Dephasing in steady-state and time-varying spectroscopy

Yu. E. D'yakov

M. V. Lomonosov Moscow State University

The Green's function $h(t)$ describing the temporal response of a medium to a resonant field is determined for arbitrary pressures p and for an arbitrary dephasing correlation $B(\tau)$. The increase in the dephasing time corresponding to Dicke contraction and the identification of $B(\tau)$ from $h(t)$ are discussed. The theory agrees with data from picosecond coherent anti-Stokes Raman spectroscopy of hydrogen at pressures in the range $p = 10^{-2}$–10 atm.

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1. The major thrust in spectroscopy has traditionally been to analyze frequency characteristics, i.e., spectra.[1,2] Recently, however, time-varying spectroscopy has appeared on the scene and has been developed successfully. In this new approach, short light pulses are used to excite a transition,[3–5] and to describe experiments in this case we need to know the temporal response of the medium, i.e., its Green's function $h(t)$. This problem is also of interest in correlation spectroscopy,[6] since the correlation function for the field transmitted through a resonant medium is also expressed in terms of $h(\tau)$.

In time-varying (and correlation) spectroscopy, the quantity corresponding to the line width $\Delta\omega$, measured in steady-state frequency spectroscopy, is the *dephasing time* τ_φ, which may be defined as the time required for the function $h(t)$ to decay to a certain level $[h(\tau_\varphi): h_{\max} = e^{-m}]$. The time τ_φ is the same as the length of the polarization pulse $P_a(t)$ excited by a very short pulse of an external field (more on this below).

The quantity $\Delta\omega$ has a mimimum in a certain pressure region $p \approx p_0$:
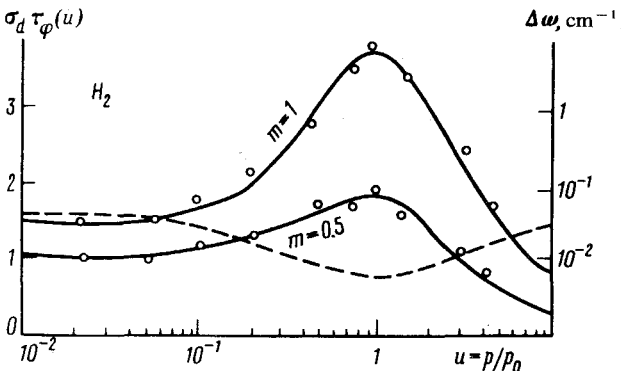

FIG. 1.

$\Delta\omega_{\min} = \Delta\omega(p_0)$ (Dicke contraction; see the dashed curve in Fig. 1). The pressure $p_0 = \sqrt{B/A}$ is a characteristic value in the sense that at this pressure the diffusion dephasing constants $D_c = AP$ and $D_d = B/p$ are equal in magnitude; these are the dephasing constants caused by collisions and the Doppler effect, respectively. This interesting and useful effect is also very informative, since if we know p_0 and $\Delta\omega_{\min}$ we find $\Delta\omega(p)$ for all p. Dicke contraction occurs, however, only for sufficiently light particles (hydrogen[7,8] and deuterium,[8] for example). For heavier particles, the function $\Delta\omega(p)$ does not have a minimum. It increases monotonically with increasing p (see, for example, the data on ammonium in Fig. 2.14 in Ref. 9).

2. In this letter we wish to call attention to some new possibilities in time-varying and correlation spectroscopy.

a) Corresponding to the minimum of $\Delta\omega(p)$, i.e., to Dicke contraction, is a maximum of the function $\tau_\varphi(p)$ at the same pressure p_0 (see the solid curves in Fig. 1). By increasing m, i.e., by expanding the range over which $P_a(t)$ is measured, we can make this maximum noticeable for *any* particles, including heavy particles, for which Dicke contraction cannot be observed.

b) In principle, by measuring $h(t)$ we could solve the *inverse problem*, i.e., find the correlation function of the dephasing noise. There is an interesting possibility here of taking this approach to measure the correlation function of the thermal velocities of particles, the velocities of turbulent flows, and, in general, the correlation functions for the velocities of any randomly moving Doppler reflectors of light, radio, and acoustic waves.

3. To demonstrate the feasibility of a) and b) we must determine the Green's function $h(t)$ for arbitrary p. This can be done by the following approach. The complex amplitudes of the fields at the entrance (a_0) and exit (a, A) of a thin layer of a medium are related to the complex amplitudes $P = \Sigma_{j=1}^N p_j$ of the resultant polarization by $a = a_0 - \gamma P$ (resonant absorption or amplification) and $A = \gamma P$ (resonant light scattering or optical frequency conversion). The observed fields are thus expressed in terms of P. To find P we work from the equation for the polarization of a single particle:

$$\dot{p}_j + [\alpha_0 + i\langle\nu\rangle + i\nu_j(t)]p_j = n_0 a_0(t) + \xi_j(t).$$

Here we have introduced random frequency fluctuations $\nu_j(t)$, i.e., the dephasing noise (which we will assume to be Gaussian), and $\xi_j(t)$, the spontaneous noise:

$$<\nu_j(t)\,\nu_l(t+\tau)> = B(\tau)\delta_{jl}, \qquad <\xi_j(t)\xi_l^*(t+\tau)> = 2C_0\delta(\tau)\delta_{jl}$$

(δ_{jl} is the Kronecker delta). As a result, we find P as the sum of an active component (i.e., a component induced by the external field a_0) and a spontaneous component: $P(t) = P_a(t) + P_{\rm sp}(t)$. Here

$$P_a(t) \approx n_0 \int_0^\infty h(\theta)\,a_0(t-\theta)\,d\theta, \quad (N \gg 1) \tag{1}$$

$$\left\langle P_{\rm sp}(t)P_{\rm sp}^*(t+\tau)\right\rangle = \frac{NC_0}{\alpha_0}\,h(|\tau|), \quad G_{\rm sp}(\omega) = \frac{NC_0}{\pi\alpha_0}\,{\rm Re}\,\chi(\omega); \tag{2}$$

The unknown Green's function $h(\theta)$ and the polarization susceptibility $\chi(\omega)$ are

$$h(\theta) = \exp[-\alpha_0\theta - i<\nu>\theta - L(\theta)] = \frac{1}{2\pi}\int_{-\infty}^{\infty}\chi(\omega)e^{i\omega\theta}d\omega \quad (\theta > 0)$$

$$\chi(\omega) = \int_0^{\infty} h(\theta)e^{-i\omega\theta}d\theta, \tag{3}$$

where

$$L(\theta) = \int_0^{\theta}(\theta - \theta')B(\theta')d\theta' = \begin{cases} \dfrac{1}{2}\sigma^2\theta^2 & (\theta \ll \tau_k), \\ D\cdot(\theta - \tau_0) & (\theta \gg \tau_k) \end{cases} \tag{4}$$

$D = \sigma^2\tau_k, \tau_k = \int_0^{\infty} R(\tau)d\tau$, and $\tau_0 = \int_0^{\infty}\tau R(\tau)d\tau/D, B(\tau) = \sigma^2 R(\tau)$ (see p. 152 in Ref. 10). We will ignore the shift of the resonance by $\langle\nu\rangle p$. Expression (1) for $P_a(t)$ is quite general, describing both linear and nonlinear methods for excitation of the resonance: single-photon excitation $(a_0 \sim b_1, \quad \omega_{12} = \omega_1)$, many-photon excitation $(a_0 \sim b_1^k, \quad \omega_{12} = k\omega_1, k - 2, 3, \ldots)$ biharmonic excitation, in particular, the method of coherent anti-Stokes Raman spectroscopy[4] $(a_0 \sim b_1 b_2^*, \omega_{12} = \omega_1 - \omega_2)$, etc. Here ω_{12} is the transition frequency, the ω_i are the frequencies of the external fields acting on the medium, and $b_i(t)$ are the amplitudes of these fields.

We consider two components of the dephasing noise, a collisional component and a Doppler component: $\nu_j = \nu_{j,c} + \nu_{j,d}, \langle\nu\rangle = \langle\nu\rangle_c$. If we assume these components to be statistically independent, then we have $B(\tau) = B_c(\tau) + B_d(\tau)$ and $L(\theta) = L_c(\theta) + L_d(\theta)$ in (4). In the collisional (diffusion) approximation we have $B_c(\tau) = 2D_c\delta(\tau)$, from which we find $L_c(\theta) = D_c\theta$, where $D_c = Ap \sim p$. For the Doppler component, for an arbitrary correlation coefficient $R_d(\tau)$, we can write the thermal velocities of the particles as $B_d(\tau) = \sigma_d^2 R_d(\tau)$, $\sigma_d^2 = k_0^2\sigma_v^2$ (k_0 is the wave number of the polarization quasiwave, and $\sigma_v^2 = kT/\mu_0$ is the variance of the thermal velocities), and we can write the correlation time as $\tau_d \sim p^{-1}$. We find $L_d(\theta) = \sigma_d^2 \int_0^{\theta}(\theta - \theta')\times R_d(\theta')d\theta'$ and then

$$L(\theta) = D_c\theta + \sigma_d^2 \int_0^{\theta}(\theta - \theta')R_d(\theta')d\theta' \tag{5}$$

In particular, if $R_d(\tau) = e^{-|\tau|/\tau d}$, we find from (5)

$$L(\theta) = D_c\theta + D_d(\theta - \tau_d + \tau_d e^{-\theta/\tau_d}), \tag{6}$$

where $D_d = \sigma_d^2\tau_d$. We introduce the dimensionless pressure $u = p/p_0$ and the parameter $\alpha = (Ap_0/\sigma_d)^2$. We can then write $D_c = \sigma_d\sqrt{\alpha}u$, $D_d = \sigma_d\sqrt{\alpha}/u$ and $\tau_d = \sqrt{\alpha}/\sigma_d u$.

4. If the transition is excited by a very short field pulse, then the response polarization pulse will have the same shape as the Green's function: $A(t) \sim P_a(t) \sim h(t)$ [this can be seen by substituting $a_0(t) \sim \delta(t)$ into (1)]. The dephasing time τ_φ is thus determined by the equation $L(\tau_\varphi) = m$ (if we ignore the natural line widths, we have $\alpha_0 = 0$). In the limit $p_0 \gg p \to$ (the Doppler limit) we have $\tau_d \to \infty$, and from (4) and (5)

we have $\tau_\varphi(p=0) = \sqrt{2m}/\sigma_d$. At sufficiently large values of $p \approx p_0$ and m, the pulse length $h(t)$ is measured nearly at its base, at $t \gg \tau_d$, and from (4) and (5) we find $L(t) \approx (D_c + D_d)t$. We then find $\tau_\varphi(p) = m/(Ap + B/p)$ and $\tau_{\varphi max}(p_0) = m/2\sigma_d\sqrt{\alpha}$. Working from the results of spectral-line theory, we can also write the following for spectra of the type in (2), which are proportional to $\mathrm{Re}\chi(\omega)$: $\Delta\omega(p=0) = \sqrt{8\ln 2}\sigma_d$, and $\Delta\omega_{min}(p_0) = 4\sigma_d\sqrt{\alpha}$. Thus we have

$$\frac{\tau_{\varphi,\,max}(p_0)}{\tau_\varphi(p=0)} = \sqrt{\frac{m}{8\alpha}}, \qquad \frac{\Delta\omega(p=0)}{\Delta\omega_{min}(p=p_0)} = \sqrt{\frac{\ln 2}{2\alpha}}. \qquad (7)$$

Relations (7) prove our assertion a): The maximum of τ_φ can be rendered noticeable for substances having an arbitrary value of α (it is sufficient to choose $m > 8\alpha$), while the minimum of $\Delta\omega$ will be observable only for substances having sufficiently small values $\alpha < \ln 2/2 \approx 0.35$. Furthermore, according to (3) and (4), the correlation function of the dephasing noise can be found from $h(t)$ or $L(t)$ by differentation, $B(\tau) = L(\tau) = (d/d\tau)^2 \ln h(\tau)$; this proves assertion b).

5. It follows from this analysis that the most informative methods are the methods of time-varying and correlation spectroscopy in which the Green's function $h(t)$ is measured directly (an example is the method of time-varying coherent anti-Stokes Raman spectroscopy[4,5]), and in which it is possible to solve the inverse problem. Spectral methods involving measurements of frequency characteristics of the type $\mathrm{Re}\chi(\omega) = \int_0^\infty h(\theta)\cos\omega\theta d\theta$ or $\mathrm{Im}\chi(\omega) = -\int_0^\infty h(\theta)\sin\omega\theta d\theta$ make it possible to reconstruct $h(t)$ by taking inverse Fourier transforms: $h(t) = (2/\pi)$.

$$\int_0^\infty \mathrm{Re}\chi(\omega)\cos\omega t d\omega = -(2/\pi)\int_0^\infty \mathrm{Im}\chi(\omega)\sin\omega t d\omega.$$

Less informative are the frequency methods, in which one measures spectra of the type $|\chi(\omega)|^2$ (in particular, steady-state coherent anti-Stokes Raman spectroscopy), since in this approach one loses information about the phase of $\chi(\omega)$, and $h(t)$ cannot be determined.

6. If a pulse $A_0(t) \sim h(t)$ is sent into a region filled with a nonresonant dispersive medium (a line of the optical fiber type for short pulses or a ring resonator for relatively long pulses), then as the pulse propagates it acquires the typical "spectron" shape; i.e., the envelope of the pulse assumes the shape of the envelope of the spectrum of the same pulse:

$$|A(t, z)| \sim |\chi(\omega = \theta/gz)|, \qquad \theta = t - z/u, \qquad g = \partial^2 k/\partial\omega^2.$$

This circumstance can be exploited to measure the function $|\chi(\omega)|$. This type of spectroscopy (involving a time sweep of the frequency spectrum) follows from the solution

$$A(t, z) = \frac{1}{\sqrt{2\pi i g z}} \int_{-\infty}^{\infty} A_0(\theta') e^{(i/2gz)(\theta - \theta')^2} d\theta' \approx \frac{e^{i\theta^2/2gz}}{\sqrt{2\pi i g z}} \int_{-\infty}^{\infty} A_0(\theta') e^{-(i\theta\theta'/gz)} d\theta'$$

of the equation $[\partial/\partial z + (1/u)(\partial/\partial t) - (ig/2)(\partial^2/\partial t^2)]A = 0$ (see, for example, p. 280 in

Ref. 10) over propagation distances $z \gg L_0$ greater than the dispersive-spreading length $L_0 = \tau_{in}^2/g$, where τ_{in} is the pulse length at the entrance (in the case at hand,[1]) $\tau_{in} = \tau_\varphi$).

7. The theory derived here for $L(\theta)$ in the form in (6) gives a good description of both the shape and length of the anti-Stokes emission pulses $|A_a(t)|^2 \approx h^2(t)$ observed in experiments with hydrogen ($\alpha \sim 0.02$) carried out by the method of time-varying coherent anti-Stokes Raman spectroscopy over a broad pressure range[5] $p = 10^{-2}\text{–}10$ atm (experimental values of τ_φ are shown by the points in Fig. 1).

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[1] An analogous result can be derived for *any* distance z because of the compression of the pulse $h(\theta)$, if we arrange a shift of the resonant frequency that is linear in the time: $\Delta\omega_{12}(t) = \dot{\omega}t$, where $\dot{\omega} = 1/gz$ [for example, by applying a Stark field of varying intensity, $\sim\Delta\omega_{12}(t)$].

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