

Resonant-absorption-enhanced Raman effect in gases

V. P. Safonov and B. M. Chernobrod

Institute of Automation and Electrometry, Siberian Branch, Academy of Sciences of the USSR

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Collisions between molecules which are at resonance with a strong field and nonresonant scattering molecules can substantially increase the effective cross section for Raman scattering.

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The sharp increase in the effective cross section for Raman scattering of molecules adsorbed on the surfaces of noble metals, "surface-enhanced Raman scattering," results from a local increase in the field of the light wave near a surface inhomogeneity.¹ Another mechanism for a local field intensification might be the proximity of a resonantly absorbing molecule to the scattering molecule. The external light field would induce an oscillating dipole moment in the resonantly absorbing molecule, which would result in the appearance near the dipole \mathbf{p} of an additional field

$$\mathbf{E}_g = \frac{1}{2} \frac{3(\mathbf{p}\mathbf{n})\mathbf{n} - \mathbf{p}}{r^3} + \text{c.c.} \quad (1)$$

At short distances r the field amplitude E_g may substantially exceed the external field amplitude E_0 and thus alter the intermolecular interaction, even giving rise to new bound states in several cases.²⁻⁴ It has been shown that the presence of resonantly absorbing impurity atoms in a solid substantially increases the efficiency of nonlinear processes such as the Raman effect⁵ and second-harmonic generation.⁶

In this letter we show that collisions of molecules which are involved in the Raman effect with molecules which are at resonance with the exciting field significantly increases the intensity of the Raman scattering in the quasistatic wing of the scattering line. In terms of elementary quantum processes, the effect may be interpreted as the transfer of excitation from the resonant molecule to the nonresonant molecule, accompanied by the emission of a photon which carries off the difference between the energies of the excited states of the molecules.

In describing the collision process we assume that the resonant molecule moves along a classical trajectory. The external field \mathbf{E}_0 induces in the resonant molecule a dipole moment which is described in the two-level approximation by

$$\mathbf{p} = \beta \mathbf{E}_0, \quad \beta = i |d_{mn}|^2 [2\hbar (1 + \frac{\kappa \Gamma^2}{\Gamma^2 + \Omega^2}) (i\Omega + \Gamma)^{-1}], \quad (2)$$

where $\kappa = 4|d_{mn}E_0|^2((2\hbar)^2\gamma\Gamma)^{-1}$, d_{mn} is a matrix element of the dipole moment of the transition with frequency ω_{mn} , Γ is the line width, γ is the probability for a spontaneous transition, and $\Omega = \omega - \omega_{mn}$. Expression (2) was derived under the assumption of homogeneous line broadening. The resonant molecule is acted upon by the field of the

dipole, E_g , in (1), where $r = [\rho^2 + (vt)^2]^{1/2}$, and ρ is the impact parameter. The probability for the emission of a photon at the Stokes frequency is

$$dW_k = \frac{c k^3}{16 \pi^2 \hbar} \left| \alpha_{iv} e'_v{}^* \int_{-\infty}^{\infty} dt E_{gi}(t) e^{i \Omega_k t + i \int_{-\infty}^t dr' \Delta U(r')} \right|^2 d\omega, \quad (3)$$

where $\Omega_k = \omega_k - \omega - \omega_{21} - \mathbf{k}\mathbf{v}$, α_{iv} is the scattering tensor, \mathbf{e}' is the polarization of the Stokes photon, $\Delta U = U_2 - U_1$, $U_{1,2}$ are the level shifts in the collision, and we assume $\Delta U = C_n/r^n$.

In the quasistatic approximation the integral in (3) is determined by the stationary-phase point $\Delta U = \Omega_k$. In this case the spectral intensity is given by

$$dI_k = \hbar \omega_k \int_{\rho_0}^{\infty} 2\pi\rho d\rho \int_0^{\infty} v dN_v \overline{dW_k} \approx \frac{k^4}{8} \left| \alpha_{iv} e_i e'_v{}^* \right|^2 \frac{|E_0|^2 |\beta|^2 N d\omega}{nC_n^{3/n} \Omega_k^{1-3/n}}, \quad (4)$$

where $\overline{dW_k}$ is the probability (3) averaged over all directions of the vector \mathbf{r} , N is the number density of resonant molecules, and ρ_0 is the minimum impact parameter. The vector \mathbf{e} does not coincide with the vector \mathbf{E}_0 , and in the case $\mathbf{E}_0 \parallel \mathbf{e}_z$ we have $\mathbf{e}(\sqrt{2/5}, \sqrt{3/10}, \sqrt{3/10})$. It is assumed here that the line shift is far greater than the reciprocal transit time, $\Delta U \gg v/\rho_0$, and if $\Delta U \ll v/\rho_0$, the line width is of order v/ρ_0 . With $v = 10^5$ cm/s and $\rho_0 = 4 \times 10^{-8}$ cm we would have 10 cm $^{-1}$.

The integrated intensity of the Raman scattering can be expressed in terms of the integrated intensity of ordinary Raman scattering in a field of amplitude E_0 with the polarization \mathbf{e} determined above:

$$dI = F dI_0, \quad dI_0 = \frac{ck^4}{8\pi} \left| \alpha_{iv} e_i e'_v{}^* \right|^2 |E_0|^2 d\omega, \quad (5)$$

where

$$F = \frac{\pi^2 N}{2\rho_0^3} \left[\frac{|d_{mn}|^2}{2\hbar \left(1 + \frac{\kappa \Gamma^2}{\Gamma^2 + \Omega^2}\right)} \right]^2 \frac{1}{\Gamma^2 + \Omega^2}. \quad (6)$$

To evaluate F we adopt the parameter values $\Omega = 0$, $\kappa < 1$, $|d_{mn}|^2 = 2.5 \times 10^{-35}$ esu, $\Gamma = 10^{10}$ s $^{-1}$, $\rho_0 = 4 \times 10^{-8}$ cm, and $N = 10^{16}$ cm $^{-3}$. We find $F \sim 10^3$.

Collisions of scattering molecules with resonantly absorbing molecules can thus increase the integrated intensity of the Raman scattering by three orders of magnitude. It should be noted that in the case of an absorbing resonant gas at these parameter values the absorption length and thus the thickness of the layer in which the enhanced Raman effect occurs are shorter than the wavelength. An amplifying medium does not suffer from this disadvantage. The method proposed by Zel'dovich and Kuz'michev⁶ for exciting the scattering, by means of coherent 2π pulses, can also be used in our case.

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