisting of an absorbing molecule and the investigated one is considered. It is shown that the cross section for Raman scattering can increase in the system by several orders of magnitude. Owing to the strong linear Stark shift, which depends on the pump field, this effect can be used for selective study of only those dipole molecules or only those parts of large molecules, which form complexes with the absorbing probing molecule. It is shown that for molecules adsorbed on a metal, besides the above mentioned amplification by the "local field," which decreases slowly with distance, there exists for the first monolayer another effective amplification mechanism, connected with the abrupt increase of the dipole moments of the transition into the virtual state on account of formation of a new state with charge transfer from the molecule to the metal.

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INTRODUCTION

Interest in experiments on the anomalous increase (by up to six orders of magnitude) of the cross section of spontaneous Raman scattering (SpRS) upon adsorption of a number of molecules on certain metallic surfaces is continuing to increase.¹ A particularly thorough study was made of the pyridine-silver (Py-Ag) system and the following experimental results were obtained:

1. A maximum increase of the cross section by 10^5 - 10^6 times.
2. The cross section depends strongly on the degree of inhomogeneity of the surface (more strongly the rougher the surface), and particularly useful are small-scale inhomogeneities, i. e., inhomogeneities of atomic scale, adsorbed atoms (adatoms).
3. The cross section depends on the frequency of the incident light (the maximum is near 1.9 eV).
4. Superimposed on the SpRS band is a structureless background several times weaker than the intensity of the anomalously amplified satellites of the SpRS. The factors that increase the intensity of these satellites (roughening of the surface, increase of the frequency of the incident light, etc.) lead simultaneously to a proportional increase of the background. Experiments with picosecond laser pulses have shown that the appearance of the background lags the appearance of the SpRS satellites.
5. The polarization is selective, namely, the cross section is a minimum if the electric vector \mathbf{E} of the incident wave is perpendicular to the surface (i. e., at the so-called p -polarization).
6. The effect reaches six orders of magnitude when the Py molecules are in direct contact with the metal, and a certain enhancement takes place also at a distance r between Py and Ag up to 50 Å (Ref. 2).
7. The anomalous SpRS lines are usually shifted relative to the position of the line of the normal SpRS by several dozen reciprocal centimeters.

8. The lines of the anomalous SpRS are more depolarized.

In this paper we attempt to explain all the foregoing experimental regularities by starting from a definite model. For estimates within the framework of this model, however, we shall have to generalize somewhat the formalism of the resonant interaction of light with a molecule³ for the case when account is taken of "neighboring" molecules and, in particular, to the case when the neighboring molecule has a transition that is at resonance with the incident pumping radiation, in contrast to the molecule from which the SpRS is observed.

§1. INTERACTION OF LIGHT WITH COMPLEXES OF TWO DIFFERENT MOLECULES

The generalization of the results of the present section to include complexes consisting of more than two molecules will be found to be quite simple. We consider therefore only the case of molecular dimers.

The interaction between the molecules of a dimer will be described, as usual, by the dipole-dipole interaction operator (a justification for using this operator as applied to polarization induced by exchange of transverse virtual photons is contained, e. g., in Ref. 4):

$$F_{12} = d_1 \hat{\alpha}_1 d_2 - d_1 (d_2 - 3n(d_2 \cdot n)) / r^3,$$

where d_1 and d_2 are the operators of the dipole moments (er_1 and er_2) of the first and second molecules, respectively, r is the distance between the molecules, and n is a unit vector along a line joining the molecules. Allowance for the quadrupole or some other paired interaction is trivial and does not change the results significantly. The Hamiltonian of a dimer interacting with a classical electromagnetic field with an electric field intensity vector \mathbf{E} is, in the dipole approximation,

$$\mathcal{H} = \mathcal{H}_{01} + \mathcal{H}_{02} + F_{12} + V_1 + V_2 = \mathcal{H}_0' + F_{12}, \quad (1)$$
$$V_1 = -Ed_1, \quad V_2 = -Ed_2.$$

We start from the chain of Bogolyubov's equations⁵ for the density matrix ρ :

$$\begin{aligned}\dot{\rho}_1 + \Gamma_1 \rho_1 &= -\frac{i}{\hbar} [\mathcal{H}_0', \rho_1] - \frac{i}{\hbar} \text{Sp}_2 [F_{12}, \rho] -, \\ \dot{\rho}_2 + \Gamma_2 \rho_2 &= -\frac{i}{\hbar} [\mathcal{H}_0', \rho_2] - \frac{i}{\hbar} \text{Sp}_1 [F_{12}, \rho] -. \end{aligned} \quad (2)$$

Here ρ_1 , ρ_2 and ρ are the respective density matrices of the first and second molecules and of the dimer as a whole. Γ_1 and Γ_2 are the relaxation operators of the first and second molecules, respectively,³ and $[A, B]$ is the commutator of the operators A and B .

Neglecting the electron exchange between molecules 1 and 2 and using a splitting of the self-consistent-field type $\rho = \rho_1 \rho_2$, we obtain

$$\begin{aligned}\dot{\rho}_1 + \Gamma_1 \rho_1 &= -\frac{i}{\hbar} [\mathcal{H}_0', \rho_1] - \frac{i}{\hbar} [d_1, \rho_1] - \hat{\alpha}_{12} \text{Sp}(d_2, \rho_2), \\ \dot{\rho}_2 + \Gamma_2 \rho_2 &= -\frac{i}{\hbar} [\mathcal{H}_0', \rho_2] - \frac{i}{\hbar} \text{Sp}(d_1, \rho_1) \hat{\alpha}_{12} [d_2, \rho_2] -. \end{aligned} \quad (3)$$

There is no longer any need for the subscripts of the spur symbol, and they will be left out. After splitting their remain under the spur symbol only matrices that characterize the particular subsystem over whose variables the summation is carried out.

We proceed to the interaction representation with the aid of the operator

$$U_0 = \exp \left\{ -\frac{i}{\hbar} (\mathcal{H}_0 + \mathcal{H}_0') t \right\}.$$

Then

$$\sigma_{mn} = (U_0^{-1} \rho U_0)_{mn} = \rho_{mn} \exp(i\omega_{mn} t).$$

$$V_{\text{int } mn} = V_{mn} \exp(i\omega_{mn} t), \quad V_{mn} = \sum_j V_{mn}^{(j)}(t) \exp(i\omega_j t),$$

where ω_j are the frequencies of the electromagnetic fields that take part in the nonlinear process. For different molecules, the classification of the levels m and n is different, i.e., m_1, n_1 and m_2, n_2 respectively. We take into account also the fact that the relaxation operator (Ref. 3, p. 17) is

$$(\Gamma \rho)_{mn} = \begin{cases} T_{mn}^{-1} \rho_{mn}, & n \neq m, \\ \sum_k (W_{mk} \rho_{mm} - W_{km} \rho_{kk}), & n = m, \end{cases}$$

T_{mn} is the relaxation time of the off-diagonal elements of the density matrix, W_{mk} is the relaxation rate of the diagonal elements of the density matrix. The first equation of (3) can then be rewritten in the form

$$\begin{aligned}\left(\frac{d}{dt} + T_{1,mn} \right) \sigma_{1,mn} &= -\frac{i}{\hbar} \sum_{k,j} \{ V_{1,mk} \sigma_{1,kn} \exp[i(\omega_{1,mk} + \omega_j) t] \\ &- \sigma_{1,mk} V_{1,kn}^{(j)} \exp[i(\omega_{1,kn} + \omega_j) t] \} - \frac{i}{\hbar} \left\{ \sum_{k,j} [d_{1,mk} \sigma_{1,kn} \exp(i\omega_{1,mk} t) \right. \\ &\left. - \sigma_{1,mk} d_{1,kn} \exp(i\omega_{1,kn} t) \right\} \hat{\alpha}_{12} \text{Sp}(d_{2,ir} \exp(i\omega_{2,ir} t) \sigma_{2,ri}), \\ \frac{d}{dt} \sigma_{mn} + \sum_k (\sigma_{mm} W_{mk} - W_{km} \sigma_{kk}) &= -\frac{i}{\hbar} \sum_{k,j} \{ V_{1,mk} \sigma_{1,km} \exp[i(\omega_{1,mk} + \omega_j) t] \\ &- \sigma_{1,mk} V_{1,km}^{(j)} \exp[i(-\omega_{1,mk} + \omega_j) t] \} - \frac{i}{\hbar} \left\{ \sum_{k,j} [d_{1,mk} \sigma_{1,km} \exp(i\omega_{1,mk} t) \right. \\ &\left. - \sigma_{1,mk} d_{1,km} \exp(-i\omega_{1,mk} t) \right\} \hat{\alpha}_{12} \text{Sp}[d_{2,ir} \sigma_{2,ri} \exp(i\omega_{2,ir} t)]. \end{aligned} \quad (4)$$

The second equation of the system (3) is transformed perfectly analogously, with the indices 1 and 2 inter-

changed. It is easy to see that in the right-sides of both equations of (4) the second sum can be combined with the first by introducing in place of $V_{mk}^{(j)}$ a new energy of interaction with the field

$$V_{1,mk}^{(j)} = V_{1,mk}^{(j)} + d_{1,mk} \exp(-i\omega_j t) \hat{\alpha}_{12} \text{Sp}[d_{ir} \sigma_{ri} \exp(i\omega_{ir} t)]. \quad (5)$$

If $V_{1,mk}^{(j)} = d_{1,mk} E_j$, then (5) can be rewritten in the form

$$V_{1,mk}^{(j)} = d_{1,mk} \{ E_j + \hat{\alpha}_{12} \text{Sp}[d_{2,ir} \exp(i(\omega_{2,ir} - \omega_j) t)] \}. \quad (6)$$

We introduce the symbol

$$P_1^{(j)} = \text{Sp}[d_{2,ir} \sigma_{2,ri} \exp[i(\omega_{2,ir} - \omega_j) t]]. \quad (7)$$

$P_j^{(2)}$ is the amplitude of the spectral component of the rapidly varying polarization with frequency ω_j . Thus, the presence of a neighboring molecule interacting with an electromagnetic field can be taken into account by adding to the field of the electromagnetic wave the field that is produced by the induced polarization of the neighboring, second molecule at the location of the first, in the quasistatic approximation. In contrast to the field E_j , this increment is not a radiation field, but just like E_j it polarizes the first molecule.

§2. CROSS SECTION FOR SPONTANEOUS RAMAN SCATTERING OF A MOLECULE LOCATED NEAR A RESONANTLY ABSORBING TWO-LEVEL SYSTEM

We consider now a particular case. We estimate the change in the cross section for spontaneous Raman scattering as a result of proximity to a resonantly absorbing two-level system. The cross section for SpRS by an isolated molecule is

$$S_{\text{SpRS}} \sim \left\{ \hbar^{-1} \sum_k \left(\frac{V_{1,1k}^{(\beta)} V_{1,k2}^{\text{Stokes}}}{\omega_{1,1k} + \omega_\beta} + \frac{V_{1,1k}^{\text{Stokes}} V_{1,k2}^{(\beta)}}{\omega_{1,1k} + \omega_{\text{Stokes}}} \right) \right\}^2. \quad (8)$$

Let a second two-level system be at resonance with the incident field E_β . We neglect the reaction of system 1, which interacts nonresonantly with the light, on the system 2 (so that the polarization amplitude P_1 of the non-resonant process is smaller by many orders than P_2 for resonant absorption). Then, neglecting the detuning and the Stark shift (Ref. 3, p. 41), we have

$$\sigma_{2,\text{stat}} \approx i\hbar^{-1} (d_{2,12} E_\beta) T \left\{ 1 + \frac{(d_{2,12} E_\beta)^2}{(\hbar^2/4\tau T)} \right\}^{-1}. \quad (9)$$

Here $\sigma_{2,\text{stat}}$ is the off-diagonal density-matrix element of the second subsystem in the quasistationary approximation, and T and τ are the times of transverse and longitudinal relaxation. The spectral component of the fast polarization component with frequency ω_β is

$$\tilde{P}_2 = i\hbar^{-1} T d_{2,12}^2 \left\{ 1 + \frac{(d_{2,12} E_\beta)^2}{(\hbar^2/4\tau T)} \right\}^{-1}. \quad (10)$$

We assume also that the excited state of the two-level molecule has a large dipole moment $d_{2,22}$, and a slow (with frequency $2\pi/\tau$) polarization component arises

$$\bar{P}_2 = 0.5(1 - \eta_2) d_{2,22} \approx 0.5 d_{2,22} \left[1 - \left(1 + \frac{(d_{2,12} E_\beta)^2}{\hbar^2/4\tau T} \right)^{-1} \right]. \quad (11)$$

Here η_2 is the population difference of the second subsystem. Using the rules formulated in §1, we can write

$$V_{1,1a}^{(\beta)} = V_{1,1a}^{(0)} + \frac{d_{1,1a} \{d_{2,12} - 3n(d_{2,12}n)\}}{\epsilon r^3} \sigma_{s,stat} \\ = d_{1,1a} \left\{ E_p + \frac{[d_{2,12} - 3n(d_{2,12}n)]}{\epsilon r^3} \sigma_{s,stat} \right\}. \quad (12)$$

Here \mathbf{n} is a unit vector along the straight line joining the first and second subsystems, r is the distance between the first and second subsystems, and ϵ is the dielectric constant at the frequency ω_p .

At $T \sim 10^{-12}$ sec, $\tau \sim 10^{-8}$ sec, $r \sim 10 \text{ \AA}$, $d_{2,12} \sim 1.4 \cdot 10^{-17}$ cgs, and $\epsilon \sim 2$, the value of $V_{1,1a}^{(\beta)}$ exceeds $V_{1,1a}^{(0)}$ by $k \approx d_{2,12}^2 T / \hbar \epsilon r^3 \sim 10^2$ times. Consequently, the nonlinear susceptibility χ is increased by k times, and the StRS cross section increases:

$$S'_{\text{SpRS}} / S_{\text{SpRS}} \sim k^2 \sim 10^4, \quad (13)$$

with

$$S'_{\text{SpRS}} / S_{\text{SpRS}} \sim 1/r^4 \quad (14)$$

and decreases relatively slowly, so that amplification takes place up to $r \leq 50 \text{ \AA}$. If molecule 1 has in the ground state a dipole moment $\sim 10^{-18}$ cgs and E_p is not too small, so that $\eta - 1 \geq 0.1 (E_p \geq 0.16 \text{ cgs})$, then the levels of molecule 1 undergo a linear Stark shift equal to several dozen reciprocal centimeters owing to the slow part of the polarization $\bar{P}_2(11)$.

Let us examine the physical meaning of the increase of the cross section (13). A possible interpretation is the following. A nonradiative energy transfer⁶ takes place, so to speak, from the resonantly absorbing molecule 2 to the molecule 1 which undergoes SpRS, with simultaneous decay into a Stokes photon and a vibrational quantum. The combined cross section for this complicated process can exceed by many orders the SpRS cross section. In a certain sense, the absorbing neighbor 2 is equivalent to introducing a resonantly absorbing level in molecule 1. Another possible interpretation is connected with "intensification of the field" by molecule 2 at the location of molecule 1. It must only be borne in mind that the real radiation field is not amplified, but a strong field of "virtual transverse photons" appears,⁴ proportional to the weak incident radiation field E_p and shifted in phase relative to the latter.

§3. COMPARISON WITH EXPERIMENT

Let us discuss in somewhat greater detail the experimental situation. As seen from the preceding analysis, to obtain an anomalous increase of the SpRS cross section we must have a system that absorbs a photon having an approximate energy 1.9 eV and with a transition dipole moment $\sim 5 \cdot 10^{-18} - 2 \cdot 10^{-17}$ cgs. Such large transition dipole moments in the visible region of the spectrum are frequent in dyes, and are typical of contacting complexes with charge transfer.⁷ In the Ag-Py system there appears to be a single formation having such a longwave spectrum and so large an oscillator strength, namely a complex of an Ag atom isolated outside the metal with the solid metal. Its lower excited state is connected with charge transfer from the Ag adatom to the Ag metal. Let us estimate, follow-

ing Mulliken,⁷ the energy of this transition (the ionization potential is $I_{Ag} = 7.58 \text{ eV}$, the work function is $W_{Ag} = 4.3 \text{ eV}$, and the distance between the Ag atom and the formed surface is $\sim 5 \text{ \AA}$):

$$h\omega \geq I_{Ag} - W_{Ag} - e^2/2r \approx 1.9 \text{ eV}. \quad (15)$$

Equation (15) takes into account the lowering of the level of the state, with charge transfer due to the interaction of the Ag^+ with its electric image in the metal. The obtained estimate (15) agrees with the experimental maximum of the SpRS cross section and with the position of the absorption bands of the pure Ag metal with specially roughed surface.⁸ Electron-hole pair absorption, due to the surface roughness, for which the state with charge transfer is so to speak a limiting case, can also lie in this region, and Eq. (15) is apparently a reasonable estimate.

The fundamental experimental regularities listed in the Introduction can be easily explained on the basis of the foregoing. Thus, the maximum of the SpRS cross section near 1.9 eV (see item 3 of the Introduction) is explained on the basis of (12) and (15): the usefulness of increasing the number of small-scale inhomogeneities (item 2) is apparently due to the increase of the number of the absorbing complexes consisting of the adatom + metal + system 2. The structureless intense background (see item 4) is due to luminescence of system 2, which is delayed in comparison with the synchronous process of emission of the SpRS satellites. The polarization selectivity indicated in item 5 of the Introduction is due to the fact that, for a state with charge transfer from a physically adsorbed atom or molecule to a metal, the moment of the transition $d_{2,12}$ is always perpendicular to the surface from symmetry considerations. The SpRS cross section decreases relatively slowly with distance from the metal surface, $\propto r^{-6}$ [see item 6 of the Introduction and Eq. (14) of the text]. The shift of the lines of the anomalous SpRS relative to the usual by several dozen reciprocal centimeters (see item 7) can be due to the linear Stark shift caused by the "slowly" varying field of the dipole $\bar{P}_2(11)$. A contribution to such a shift, however, can be made also by the double-layer field in an electrolytic cell, by intermolecular interaction, and others. As for the depolarization of the Stokes component relative to the incident pump radiation, it is due to the fact that the polarizations of the Stokes and anti-Stokes components depend more readily on the orientation of the Py molecule relative to the system 2 than to the polarization of the incident wave (see item 8 of the Introduction).

What remains unexplained is only item 1, inasmuch as under reasonable assumptions concerning the parameters of the system 2, and reasonable distances r between the Py and the system 2, it is impossible to explain such large cross sections for the first monomolecular Py layer (in an electrolytic cell, where gains $\sim 10^5 - 10^6$ were obtained, there can be only one monolayer of Py on the Ag).

For the Py molecules situated within the first monomolecular layers near the surface of the Ag metal, there should exist also another mechanism, not pre-

viously considered, for increasing the SpRS cross section. The point is that adsorption should give rise in Py to a new very intense (with large transition dipole moment) absorption band due, according to Mulliken,⁷ to the charge transfer from Py to the metal. An estimate with the aid of Eq. (15) yields for this transition $\hbar\omega$ 3.5 eV. The pumping for the SpRS lies in the longer-wavelength region, and furthermore the resonant SpRS is not always convenient from the point of view of increasing the intensity of the Stokes component since it is intensively absorbed. However, the appearance in Py of a new transition k' with $d'_{1k}, d'_{k2} \sim (1-2) \cdot 10^{-17}$ cgs results, upon substitution in (8), in a gain

$$S'_{\text{SpRS}}/S_{\text{SpRS}} \sim (d'/d)^2 \sim 10^4 - 10^6. \quad (16)$$

Thus, when analyzing the experimental data the amplification mechanisms (13) and (16) must be taken into account jointly, and we have for the surface monomolecular layer

$$S'_{\text{SpRS}}/S_{\text{SpRS}} \sim (d'/d)^2 k^2 \sim 10^8 - 10^9,$$

where the first term in the product is connected with the increase of the dipole moments of the virtual transition and the other, so to speak, with the amplification of the field.

CONCLUSION

The considered effect of amplification by a local field will manifest itself not only on the surface but also in the bulk. In particular, owing to the strong Stark shift, which depends on the pump field, one can plot only the spectra of those molecules or only of those parts of large molecules, e.g., proteins, with which the probe molecules that absorb the pump radiation form associates.

The considered effect makes apparently a certain contribution in resonant SpRS of aromatic molecules, when the π system absorbs resonantly the pump radiation, and oscillations of the σ system are radiated, e.g., in resonant Raman scattering by the vibrations of C-H bonds.

This effect can be used also to increase the cross section for other spontaneous processes, such as anti-Stokes spontaneous Raman scattering, three-photon spontaneous Raman scattering, and others.

When calculating parametric processes in such composite media it is necessary simply to increase the polarizabilities κ in the standard equations (Ref. 3, p. 176) by a factor k (if the absorber is introduced only at one j -frequency) and to add a term connected with the absorption:

$$dA_j/dz \sim -(d_{z,ii}e)^2 \eta_2 A_j,$$

where A_j is the amplitude of the electric field intensity, e is a unit vector of the polarization of the wave, and η_2 is the population difference of the absorbing substance. It is easily seen that the parametric processes in composite media have always much smaller conversion coefficients (by one or two orders) than in the case of "genuine" resonance, due to the absence of the "interference" term $\sim d \times \eta$. One cannot exclude, however, situations wherein it is technically simpler to produce the composite medium than to choose one substance with the appropriate resonance.

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