SEMINAR 5

TIME-RESOLVED NEAR-RESONANCE PHOTON SCATTERING FROM COLLISIONALLY PERTURBED MOLECULES *

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Recent time-resolved photon-scattering experiments [1,2] have monitored the continuous "transition" from resonance fluorescence to near-resonance Raman scattering. A tunable laser pulse was scattered from a single rotational-vibrational level of the $B^3\Pi$ state of I_2 around 5145 Å. The time-profile of the scattered light was monitored at various values of the mean energy of the light pulse, using several gas pressures (0.03 torr and 0.25 torr). The pulse extinction time (~3 nsec) was considerably shorter than the level lifetime ($\Gamma^{-1} \sim 1$ μsec). The following experimental features were observed [1,2]:

(i) The time-resolved decay pattern is characterized by two types of modes: a long-lived mode with lifetime Γ^{-1}, and a mode characterized by the shorter lifetime of the pulse. At resonance ($\Delta = 0$), where Δ is the energy difference between the mean energy of the pulse and the molecular transition, only the "molecular" long-lived term [$\sim\exp(-\Gamma t)$] is observed.

(ii) The relative contribution, $\{R\}$, of the molecular long-lived component

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to the total intensity of the scattered light decreases on tuning Δ away from resonance, and becomes approximately constant at large Δ values.

(iii) Increasing the I_2 pressure results in an enhancement of the ratio $\{R\}$.

A basic result of the theory of resonance scattering [3] is that the time-delay, $\langle \Delta t \rangle$, of a wavepacket due to its interaction with a target is $\langle \Delta t \rangle = 2\Gamma/(\Delta^2 + \Gamma^2)$. On resonance we have $\langle \Delta t \rangle = 2/\Gamma$, a result compatible with observation (i) above. However, as $\Delta \to \infty$, $\langle \Delta t \rangle \to 0$, i.e., far off-resonance only a direct scattering process prevails. This general conclusion is incompatible with observation (ii) as $\{R\}$ should vanish when $\Delta \to \infty$. We are thus led to the conclusion that even at pressures as low as 0.03 torr, collisional effects play an important role in photon scattering in this system.

We shall present here the results of a quantum-mechanical treatment [4–6] of photon scattering by collisionally perturbed molecules. The various decay matrices (including spontaneous emission) appear naturally in our formalism, avoiding the phenomenological treatment of the relevant decay processes made in previous works. We shall subsequently specialize to a simple molecular model, which yields qualitative agreement with the recent experimental results for the pressure dependence of time-resolved photon scattering from I_2 [1,2].

The total Hamiltonian for our system is [5,6]

$$\begin{aligned} H &= H_0 + H_v , \\ H_0 &= H_m + H_b + H_r , \\ H_v &= H_{mr} + H_{mb} . \end{aligned} \tag{1}$$

The various terms in eq. (1), as well as the relevant eigenstates of H_0, are defined in table 1.

We consider a molecule characterized by a single ground level $|g\rangle$ which is radiatively coupled (near resonance) to another single electronically excited rotational level $|j\rangle = |sj, \text{vac}\rangle$. $|j\rangle$ is a part of a rotational manifold $\{|i\rangle\}$. We further assume that inelastic molecular collisions can induce transitions within the manifold, as well as predissociation. Vibrational relaxation is neglected, as vibrational energy differences are considerably larger than rotational spacings. Also, we neglect electronic relaxation (other than predissociation). In a simple model calculation, all the $\{|i\rangle\}$ levels are assumed to have the same radiative lifetime Γ_s^{-1} whereupon the rate of spontaneous emission is

$$F(\Delta, t) = \Gamma_s P_s(\Delta, t) , \tag{2}$$

where $P_s(\Delta, t)$ is the total population of the excited band $\{|i\rangle\}$ obtained by taking the trace of the density matrix, $\rho_{mrb}(t)$, for the entire system, over

Table 1
Definition of the system's Hamiltonian and the zero-order eigenstates

Term	Definition	Eigenstates
H_m	Molecular Hamiltonian	$\|g\rangle$ ground state $\left.\begin{matrix}\|s1\rangle \\ \|s2\rangle \\ \vdots \\ \|sn\rangle\end{matrix}\right\}$ a set of closely lying excited states
H_r	Free radiation field Hamiltonian	$\|vac\rangle$ vacuum state $\|k\rangle$ one-photon state (k being the photon wave vector)
H_b	Bath Hamiltonian	$\|b\rangle$ bath states
$H_m + H_r$	Combined radiation + molecular Hamiltonian	$\|g, k\rangle \equiv \|k\rangle$ $\|si, vac\rangle \equiv \|i\rangle$ (in the rotating wave approximation)
$H_0 = H_m + H_r + H_b$	Zero-order Hamiltonian	
H_{mr}	Molecule-radiation interaction	
H_{mb}	Molecule-bath interaction	

the bath and over the $\{|i\rangle\}$ states,

$$P_s(\Delta, t) = \sum_b \sum_i \langle i, b|\rho_{mrb}(t)|i, b\rangle . \tag{3}$$

Eqs. (2) and (3) describe molecules corresponding to a single velocity-group. The experimental photon counting rate $\{F(\Delta, t)\}$ from a gas at thermal equilibrium is obtained by convoluting eq. (2) with the Doppler profile $f(\Delta)$

$$\{F(\Delta, t)\} = \int d\Delta' F(\Delta', t) f(\Delta - \Delta') \equiv F * f , \tag{4}$$

where

$$f(\Delta) = (\pi\beta^2)^{-1/2} \exp(-\Delta^2/\beta^2) \tag{5}$$

and β is the Doppler width.

Using the equation of motion of the density matrix in Liouville space [7,8]

we obtain, to second order in the applied field, and within the framework of the rotating-wave approximation [5]

$$P_s(\Delta, t) = -2 \,\mathrm{Re} \sum_i |\mu_{jg}|^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathrm{d}\tau \, \mathrm{d}\tau' \, \theta(t-\tau)$$

$$\times \theta(t-\tau') \, \varphi(\tau)\varphi(\tau') \, \langle\langle ii|\underset{\approx}{G}_1(t-\tau)|jj\rangle\rangle \langle\langle jk|\underset{\approx}{G}_2(t-\tau')|jk\rangle\rangle \,. \tag{6}$$

Here θ is the Heavyside step function, μ_{jg} is the transition dipole matrix element and $\varphi(\tau)$ is the envelope of the light pulse,

$$E(\tau) = \varphi(\tau) \exp[-i\bar{k}(c\tau - z)] \,, \tag{7}$$

$\underset{\approx}{G}_1$ and $\underset{\approx}{G}_2$ are tetradic retarded propagators related to the relaxation matrices for populations (T_1) and for optical coherence (T_2), respectively. We are using here the double bracket notation [7,8], where $|\alpha\beta\rangle\rangle$ is the Liouville-space vector corresponding to the transition operator $|\alpha\rangle\langle\beta|$.

We have derived [5,6] explicit formal expressions for $\underset{\approx}{G}_1$ and $\underset{\approx}{G}_2$ using the Fano-Zwanzig projection-operators technique [9,10]. Assuming short correlation times for collisions with the bath, these reduce to the form

$$\underset{\approx}{G}_1(t) = \theta(t) \exp(-\tfrac{1}{2} \underset{\approx}{\Gamma}_1 t) \,, \tag{8a}$$

$$\underset{\approx}{G}_2(t) = \theta(t) \exp[-(i\underset{\approx}{\Omega} + \underset{\approx}{\Gamma}_2) t] \,, \tag{8b}$$

where $\underset{\approx}{\Omega}$ and $\underset{\approx}{\Gamma}_i$ correspond to the line-frequency and the damping matrices respectively.

For a two-level system ($|g\rangle$ and $|j\rangle$) the matrices $\underset{\approx}{G}_1$ and $\underset{\approx}{G}_2$ are scalars and we get

$$P_s(\Delta, t) = P_j(\Delta, t) = |\mu_{jg}|^2 \int_{-\infty}^{t} \int_{-\infty}^{t} \mathrm{d}\tau \, \mathrm{d}\tau' \varphi(\tau) \, \varphi(\tau')$$

$$\times \exp[-\tfrac{1}{2}\Gamma_1(2t - \tau - \tau')] \exp[(i\Delta - \hat{\Gamma})(\tau' - \tau)] \,, \tag{9}$$

where

$$\hat{\Gamma} = \Gamma_2 - \tfrac{1}{2}\Gamma_1 = \frac{1}{T_2} - \frac{1}{2T_1} \,, \tag{9a}$$

and

$$\Delta = E_j - E_g - \hbar\bar{k}c \,, \tag{9b}$$

is the off-resonance parameter. Strictly speaking, the level energies E_j, E_g should be corrected by a frequency shift included in Ω. However, since we are interested in a simple model we shall hereafter neglect this shift. In a more complicated situation the matrices $\underset{\approx}{G}_1$ and $\underset{\approx}{G}_2$ can be generally calculated using the formalism described elsewhere [5,6].

We shall now confine the discussion to a simple model for the multilevel system. We take $\underset{\approx}{\Gamma}_1$ to be an $n \times n$ matrix

$$\langle\langle jj|\underset{\approx}{\Gamma}_1|ii\rangle\rangle = \Gamma_1'\delta_{ij} - (1-\delta_{ij})\,\Gamma_1'' \qquad (i,j = 1,2,3,\ldots,n)\,, \tag{10}$$

assuming that all the n excited levels are characterized by the same damping rate Γ_1' and cross relaxation Γ_1'', the tetradic vector $\Sigma_i\langle\langle ii|$ is then an eigenvector of $\underset{\approx}{\Gamma}_1$, with the eigenvalue

$$\Gamma_1 = \Gamma_1' - (n-1)\,\Gamma_1''\,. \tag{11}$$

This property enables us to simplify eq. (6) considerably, making the replacement $\Sigma_i\langle\langle ii|G_1(\tau) = \Sigma_i\langle\langle ii|\exp(-\Gamma_1\tau)$. Next, we consider the T_2 propagator $\underset{\approx}{G}_2$. In the case of a sharply-defined near resonance transition $|g\rangle \rightarrow |j\rangle$ we need only the single term [7]

$$\Gamma_2 \equiv (\underset{\approx}{\Gamma}_2)_{j\bar{k},j\bar{k}} = \tfrac{1}{2}(\Gamma_j + \Gamma_{\bar{k}}) + \Gamma_2'\,, \tag{12}$$

where $\frac{1}{2}(\Gamma_j + \Gamma_{\bar{k}})$ is a T_1 contribution to T_2, whereas Γ_2' represents true T_2 processes (i.e., the contribution of phase-changing collisions). Neglecting the relaxations in the ground state, we have $\Gamma_{\bar{k}} = 0$ and $\Gamma_j = \Gamma_1'$. Thus $\Gamma_2 = \frac{1}{2}\Gamma_j + \Gamma_2' = \frac{1}{2}\Gamma_1' + \Gamma_2'$.

Using the relaxation matrices eqs. (10) and (12), the photon counting rate now assumes the same form as for the two-level system eqs. (2), and (9) where Γ_1 and Γ_2 are defined by eqs. (11) and (12). Eqs. (9) may be rearranged and the experimental photon counting rate at finite pressure, eq. (2), is finally expressed in the form of the triple convolution

$$F(\Delta, t) = \iint \mathrm{d}\Delta'\,\mathrm{d}\Delta'' F^0(\Delta - \Delta', t)$$

$$\times\, L(\Delta' - \Delta'')\, f(\Delta'') = F^0 * L * f\,. \tag{13}$$

Here F^0 is the photon counting rate given by eq. (9) with $\hat{\Gamma} = 0$. It depends on Γ_1 only, and since Γ_1 includes pressure-independent contributions (whereas $\hat{\Gamma}$ includes only collisional effects), we can regard it as an "isolated-mole-

cule" photon counting rate. At finite pressures, however, Γ_1 includes collisional contributions (such as predissociation) as well. The function L in eq. (13) is a Lorentzian

$$L(\Delta) = (\hat{\Gamma}/\pi)/(\Delta^2 + \hat{\Gamma}^2)\,, \tag{14}$$

whose width is given by

$$\hat{\Gamma} = \Gamma_2 - \tfrac{1}{2}\Gamma_1\,. \tag{14a}$$

In order to provide a quantitative interpretation of the recent experimental data [1,2] we shall consider the following model for the light-pulse envelope

$$\varphi(t) = \begin{cases} \exp(\frac{1}{2}\gamma_1 t) & t < 0 \\ 1 & 0 < t < T \\ \exp[-\frac{1}{2}\gamma_1 (t - T)] & t > T\,. \end{cases} \tag{15}$$

For the "isolated-molecule" case we can then write

$$F^0(\Delta, t) = |\Phi(\Delta, t)|^2\,, \tag{16}$$

where, for $t > \Gamma$, $\Phi(t)$ is given by [4]

$$\Phi(t) = A_p \exp[-\tfrac{1}{2}\gamma_2 (t - T)] - A_s \exp[-(i\Delta + \tfrac{1}{2}\Gamma_1)(t - T)]\,, \tag{17}$$

with

$$A_p = \left[\Delta + \frac{i}{2}(\Gamma_1 - \gamma_2)\right]^{-1}\,, \tag{17a}$$

$$A_s = \left[\Delta + \frac{i}{2}(\Gamma_1 - \gamma_2)\right]^{-1} - \left(\Delta + \frac{i}{2}\Gamma_1\right)^{-1} + \exp(-\tfrac{1}{2}\Gamma_1 T + i\Delta T)\left\{\left(\Delta + \frac{i}{2}\Gamma_1\right)^{-1} - \left[\Delta + \frac{i}{2}(\Gamma_1 + \gamma_1)\right]^{-1}\right\}\,. \tag{17b}$$

The ratio $\{R\}$ of the long-lived component (I_M) to the total scattered inten-

sity (I_T) defined at $t = T$ is thus

$$\{R\} \equiv I_M/I_T = \frac{|A_s|^2 * f * L}{|\Phi(T)|^2 * f * L} \,. \tag{18}$$

Eqs. (13) through (18) constitute our basic results. In figs. 1 and 2 we present some numerical model calculations for $\{F(\Delta, t)\}$ *versus* t at several values of Δ and for $\{R\}$ *versus* Δ for various values of $\hat{\Gamma}/\Gamma_1$. The results are in qualitative agreement with all the experimental features [1,2]. In particular, we note that:

(i) For $t > T$, the decay pattern consists of a short-lived component (with lifetime $\simeq \gamma_2^{-1}$) and a long-lived molecular component (with lifetime Γ_1^{-1}). The ratio $\{R\}$ of eq. (18) is unity at exact resonance ($\Delta = 0$) and decreases as Δ increases.

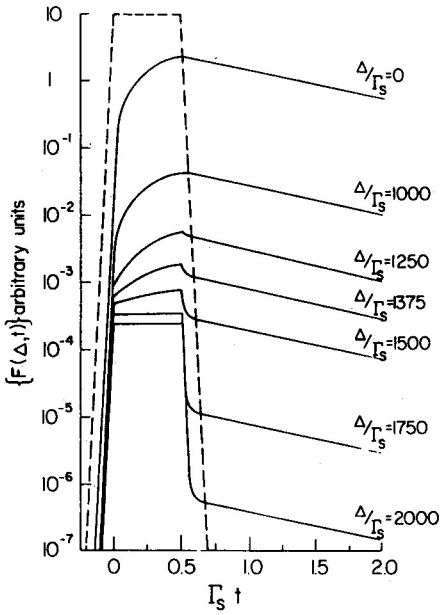

Fig. 1. The time resolution of the photon counting rate $\{F(\Delta, t)\}$ (in arbitrary units) in the absence of collisions for various values of the off-resonance energy Δ, the Doppler width (in units of the radiative damping) is $\beta/\Gamma_s = 500$; the rise and fall times of the pulse are γ_1/Γ_s $\gamma_2/\Gamma_s = 100$; the inverse duration of the pulse is $T^{-1}/\Gamma_s = 2$. The dotted line is proportional to the pulse time-resolved intensity.

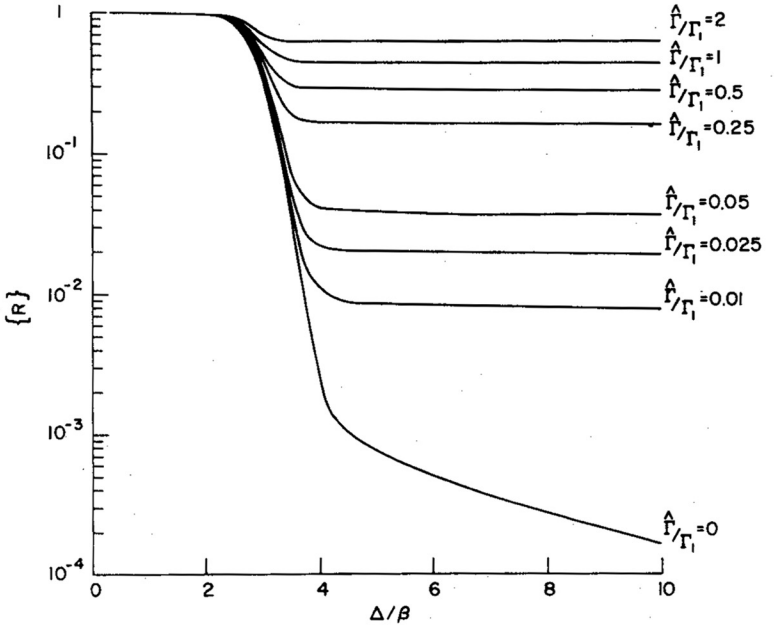

Fig. 2. The intensity ratio $\{R\}$ between the slowly decaying component and the total photon-counting rate, evaluated at $t = T$, as a function of the off-resonance parameter Δ, at different values of the collision-rboadening rate $\hat{\Gamma}$. Other parameters same as in fig. 1.

(ii) In the "isolated-molecule" case ($\hat{\Gamma} = 0$) we have for $\Delta \gg \beta, \gamma_1, \gamma_2$,

$$I_M \propto \Delta^{-4} , \tag{19a}$$

$$I_T \propto \Delta^{-2} , \tag{19b}$$

and consequently

$$\{R\} \propto \Delta^{-2} . \tag{19c}$$

This result concurs with our general argument which rests on the lifetime matrix formalism described earlier. However, at finite pressures, I_M and I_T should be convoluted with the Lorentzian (14). As a result they both behave asymptotically as Δ^{-2}, and $\{R\} \to$ const. (see fig. 2) in agreement with the experimental results [1,2].

(iii) Since F^0 is a decreasing function of Δ, and therefore values of Δ' satis-

fying $|\Delta - \Delta'| < \Delta$ influence the convolution (13) more than Δ' values satisfying $|\Delta - \Delta'| > \Delta$, the convolution of F^0 with L results in a behavior more closely resembling the resonance ($\Delta = 0$) case. This observation explains why $\{R\}$ increases with increasing $\hat{\Gamma}$ (which in turn is proportional to pressure), in agreement with experiment.

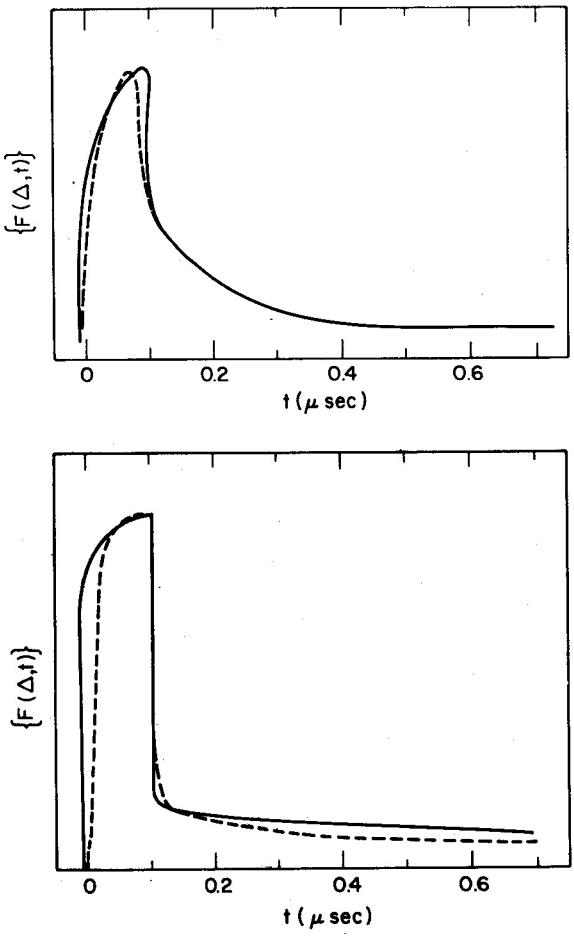

Fig. 3. Comparison of the experimental results (dashed line) of the resolved photon scattering in I_2 with our model calculations (solid line) $\Delta = 1.7$ GHz, $\beta = 0.4$ GHz, $\hat{\Gamma} = 14$ MHz(P/torr), $\gamma_1 = \gamma_2 = 0.75$ GHz, $T = 0.1$ μsec. (a) $P = 0.03$ torr, $\Gamma_1 = 0.9$ MHz. (b) $P = 0.25$ torr, $\Gamma_1 = 4.5$ MHz.

We shall now turn to a detailed comparison of the conclusions of our model with experiment. To do so, we first summarize the relevant available experimental data on I_2 near 5145 Å:

(i) From fluorescence quenching experiments [11] it was found that the levels of I_2 around 5145 Å are subjected to spontaneous and collisionally induced predissociation. We have

$$\Gamma_1 = \Gamma_s + a(P/\text{torr}), \tag{20}$$

where (at room temperature)

$$a = 2.264(\sigma/\text{Å}^2). \tag{20a}$$

Here

$$\sigma = 70\ \text{Å}^2 \tag{20b}$$

is the cross section for collisionally induced predissociation. $\Gamma_s = 4.2 \times 10^5$ sec^{-1} is the inverse lifetime of the collision-free molecule (including spontaneous predissociation and radiative damping).

(ii) $\hat{\Gamma}$ may be evaluated [6] from high-resolution spectral measurements [2]. The ratio of the integrated intensities of the sharp Raman lines and of

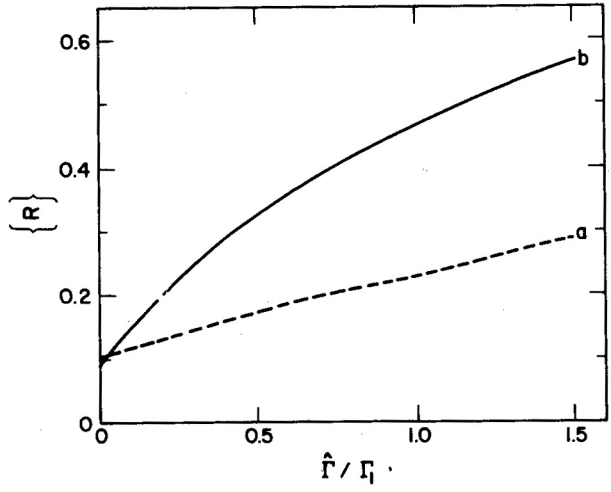

Fig. 4. The intensity ratio $\{R\}$ between the slowly decaying component and the total photon-counting rate, evaluated at $t = T$, as a function of the off-resonance parameter Δ, at different values of the collision-broadening rate $\hat{\Gamma}$. Other parameters same as in fig. 3. (a) $P = 0.03$ torr. (b) $P = 0.25$ torr.

Table 2
Comparison of the calculated intensity ratio $\{R\}$ (eq. (18)) with the experimental results (The off-resonance energy $\Delta = 1.7$ GHz, $\beta = 0.4$ GHz, $\gamma_1 = \gamma_2 = 0.75$ GHz and $T = 0.1$ μsec)

		$P = 0$	$P = 0.03$ torr	$P = 0.25$ torr
Γ_1	from self quenching data (MHz)[a]	0.42	0.9	4.5
$\hat{\Gamma}$	(MHz)[b]	0	0.43	3.6
$\{R\}$	theory	0.10	0.17	0.42
$\{R\}$	experiment	unavailable	0.14	0.45

a) Ref. [11].
b) Estimated from the value of $\hat{\Gamma}/\Gamma_1$ obtained from the energy resolved spectral data of ref. [2], and the value of Γ_1 obtained from the self-quenching data of ref. [11].

the broadened "redistribution" term [2] (0.8 at 0.25 torr) is just $\hat{\Gamma}/\Gamma_1$. We can then estimate $\hat{\Gamma} = 14$ MHz (P/torr).

(iii) The pulse parameters [1] (eq. (15)) were taken as $T = 0.1$ μsec and $\gamma_1 = \gamma_2 = 0.75$ GHz. The Doppler width is $\beta = 0.4$ GHz. The off-resonance parameter in ref. [2] was $\Delta = 1.7$ GHz.

Using all these data we have calculated the time profile of the scattered light at the pressures studied experimentally [2] (0.03 torr and 0.25 torr), as presented in fig. 3. To gain an insight in the sensitivity of our results to the variations of $\hat{\Gamma}$ we plot $\{R\}$ *versus* $\hat{\Gamma}$ in fig. 4. The qualitatively good agreement of our calculations with experiment is evident from table 2.

We have thus advanced a simple solvable model for scattering of a weak light pulse from a collisionally perturbed molecular resonance. The same solution could be obtained from the Bloch equations to second order in the applied field. Extension of the treatment to strong light pulses (i.e., saturation effects) may be obtained by a numerical solution of the Bloch equations. From the experimental point of view it will be interesting to (a) perform further studies with foreign gas broadening, (b) investigate the dependence of the time profile on the light intensity, and (c) try to study time-resolved photon scattering resulting from excitation by two photons travelling in opposite directions [12]. Doppler-free scattering experiments of the latter type will result in new information regarding some salient features of collisional effects.

Note added in proof. The numerical results presented here are in qualitative agreement with experiment. A more detailed and quantitative comparison with experiment is presented in ref. [6].

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