# Time-resolved light scattering from a collisionally perturbed molecular resonance

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Time-resolved near-resonance photon scattering in a gas is expressed in terms of a triple convolution of the photon counting rate from a single resonance (characterized by a total width which contains additive contributions from radiative decay, spontaneous predissociation, and collisionally induced predissociation) with a Lorentzian profile, which incorporates the effects of collisionally induced intrastate cross relaxation and phase shifts, and with a Doppler–Gaussian profile. This theory provides a quantitative picture for the recent experimental data of Rousseau, Patterson, and Williams [Phys. Rev. Lett. **34**, 1306 (1975)] on photon scattering from collisionally perturbed molecular iodine.

The experimental work of Williams, Rousseau, and Dworetsky[1] on time-resolved photon scattering from molecular iodine triggered considerable theoretical activity in this field.[2–7] Indeed, the fundamental problem of the "transition" from resonance fluorescence to near-resonance photon scattering from a molecular resonance is intimately related to the general areas of radiationless transitions[2] and resonance Raman scattering[1,8,9] in molecules and solids. In the work of Williams *et al.*,[1] the time-resolved photon scattering was determined as a function of the off-resonance energy $\Delta = |\bar{E}_s - \bar{k}|$, separating the center, $\bar{E}_s$, of the molecular resonance and the center, $\bar{k}$, of the photon wavepacket. The exciting light pulse is characterized by the amplitude[2,3]

$$\varphi(t) = \begin{cases} \exp(\gamma_1 t/2) & t<0 \\ 1 & 0<t<T \\ \exp[-\gamma_2(t-T)/2] & t>T\,, \end{cases} \tag{1}$$

where $\gamma_1^{-1}$ and $\gamma_2^{-1}$ correspond to the risetime and to the falltime of the pulse, respectively, while $T$ is the pulse duration and $T \gg \gamma_1^{-1}$, $\gamma_2^{-1}$. Additional physical parameters are the width $\Gamma_1$ of the molecular resonance, which at zero pressure incorporated additive contributions[2,3,10] from radiative decay and spontaneous predissociation,[10,11] and the Doppler width $\beta$, where $\beta \gg \Gamma_s$. The following experimental observations were recorded:[1]

(a) In the case of resonance excitation, i.e., $\Delta < \beta$, only a long, molecular-type, decay component was observed.

(b) When the off-resonance energy is large, i.e., $\Delta > \beta$, $\gamma_1 + \gamma_2 > \Gamma_1 \sim T^{-1}$, two major decay modes are exhibited for $t > T$, characterized by the lifetimes $\gamma_2^{-1}$ and $\Gamma_1^{-1}$.

(c) At moderately low pressures ($p = 0.03$ torr), the relative contribution, $\{R\}$, of the long-lived decay component to the total intensity at $t = T$ is a slowly varying function of $\Delta$ at off resonance, becoming constant at large values of $\Delta$.

(d) Increasing the pressure to 0.25 torr results in an appreciable enhancement of the intensity ratio $\{R\}$ at off resonance.

The time-resolved photon counting rate from a single molecule, which was investigated by several groups,[2–8] depends crucially on the energy distribution of the Fourier components $A_k$ of the exciting pulse, in particular on whether $A_k$ decays assymptotically slower or faster than the Lorentzian line shape of the "isolated" molecular resonance. In the former case, for example, for an exponentially decaying pulse[2,4] $\varphi(t) = 0$ $(t<0)$, $\varphi(t) = \exp(-\gamma_2 t)$ $(t>0)$, or for a rectangular pulse function[2] $\varphi(t) = 0$ $(t<0)$, $\varphi(t) = \text{const}(0<t<T)$, $\varphi(t) = 0$ $(t>T)$, $\varphi(t)$ will have sufficient Fourier components at resonance so that the long molecular component will be prominent in the photon-scattering pattern. In the latter case, e.g., the limiting case of Eq. (1) with $T = 0$,[5] or the realistic pulse shape,[2,3,6] Eq. (1), both direct scattering and a molecular decay component will be exhibited. Several papers[2,5] have independently concluded, in contrast to the original interpretation,[1] that the time-resolved photon scattering from an "isolated" molecular resonance is characterized by two types of lifetimes $\gamma_2^{-1}$ and $\Gamma_1^{-1}$, and no new observable decay modes are exhibited when the excitation is tuned away from resonance, in agreement with observation (a). The work of Berg, Langhoff, and Robinson[5] and of Hilborn[7] cannot account for the experimental features (b) and (c). A quantitative calculation[2,3,6] for scattering of the pulse given by Eq. (1) from an isolated molecular resonance including the effect of Doppler broadening,[12] results in the asymptotic relation $\{R\} \propto \Delta^{-2} (\Delta \gg \beta)$, rather than $\{R\} = \text{const} (\Delta \gg \beta)$. To overcome this difficulty, Metiu, Ross, and Nitzan[6] have proposed that our use[2,3] of uncertainty-limited photon wavepackets should be modified, allowing for independent time and energy profiles of the light pulse, and that a Lorentzian distribution function of one-photon wavepackets accounts for observation (b). On the other hand, we have proposed[3] that in this system, even at the lowest pressure (0.03 torr) which was experimentally studied, collisional perturbations dominate the time-resolved photon scattering pattern. The role of col-

  

lisional perturbations on time-resolved near-resonant photon scattering was studied by Huber[8b] and by the present authors.[3] In Huber's work,[8b] a two-level system was considered where phase shifts were simulated by random fluctuations of the energy separation. Our approach,[3] which rests on the effective-Liouvillian formalism, handles a manifold of excited levels and allows for cross-relaxation effects between these states. The purpose of the present note is twofold. First, we would like to point out that the recent quantitative experimental observations of Rousseau, Patterson and Williams[13] of time-resolved (and energy-resolved) photon scattering from molecular $I_2$ using 5145 Å excitation at $p = 0.03$ torr and at $p = 0.25$ torr, provide an overwhelming support to our original approach. Second, we would like to provide a generalization of our previous treatment[3] and to present a complete analysis of time-resolved photon scattering from a realistic molecular system subjected to radiative decay, spontaneous predissociation, collisionally induced predissociation, collisionally induced cross relaxation within the excited manifold, and phase-changing collisions (true $T_2$ processes) as is appropriate[3,11] for the $B^3\Pi$ state of $I_2$.

The theory of simultaneous collisional and radiative damping effects in a molecular system was previously handled by us[3] utilizing an effective-Liouvillian formalism, and these results will be now generalized to incorporate the effects of collisionally induced predissociation. First we would like to emphasize that pressure broadening effects cannot be elucidated by a naive extension of the results for photon scattering from an isolated molecule by just modifying the molecular decay width $\Gamma_1$ with the addition of a pressure-dependent term. The photon counting rate under collisional perturbations involves both $T_1$-type (level relaxation) processes and $T_2$-type (line broadening) contributions. In the present case the following collisional effects have to be considered:

I. collisionally induced predissociation ($T_1$ process);

II. vibrational–rotational cross relaxation ($T_1$ processes);

III. relaxation of optical coherences between the lower and upper states due to phase-changing collisions ($T_2$ process).

The level scheme for simultaneous collisional and radiative coupling is portrayed in Fig. 1. We consider a manifold $\{|si\rangle\}$ of $n$ vibrational–rotational levels

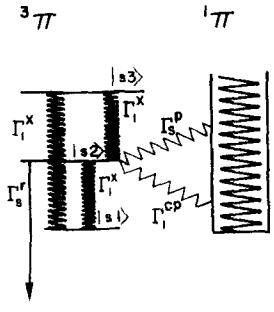


FIG. 1. A schematic energy level scheme for spontaneous radiative and nonradiative decay together with collisional perturbations of a molecular system.

corresponding to the $B^3\Pi$ electronic configuration. The $T_1$ relaxation processes are specified in terms of the following damping matrix:

$$(\Gamma_1)_{ii} = \Gamma_s + \Gamma_1^{cp} + (n-1)\Gamma_1^x , \tag{2}$$

$$\Gamma_s = \Gamma_s^r + \Gamma_s^p , \tag{2'}$$

$$(\Gamma_1)_{ij} = -\Gamma_1^x \quad (i \neq j) . \tag{3}$$

The indices $i$ and $j$ refer to $|si, si\rangle\rangle$ and $|sj, sj\rangle\rangle$ in the double bracket notation.[14,15] $\Gamma_s$ is the total width of the "collision free" $|si\rangle$ level consisting of additive contributions from radiative decay, $\Gamma_s^r$, and from spontaneous predissociation $\Gamma_s^p$; $\Gamma_1^{cp}$ is the contribution of collisionally induced predissociation. $\Gamma_1^x$ is the cross-relaxation rate, its negative sign results from general unitary properties.[14] In expressing the diagonal damping terms and the off-diagonal cross-relaxation terms of the $T_1$ matrix, we have involved the assumption of "level democracy" assuming that there are altogether $n|si\rangle$ levels all of which are characterized by the same damping and cross-relaxation rates. The damping matrix for $T_2$ processes is diagonal, within the framework of the rotating-wave approximation, and for our "democratic" level scheme it assumes the form

$$(\Gamma_2)_{ij} = \{\tfrac{1}{2}[\Gamma_s + \Gamma_1^{cp} + (n-1)\Gamma_1^x] + \Gamma_2^{ps}\}\delta_{ij} , \tag{4}$$

where $i \equiv |si, gk\rangle\rangle$, $|gk\rangle$ being a one-photon ground electronic state. $\Gamma_2^{ps}$ corresponds to phase shift contributions, i.e., proper $T_2$ processes. The photon counting rate $\langle F(t)\rangle$ is expressed in the form[3]

$$\langle F(t)\rangle = \int_{-\infty}^{\infty} d\Delta' \int_{-\infty}^{\infty} d\Delta'' I(\Delta'', t) f(\Delta' - \Delta'') C(\Delta - \Delta') \equiv I * f * C , \tag{5}$$

where * stands for a convolution. Equation (15) constitutes a triple convolution of the photon counting rate from a single resonance

$$I(\Delta, t) = \left| \int_{-\infty}^{t} d\tau\, \varphi(t) \exp[-\Gamma_1(t-\tau) - i\Delta(t-\tau)] \right|^2 \tag{6}$$

which is characterized by the decay width

$$\Gamma_1 = \Gamma_s^r + \Gamma_s^p + \Gamma_1^{cp} = \sum_j (\Gamma_1)_{ij} \tag{7}$$

with a Doppler–Gaussian distribution

$$f(\Delta) = (\pi\beta^2)^{-1/2} \exp(-\Delta^2/\beta^2) \tag{8}$$

and with a Lorentzian-type collisional term

$$C(\Delta) = (\hat{\Gamma}/2\pi)/(\Delta^2 + \hat{\Gamma}^2) , \tag{9}$$

where

$$\hat{\Gamma} = \Gamma_2^{ps} + \tfrac{1}{2}(n-1)\Gamma_1^x = (\Gamma_2)_{ii} - \tfrac{1}{2}\Gamma_1 . \tag{10}$$

The collisional width $\hat{\Gamma}$ in Eq. (9) incorporates only effects due to intrastate cross relaxation and to "proper" $T_2$-type processes originating from phase-changing collisions.

Utilizing Eqs. (1) and (6) we can now separate $I$ for $t \geq T$ into two components

$$I(\Delta, t) = I_p(t) + I_m(t) , \quad t \geq T . \tag{11}$$

$I_p(t)$ and $I_m(t)$ correspond to "direct" photon scattering and to molecular fluorescence specified in terms of the molecular decay time $\Gamma_1^{-1}$, respectively. These are given by

$$I_p(t) = |A_p|^2 \exp[-\gamma_2(t-T)] - 2\,\mathrm{Re}\{A_p^* A_s \times \exp[i\Delta(t-T)] \exp[-\tfrac{1}{2}(\gamma_2+\Gamma_1)(t-T)]\}\,, \quad (12a)$$

$$I_m(t) = |A_s|^2 \exp[-\Gamma_1(t-T)]\,, \quad (12b)$$

where

$$A_p = [\Delta + \tfrac{1}{2}i(\Gamma_1 - \gamma_2)]^{-1} \quad (13a)$$

and

$$A_s = [\Delta + \tfrac{1}{2}i(\Gamma_1 - \gamma_2)]^{-1} - (\Delta + \tfrac{1}{2}i\Gamma_1)^{-1} + \exp[-\tfrac{1}{2}\Gamma_1 T + i\Delta T] \times \{(\Delta + \tfrac{1}{2}i\Gamma_1)^{-1} - [\Delta + \tfrac{1}{2}i(\Gamma_1+\gamma_1)]^{-1}\}\,. \quad (13b)$$

The relative contribution of the long-lived molecular component to the total photon counting rate at $t = T$ is given by

$$\{R\} = \frac{I_m(T) * f * C}{[I_p(T) + I_m(T)] * f * C}\,. \quad (14)$$

Concerning the general features of the time-resolved photon scattering, we note that the short decay component $\langle I_p(t)\rangle \equiv I_p * f * C$ originates from a "direct" quantum mechanical scattering process while the "molecular" component $\langle I_m(t)\rangle \equiv I_m * f * C$ arises from the decay of collisionally perturbed molecular states, in a manner independent of the variation of the exciting pulse. Different Fourier components of the light pulse contribute to $\langle I_p\rangle$ and $\langle I_m\rangle$. Collisional effects enter in two different ways in this formalism. First, the contribution of $\Gamma_1^{c,p}$ to $\Gamma_1$, Eq. (7), modifies the decay time of $\langle I_m(t)\rangle$. Second, the width $\hat{\Gamma}$ of the collisionally induced Lorentzian line shape, Eqs. (9) and (10), is crucial in determining the photon counting rate, Eq. (6). The collisionally broadened Lorentzian line spans a large contribution of the Fourier components of the pulse near resonance, resulting in a dramatic pressure induced increase of $\{R\}$.

The following general conclusions now emerge:

(1) The decay time for the direct scattering $\langle I_p(t)\rangle$ is the pulse decay time $\gamma_2^{-1}$, which is independent of pressure. (Note that $\gamma_2 \gg \Gamma_1$ and that the second "interference type" term in Eq. (12a) is smoothed out by the convolution, Eq. (5).

(2) The decay time for the "molecular" decay component $I_m(t)$ is $\Gamma_1^{-1} = (\Gamma_s^r + \Gamma_s^p + \Gamma_1^{c,p})^{-1}$, according to Eq. (7). This lifetime does not originate solely from collisional redistribution[13] but includes additive widths due to spontaneous radiative and nonradiative decay of the isolated resonance and collision-induced predissociation. The molecular decay component exhibits a pressure dependence expected for the latter process, so that

$$\Gamma_1(\mathrm{sec}^{-1}) = \Gamma_s + a(P/\mathrm{torr})\,, \quad (15)$$

where $a = 2.264\times10^5\ (\sigma/\text{Å}^2)$, where $\sigma$ is the cross section for collision-induced predissociation.

(3) For the isolated resonance $I_m(t) \propto \Delta^{-4}$ for $\Delta \gg \beta$, and convolution of this result with the Lorentzian pressure-broadened line shape, Eq. (9), results in the asymptotic relation $\langle I_m(t)\rangle \propto \Delta^{-2}$. On the other hand, $I(t) \propto \Delta^{-2}$ and $\langle I(t)\rangle \propto \Delta^{-2}$ for $\Delta \gg \beta$. Thus, $\{R\}$ for the extreme off-resonance situation is independent of $\Delta$ when collisional perturbations prevail.

TABLE I. Decay rates $\Gamma_1$ and $\hat{\Gamma}$ and the fractional intensity $\{R\}$ of the long-lived component in time-resolved photon scattering from a single-vibrational–rotational level of $B\,^3\Pi$ state of $I_2$ at 5145 Å. The off-resonance energy $\Delta = 1.7\times10^9$ Hz, $\beta = 1.7\times10^9$ sec$^{-1}$, $\gamma_1 = \gamma_2 = 3.3\times10^8$ sec$^{-1}$, and $T = 10^{-7}$ sec.

| | $P=0$ | $P=0.03$ torr | $P=0.25$ torr |
|---|---|---|---|
| $\Gamma_1$ from self-quenching data[a] | $4.2\times10^5$ sec$^{-1}$ | $9\times10^5$ sec$^{-1}$ | $4.5\times10^6$ sec$^{-1}$ |
| $\Gamma_1$ direct decay[b] | Unavailable | $>5\times10^5$ sec$^{-1}$ [d] | $3.3\times10^6$ sec$^{-1}$ |
| $\hat{\Gamma}$[c] | 0 | $4.3\times10^5$ sec$^{-1}$ | $3.6\times10^6$ sec$^{-1}$ |
| $\{R\}$ (theory) | $5\times10^{-4}$ | 0.08 | 0.37 |
| $\{R\}$ (experiment)[b] | Unavailable | 0.14 | 0.45 |

[a] Reference 10(a).
[b] Reference 11.
[c] Estimated from the value of $\hat{\Gamma}/\Gamma_1$ obtained from the energy resolved spectral data of Ref. 11, and the values of $\Gamma_1$ obtained from the self-quenching data of Ref. 10(a).
[d] This experimental value constitutes a lower limit for $\Gamma_1$ in view of the "exodus" of excited molecules from the range of the slits of the monochromator (see Ref. 13).

(4) The collisionally induced Lorentzian linewidth $\hat{\Gamma}$, Eq. (10), is proportional to $p$,

$$\hat{\Gamma} = b(p/\mathrm{torr}). \quad (16)$$

These expectations are fully borne out by the experimental data summarized in Table I. From the independent detailed lifetime and self-quenching data[11] for the $B$ state of $I_2$ near 5145 Å, we take $\Gamma_s = 4.2\times10^5$ sec$^{-1}$ and $\sigma = 70$ Å$^2$ in Eq. (15), whereupon $a = 1.58\times10^7$ sec$^{-1}$. The values of $\Gamma_1$ calculated for the two pressures studied in the time-resolved experiments (Table I) are in good agreement with the quenching data. We note that collisional quenching effects on $\Gamma_1$ are already appreciable at $p = 0.03$ torr, in agreement with the experimental observation.[11] What is now required is an independent information concerning $\hat{\Gamma}$, Eq. (16). This can be obtained from the high-resolution spectral measurements of Rousseau *et al.*,[13] which yield the ratio of the width due to phase shifts ($\gamma_E$ in the notation of Ref. 13) to $\Gamma_1$: $\gamma_E/\Gamma_1 = 0.8$ at $p = 0.25$ torr. In that treatment,[13] the contributions of cross relaxation were disregarded. When these are incorporated we can identify $\gamma_E$ with $\hat{\Gamma}$, and the energy-resolved experiment[13] yields $\hat{\Gamma}/\Gamma_1 = 0.8$ at $p = 0.25$ torr. Thus, $\hat{\Gamma} = 3.6\times10^6$ sec$^{-1}$ at $p = 0.25$ torr, whereupon $b = 14\times10^6$ sec$^{-1}$ in Eq. (16) and $\hat{\Gamma} = 4.3\times10^5$ sec$^{-1}$ at $p = 0.03$ torr. These results yield $\sigma = 64$ Å$^2$ for the cross section for cross relaxation and phase shifts. We note that it is accidentally close to the value of $\sigma = 70$ Å$^2$, although in general we expect that $\hat{\Gamma} \neq \Gamma_1^{c,p}$.

In Fig. 2 we portray the results of numerical simulations of the time-resolved photon scattering from $I_2$ at 5154 Å using Eqs. (5)–(10) and (15), together with the pulse parameters[16] $\gamma_1 = \gamma_2 = 3.3\times10^8$ sec$^{-1}$ and $T = 10^{-7}$ sec, the off-resonance energy $\Delta = 1.7\times10^9$ Hz, the Doppler width $\beta = 1.7\times10^9$ sec$^{-1}$, and the molecular pa-

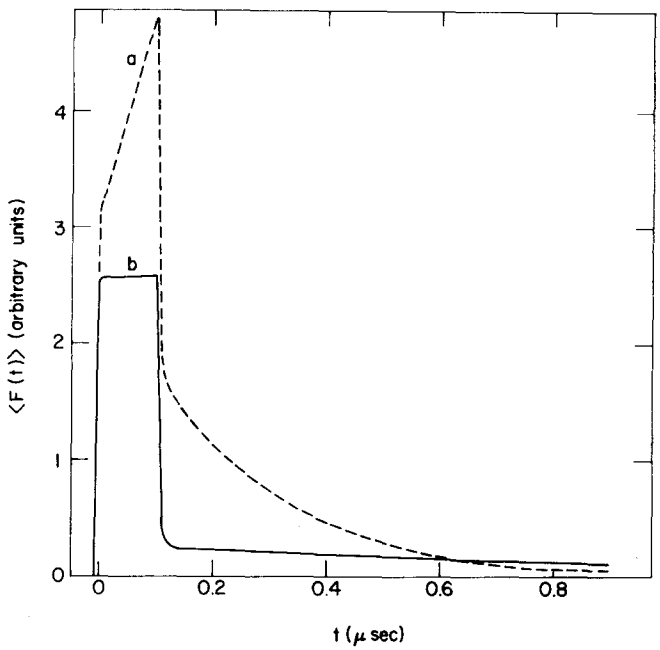


FIG. 2. Numerical simulations of time-resolved near-resonance photon scattering from a single-vibrational–rotational level of $I_2$ at 5145 Å. $\Delta = 1.7$ GHz, $\beta = 1.7\times10^9$ sec$^{-1}$, $\gamma_1 = \gamma_2 = 3.3\times10^8$ sec$^{-1}$, $T = 10^{-7}$ sec. (a) $P = 0.03$ torr, $\Gamma_1 = 0.91\times10^6$ sec$^{-1}$, $\hat{\Gamma} = 0.47\ \Gamma_1$; (b) $P = 0.25$ Torr, $\Gamma_1 = 4.5\times10^6$ sec$^{-1}$, $\hat{\Gamma} = 0.83\ \Gamma_1$.

rameters $\Gamma_s = 4.2\times10^5$ sec$^{-1}$, $a = 1.58\times10^7$ sec$^{-1}$, and $b = 1.4\times10^7$ sec$^{-1}$. The numerical results bear a striking resemblance to the experimental data of Rousseau *et al.* In Fig. 3 and 4 we present the results of model calculations for the intensity ratio $\{R\}$, Eq. (14), for several values of $\Delta/\beta$ at $p = 0$, 0.03 torr and 0.25 torr and for various values of the ratio $\hat{\Gamma}/\Gamma_1$ at finite pressures. We note that at $p = 0$ (i.e., $\hat{\Gamma} = 0$ and $\Gamma_1 = \Gamma_s$), $\{R\} = 5\times10^{-4}$, which is much lower than the experimental value $\{R\} = 0.14$ at $p = 0.03$ torr. Thus, even at the lowest pressure studied[13] the entire contribution to

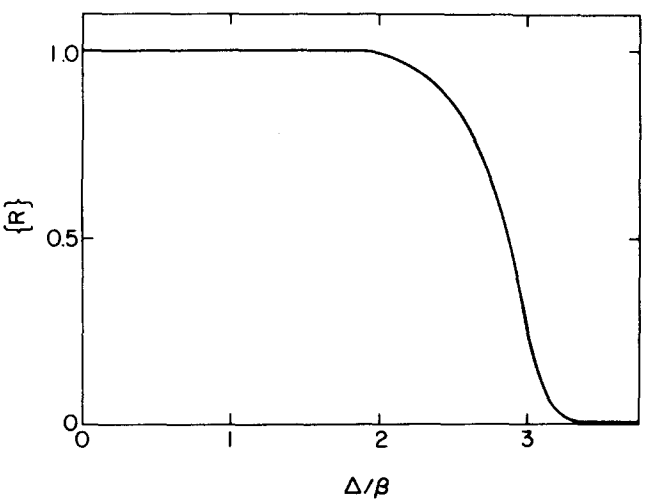


FIG. 3. The dependence of the fractional intensity ratio $\{R\}$ of the long decay component on the off-resonance energy $\Delta$ at zero pressure.

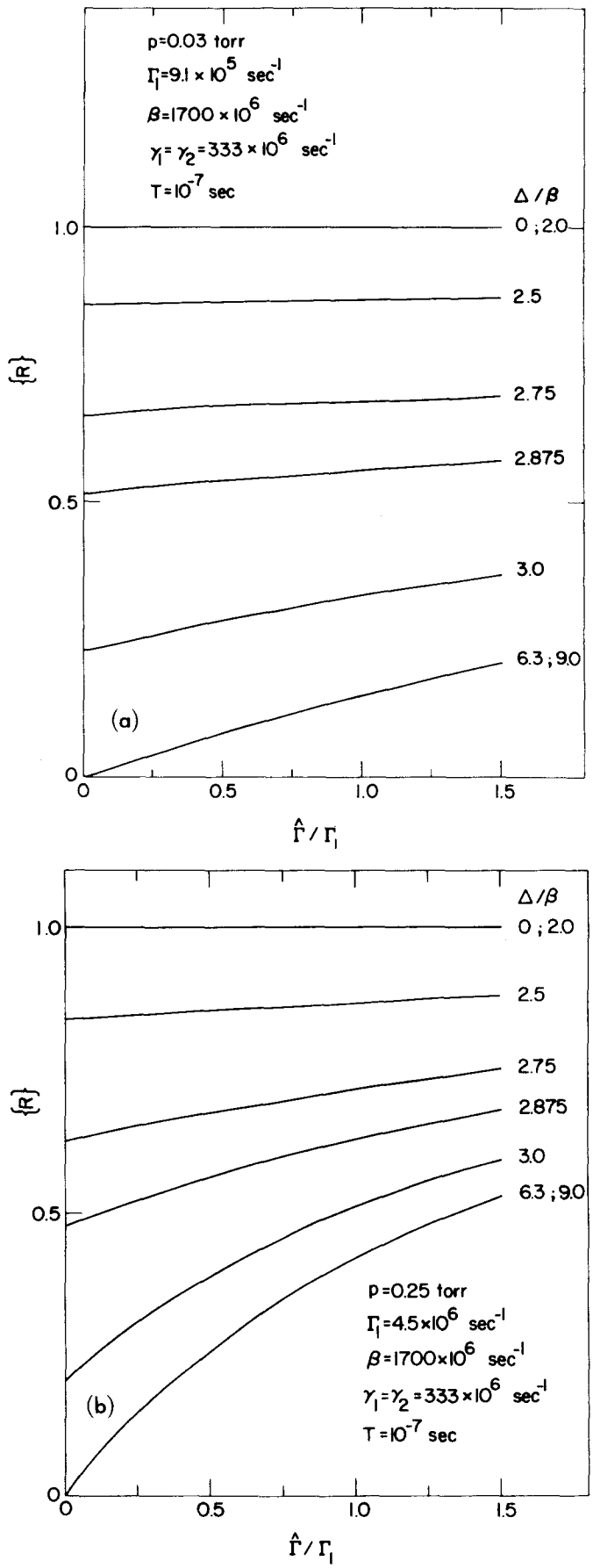


FIG. 4. The dependence of the fractional intensity ratio $\{R\}$ of the long decay component of the off-resonance energy and on $\hat{\Gamma}/\Gamma_1$ at finite pressure. 4(a) $p = 0.03$ torr, 4(b) $\beta = 0.25$ torr.

the intensity of the "molecular" decay mode originates from collisional line broadening effects. Finally, we would like to point out that, as is evident from Table I, our theory provides a quantitative account for the time-resolved photon scattering data of Rousseau *et al.*[13]

We conclude that in view of the long decay time $\Gamma_s \simeq 4.2\times10^5$ sec$^{-1}$ of this level of $I_2$ in the collision free molecule, time-resolved photon scattering over the entire pressure range studied up to date[13] is dominated by collisional perturbations, which are adequately accounted for in terms of our theory. Some detailed interesting features of collisional perturbations in this one-photon experiment can not be disentangled, as the photon counting rate, Eq. (5), includes a convolution over the Doppler width, which erodes much of the relevant information. The effects of Doppler broadening can be eliminated by the application of two-photon spectroscopy,[17] utilizing two photons travelling in opposite directions. A theory of time-resolved photon scattering under such two-photon excitation was worked out[18] and is expected to unveil new and pertinent information concerning collisional damping effects.


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