საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 8, №1, 2014
BULLETIN OF THE GEORGIAN NATIONAL ACADEMY OF SCIENCES, vol. 8, no. 1, 2014

Physical Chemistry

New Formulas of Spectral-Line Excitation Profiles for Coherent Anti-Stokes Raman Scattering by Molecules in Solutions

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(Presented by Academy Member Givi Tsintsadze)

ABSTRACT. The inhomogeneity of the surrounding of scattering molecules significantly affects the intensity distribution in coherent anti-Stokes Raman scattering (CARS) spectra and excitation profiles. A theoretical expression is obtained that describes the excitation profile of an arbitrary relationship between the relaxation constant Γ of the vibronic levels of the excited electronic state and parameter σ, characterizing the inhomogeneity of the environment. The possible influence of inhomogeneity on the CARS spectral lines is also discussed in the paper. *© 2014 Bull. Georg. Natl. Acad. Sci.*

Key words: *coherent anti-Stokes Raman spectroscopy (CARS), excitation profiles, influence of surrounding inhomogeneity.*

Coherent anti-Stokes Raman spectroscopy (CARS) is a form of spectroscopy used primarily in chemistry, physics, biology and related fields. It is sensitive to the same vibrational signatures of molecules as seen in Raman spectroscopy, typically the nuclear vibrations of chemical bonds. Unlike Raman spectroscopy, CARS employs multiple photons to address the molecular vibrations, and produces a coherent signal. As a result, CARS is the order of magnitude stronger than spontaneous Raman emission.

In the CARS process, three waves, two at the pumping frequency ω_1 and one at the Stokes frequency ω_1 interact with a molecule. Nonlinear optical effects caused by the so-called $\chi^{(3)}$ mechanism ($\chi^{(3)}$ is the third-order nonlinear susceptibility) led to the formation of new coherent radiation at the anti-Stokes frequency $\omega_3 = 2\,\omega_1 - \omega_2$. The efficiency of such a process attained in any medium grows sharply as the difference $\Delta \equiv \omega_1 - \omega_2$ approaches the frequency of Raman – active transition $\Omega_{n_g} \equiv \varepsilon_{n_g} / \hbar$.

In view of the relatively small width Γ_{n_g} (several cm^{-1}) of the vibronic states $|n_g\rangle >$ relative to the ground electronic state of the molecule, the CARS spectrum, i. e. the dependence of the intensity of the radiation generated at the frequency $\omega_3 = \omega_1 + \Delta$ on Δ for fixed values of ω_1, has a quasidiscrete character.

Nonzero intensities are actually attained for $\Delta \simeq \varepsilon_{n_g}$. To obtain the corresponding excitation profile one scans the frequencies ω_1 and ω_2 in such a way that $\Delta \equiv \omega_1 - \omega_2 \simeq \varepsilon_{n_g}$ is fulfilled all the time. According to [1], the shape of the band of the excitation profile possesses increased sensitivity to different broadening mechanisms – homogeneous (primarily relaxation) and inhomogeneous (frequently fluctuating), which in its own way can promote unique solution to both problems identifying the contributions of the separate mechanisms of excitation profile broadening and determining the parameters characterizing the change of the equilibrium geometry molecules in the excited electronic state. This paper is devoted to a study of the simultaneous effect of condensed medium and intramolecular processes on the excitation profile of CARS spectral lines.

According to [2], one may reduce the effect of the medium (inhomogeneity of the surroundings of the scattering molecules in solution) on the formation of the excitation profile of CARS spectral lines, as in weakly polar and nonpolar solvents, to an averaging function, which describes the intensity distribution in the CARS spectra and of the intensity distribution in the CARS spectra and of the corresponding excitation profiles within the framework of the so-called fundamental theory of the model of vibronic interactions

$$P_{n_g}(\omega_1) \simeq \left| \chi_{n_g}^{(3)}(\omega_1) \equiv \sum_{K_{e=0}}^{\infty} \sum_{m_{e=0}}^{\infty} \chi_{n_g}^{K_e, m_e}(\omega_1) \right|^2, \tag{1}$$

where

$$\chi_{n_g}^{K_e, m_e} \simeq \mu_{eg}^4 \frac{< O_g \mid m_e >< m_e \mid n_g >< n_g \mid K_e >< K_e \mid O_g >}{(\omega_1 - \omega_{eg} - \varepsilon_{\kappa_e} + i\Gamma_{\kappa_e})(\Delta - \varepsilon_{n_g} + \Gamma_{n_g})(\omega_3 - \omega_{eg} - \varepsilon_{m_e} + i\Gamma_{m_e})}. \tag{2}$$

In (2) μ_{eg} is the electric dipole moment on the transition; $\mid k_e >$ and $\mid m_e >$ are the vibronic states of the excited electron level with energies ε_κ and ε_m measured with $\omega_{eg}\,(\hbar \equiv 1)$; and Γ_{k_e} and Γ_{m_c} are phenomenologogically introduced relaxation constants. One may treat (2) as the probability amplitude of a four – step process of virtual transition described by the fourth-order perturbation theory for the interaction of radiation with a molecule.

In view of the coherence of the CARS process, according to [2] one may perform all averaging, including that over the variations of ω_{eg}, for probability amplitudes, i.e., for the square of the absolute value of (2). One must average (2) over a Gaussian distribution

$$\rho\left(\omega_{eg}\right) = \left(\sqrt{2}\pi\sigma\right)^{-1} \exp\left[-\left(\omega_{eg} - \varpi_{eg}\right)^2 / 2\sigma^2\right], \tag{3}$$

because variations of the local environment, as a consequence of fluctuations, have a Gaussian character in the majority of actual case. The correct averaging of $\chi_{n_g}^{(3)}$ over the distribution of (3) was first performed in [2]. However, both the further theoretical analysis of the final expressions obtained there and their use in quantitative computations are extremely difficult.

Having substituted $\Delta \equiv \omega_1 - \omega_2 \simeq \varepsilon_{n_g}$ in (2) and transforming the remaining part of the denominator into the form

$$\frac{(\omega_1 - \omega_{eg} - \varepsilon_{\kappa_e} + i\Gamma_{\kappa_e})^{-1} - (\omega_3 - \omega_{eg} - \varepsilon_{m_e} + i\Gamma_{m_e})^{-1}}{(\omega_3 - \omega_1) + (\varepsilon_{k_e} - \varepsilon_{m_e}) + i(\Gamma_{m_e} - \Gamma_{\kappa_e})}, \tag{4}$$

it is not difficult to carry out the averaging of $\chi_{n_g}^{(3)}(\omega_1)$ with respect to Eq.(3) with consideration of

$$\ll (\omega_1 - \omega_{eg} - \varepsilon + i\Gamma)^{-1} \gg -\frac{i}{\sigma}\sqrt{\frac{\pi}{2}}W\left(\frac{\omega - \omega_{eg} - \varepsilon + i\Gamma}{\sqrt{2}\sigma}\right). \tag{5}$$

Here $W(z)$ is a complex function [3].

$$W(z) = \frac{i}{\pi}\int_{-\infty}^{\infty}\frac{\exp(-t^2)dt}{z-t} = \exp(-z^2)erfc(-iz) \quad (\mathrm{Im}\, z > 0) \tag{6}$$

connected by a simple relation with the plasma dispersion function

$$Z(\upsilon + i\xi) = i\sqrt{\pi}W(\upsilon + i\xi). \tag{7}$$

We separate the real (Ψ) and imaginary (φ) parts of the function $W(z \equiv \upsilon + i\xi)$ from (6) for arbitrary values of ξ and υ in the form of rapidly converging series of [4,5] (see (8) and (9) of [4]). Below we present simpler, but still accurate expressions for the functions

$$\Psi(\upsilon;\xi) = \exp(-\upsilon^2)\{\exp(\xi^2)\cos(2\xi\upsilon)[1 - cth(2\pi\xi)] + (2\xi/\pi)\sum_{n=-\infty}^{\infty}\exp(-n^2/4)\cosh(n\upsilon)/(n^2 + 4\xi^2)\} \tag{8}$$

$$\varphi(\upsilon;\xi) = \exp(-\upsilon^2)\{\exp(\xi^2)\sin(2\xi\upsilon)[\mathrm{cth}(2\pi\xi) - 1] + (1/\pi)\sum_{n=-\infty}^{\infty}n\exp(-n^2/4)\sinh(n\upsilon)/(n^2 + 4\xi^2)\} \tag{9}$$

which were obtained from [3] with the aid of the summation

$$(2\xi/\pi)\sum_{n=-\infty}^{\infty}\exp(-n^2/4)(n^2 + 4\xi^2)^{-1} = \exp(\xi^2)[\mathrm{cth}(2\pi\xi) - erf(\xi)]. \tag{10}$$

We recall that $\Psi(\upsilon;\xi) \equiv \mathrm{Re}W(\upsilon;\xi)$ is called the Voigt function in spectroscopy. In the general case, it determines the dependence of the different spectral coefficients on frequency (υ is the dimensionless detuning of the resonance frequency) and plays an important role in all questions connected with the interpretation of the line share. It is not difficult to show that near the maximum $(|\upsilon| < 1)$ (and more accurately the smaller the fundamental parameter $\xi \equiv \Gamma/\sqrt{2\sigma}$). That is, one may approximate $\Psi(\upsilon;\xi)$ with

$$\Psi(\upsilon;\xi) \simeq \exp(-\upsilon^2)[a(\xi) - b(\xi)\cos(2\xi\upsilon)], \;\; \xi(\upsilon) < 1 \tag{11}$$

with coefficients

$$a(\xi) = 1/\sqrt{\pi}\xi; \quad b(\xi) = \exp(\xi^2)erfc(\xi) - (\sqrt{\pi}\xi)^{-1}, \tag{11'}$$

When the inhomogeneous (Gaussian) broadening mechanism dominates the homogeneous (Lorentzian).

So far as the far wings of the Voigt curve symmetrical with respect to $\upsilon = 0$ are concerned, they approximate the shape of the Lorentzian line

$$\Psi(\upsilon;\xi) \simeq [\xi/\sqrt{\pi}(\xi^2 + \upsilon^2)][1 + \upsilon^2/(\xi^2 + \upsilon^2)^2], \;\; \xi|\upsilon| > 1, \tag{12}$$

where the expression in the second set of brackets gives a correction to the Lorentzian line for the wing of a Voigt curve.

Finally, so far as returning to analysis of (1)-(3), it is easy to find the antisymmetric function $\varphi(-\upsilon;\xi) = -\varphi(\upsilon;\xi)$ [(8)], which describes the dispersion curve, according to (7) and (8), by simple differentiation of $\Psi(\upsilon;\xi)$

$$\varphi(\upsilon\xi) = (2\xi)^{-1}\partial\Psi/\partial\upsilon + (\upsilon;\xi)\Psi(\upsilon;\xi). \tag{13}$$

Returning to the averaging of the expression for $\chi_{n_g}^{(3)}(\omega_1)$ over the distribution of (3) taking into account (2), (5), (8) and (9), we find it more difficult to write

$$\ll \chi_{n_g}^{K_e,m_e}(\omega_1) \gg = \frac{\mu_{eg}^4}{\Gamma_{n_g}\sigma} = \sqrt{\frac{\pi}{2}} \frac{< O_g \mid m_e >< m_e \mid n_g >< n_g \mid n_g >< \kappa_e \mid O_g >}{(\varepsilon_{n_g} - \varepsilon_{\kappa_e} + \varepsilon_{m_e})(\Gamma_{m_e} - \Gamma_{\kappa_e})} \times$$

$$\varphi(\upsilon_{m_e};\xi_{m_e}) - \{(\Gamma_{m_e} - \Gamma_{\kappa_e})[\varphi(\upsilon_{m_e};\xi_{m_e}) - \varphi(\upsilon_{\kappa_e};\xi_{\kappa_e})] - (\varepsilon_{n_g} - \varepsilon_{\kappa_e} + \varepsilon_{m_e}) \times [\Psi(\upsilon_{\kappa_e};\xi_{\kappa_e}) - \Psi(\upsilon_{m_e};\xi_{m_e})] +$$

$$i(\Gamma_{m_e} - \Gamma_{\kappa_e})[\Psi(\upsilon_{\kappa_e};\xi_{\kappa_e}) - \Psi(\upsilon_{m_e};\xi_{m_e})] + i(\varepsilon_{n_g} - \varepsilon_{\kappa_e} + \varepsilon_{m_e})[\varphi(\upsilon_{m_e};\xi_{m_e}) - \varphi(\upsilon_{\kappa_e};\xi_{\kappa_e})]\} \tag{14}$$

where

$$\upsilon_{\kappa_e} \equiv \frac{\omega_1 - \omega_{eg} - \varepsilon_{\kappa_e}}{\sqrt{2}\sigma}; \quad \upsilon_{m_e} \equiv \frac{\omega_1 - \varpi_{eg} - \varepsilon_{m_e} - \varepsilon_{n_g}}{\sqrt{2}\sigma}; \quad \xi_{\kappa_e m_e} \equiv \frac{\Gamma_{\kappa_e m_e}}{\sqrt{2}\sigma}.$$

According to (14), $\ll \chi_{n_g}^{K_e,m_e} \gg$ is a complex quantity whose real and imaginary parts make identically significant contributions to the intensity distribution in CARS spectra and to the formation of the corresponding excitation profiles.

For the purpose of simplifying further analysis of (13) we treat the case of the presence of only one active vibrational degree of freedom with a frequency Ω that does not change as a result of electronic excitation and a dimensionless shift Q_0 of the equilibrium position along the normal coordinate. A simple analysis of (13) shows that only terms with $\varepsilon_{n_g} + \varepsilon_\kappa - \varepsilon_m \approx 0$ make a basic contribution to the double sum, i.e., those terms corresponding to the so-called double resonance make a significant contribution:

$\omega_1 - \omega_{eg} - \varepsilon_{\kappa_e} = \omega_3 - \omega_{eg} - \varepsilon_{m_{eg}}$. Therms with $m_e = \kappa_e + 1$ $(\kappa_e = 0,1,...)$ will correspond to the resonance condention for the excitation profile of the fundamental spectral lines with $n_g = 1$ of CARS. We note that $\ll \chi_{1_g}^{(3)} \gg$ does not have a singularity in view of the parameters corresponding to different vibrational levels of the excited electronic state. Therefore, $\ll \chi_\kappa^{(3)} \gg$ is approximated by the sum of therms with $m_e = \kappa_e + 1$ more accurately the smaller the difference $\left|\Gamma_{m_e} - \Gamma_{m_e}\right|$ in comparison with the frequency Ω of the active vibration. A stricter criterion has the form

$$\frac{Q}{\left|\Gamma_{m_e} - \Gamma_{\kappa_e}\right|} \times \frac{\left|\exp(\xi_{m_e}^2) erfc(\xi_{m_e}) - \exp(\xi_{\kappa_e}^2) erfc(\xi_{\kappa_e})\right|}{\exp(\xi_{\kappa_e}^2) erfc(\xi_{\kappa_e})} \gg 1, \tag{15}$$

where we made use of the value of the Voigt function at its maximum $\Psi(\upsilon;\xi) = \exp(\xi^2) erfc(\xi)$.

For the purpose of studying the possible influence of the effects of inhomogeneity on the shape of the CARS spectral lines, it is convenient to tune ω_1 in resonanse with ϖ_{eg} and to investigate the components of $\chi^{(3)}$ as a function of the detuning $\Delta = \omega_1 - \omega_2$. Having denoted $\delta\Omega \equiv \Delta - \varepsilon_{I_g}$ we find it not difficult to write from (2) and (4)

$$\mathrm{Re}_{\varphi_{1g}^{Q_e,I_e}} = const \frac{\delta\Omega\left[\Psi\left(\frac{\delta\Omega}{\sqrt{2}\sigma};\xi_{1'}\right) - \Psi\left(0;\xi_{0'}\right)\right] + \Gamma_{1g}\varphi\left(\frac{\delta\Omega}{\sqrt{2}\sigma};\xi_{1'}\right)}{\delta\Omega^2 + \Gamma_{1g}^2}, \tag{16}$$

$$\mathrm{Im}\,\chi_{1g}^{0_e,1_e} = const \frac{\Gamma_{1g}\left[\Psi\left(\frac{\delta\Omega}{\sqrt{2}\sigma};\xi_{1'}\right) - \Psi\left(0;\xi_{0'}\right)\right] + \left(\frac{\delta\Omega}{\sqrt{2}\sigma};\xi_{1'}\right)}{\delta\Omega^2 + \Gamma_{1g}^2}. \tag{17}$$

As a consequence, according to (16) and (17), the questions of when and how inhomogeneity of the surroundings affects the shape of a CARS spectral line depends essentially on the characteristic scale of the change of the functions $\Psi(\delta\Omega/\sqrt{2}\delta;\xi)$ and $\varphi(\delta\Omega/\sqrt{2}\delta;\xi)$, i.e., on their sensitivity as functions to $\delta\Omega/\sqrt{2\sigma}$ for arbitrary, but fixed for each specific case, ξ. Practically, in oll actual cases, it is reasonable to consider $\delta\Omega \sim \Gamma_{1g}$, i.e., $\delta\Omega/\sqrt{2}\sigma$, when one may approximate $\Psi(\upsilon;\xi)$ with the aid of (11); but according to (13), one approximates $\varphi(\upsilon;\xi)$, by the function

$$\varphi(\upsilon;\xi) \simeq -b(\xi)\exp(-\upsilon^2)\sin(2\xi 2\upsilon) = \left[\left(\sqrt{\pi}\xi\right)^{-1} - \exp(\xi^2)erfc(\xi)\right]\exp(-\upsilon^2)\sin(2\xi 2\upsilon). \qquad (18)$$

This simplifies maximally both the theoretical and quantitative analysis of the possible effect of the inhomogeneity of the surroundings of the molecules on the shape of a CARS spectral line for σ not exceeding one or two tens of cm^{-1}.

We note in conclusion that other terms of the double sum in (14) together with the resonance terms (with $m_e = \kappa_e + 1$ in (14)) make a significant contribution to both the excitation profile and the natural spectra of CARS. Their consideration is also necessary for a quantitative treatment of the experimental data for the excitation profile and CARS lines, and this will be treated in detail in the example of the biologically important molecule, β-carotene, in a separate work. We add here that an analogous procedure for studying the effect of a Gaussian inhomogeneity on the excitation profile of resonance Raman scattering lines [6] was successfully tested on carotinoids [7-9].

ფიზიკური ქიმია

ახალი ფორმულები გამხსნელებში მოლეკულების მიერ სინათლის კოჰერენტული ანტისტოქსური გაბნევის შესაბამისი აგზნების პროფილებისათვის

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(წარმოდგენილია აკადემიკოს გ. ცინცაძის მიერ)

კონდენსირებულ გარემოში მოლეკულების (მინარევული ცენტრების) მიერ სინათლის კოჰერენტული-ანტისტოქსური გაბნევის სპექტრებსა და შესაბამის აგზნების პროფილებზე გარემოს არაერთგვაროვნება საგრძნობ ზემოქმედებას ახდენს. ნაშრომში გაანალიზებულია გარსის აგზნების პროფილებზე გარემოს არაერთგვაროვნებისა და მოლეკულის შიდა რელაქსაციური პროცესების

ერთდროული და თანაზომიერი ზემოქმედების შედეგები. შედეგები ზოგადია და არაერთგვაროვნების მახასიათებელის (σ) და რელაქსაციური პარამეტრის (Γ) ნებისმიერი თანაფარდობისათვის სამართლიანია.

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Received December, 2013