APPLICATION OF THE BLOCH EQUATIONS TO
TIME-RESOLVED NEAR-RESONANCE LIGHT SCATTERING IN A GAS

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We apply the Bloch equations to the study of time-resolved near-resonance photon scattering from a collisionally perturbed molecule. An explicit result is derived for weak fields. Application of these results to photon scattering from collisionally perturbed molecular iodine is briefly considered.

The fundamental problem of the "transition" from resonance fluorescence to near-resonance Raman scattering from a molecular resonance has been of considerable experimental [1–3] and theoretical [4,5] interest. A new light was shed on this problem by recent experiments in which the time-resolved intensity of the scattered light was measured [6,7]. In these studies, a light pulse was scattered by resonance excitation to a single vibrational–rotational level of the $B^3\Pi$ state of I_2, at pressures of 0.03 torr and 0.25 torr. Several theoretical studies were made [8–15] trying to provide an adequate interpretation of the recent experimental information, which is

(1) the time-resolved decay pattern is characterized by two types of decay modes, one governed by a molecular lifetime ($\approx \mu$s) and the other by the extinction time of the pulse ($\approx$ ns);

(2) the relative contribution, $\{R\}$, of the molecular long-lived decay mode to the total scattered intensity is a decreasing function of the off-resonance energy difference Δ (i.e. the separation between the mean photon-energy and the molecular resonance energy) for values of Δ of the order of the Doppler width β;

(3) off resonance ($\Delta \gg \beta$), $\{R\}$ becomes approximately

constant, independent of Δ;

(4) increasing the I_2 pressure from 0.03 torr to 0.25 torr results in a considerable enhancement of $\{R\}$.

Without alluding to any specific theoretical models we may recall a basic result of the theory of resonance scattering [16] which tells us that the time-delay, $\langle \Delta t \rangle$, of a wave packet due to its interaction with a two-level target is $\langle \Delta t \rangle = 2\Gamma/(\Gamma^2 + \Delta^2)$, where Γ is the width of the resonance. Exactly on resonance ($\Delta = 0$), we have $\langle \Delta t \rangle = 2/\Gamma$, a result compatible with observation (1). However, for $\Delta \to \infty$ we have $\langle \Delta t \rangle \to 0$; i.e. far off resonance only a direct scattering process prevails, a conclusion which is incompatible with observation (3). We thus conclude [8–10] that even at pressures as low as 0.03 torr, collisional effects play an important role in the photon scattering process in this system.

Collisional effects on time-resolved photon scattering can be handled by considering the time-evolution of the entire system, using the Liouville-space formalism (with Fano–Zwanzig projection-operator techniques) in the ω (frequency) representation [9,10]. A basic approximation introduced in the course of this derivation is the assumption of short memory times of the thermal bath, allowing us to neglect transient effects of the col-

lisions. Under this condition the system can be alternatively described by the Bloch–Redfield equations [17].

In the present note we shall utilize the Bloch equations to the study of time-resolved near-resonance photon scattering from a collisionally perturbed molecule. This approach has the merit that (using a classical representation of the applied field) saturation effects can be introduced more readily to its perturbative solution. In the derivation of the solution we invoke the following assumptions concerning the molecular level-scheme, its coupling to the radiation field and how it is affected by collisions:

(1) The molecule is characterized by a single ground state $|g\rangle$, well separated in energy from a manifold of closely lying n excited levels $\{|k\rangle\}$, $(k = 1, \dots n)$. The light pulse is near resonance with a single transition $|g\rangle \to |j\rangle$, where $|j\rangle$ belongs to the $\{|k\rangle\}$ manifold.

(2) Optical coherence prevails between $|g\rangle$ and $|j\rangle$, and is eroded by the effects of collisional relaxation. Provided that the spacings between the various $|k\rangle$ levels are large compared to their inverse lifetimes (sharp resonance), we can neglect transfer of coherence by cross relaxation between $|j\rangle$ and other levels.

(3) Collisions result in population changes (T_1 processes) by inducing transitions between the $\{|k\rangle\}$ levels (intraband relaxation) as well as causing relaxation from the manifold (e.g. predissociation). In addition, collisions lead to the damping of coherence (T_2 processes).

Under these assumptions, the Bloch equations [17] for the system may be written in the rotating-frame representation (for a single molecular velocity-group) in the form

$$\dot{\rho}_{\pm}(t) = \pm i\Delta\rho_{\pm} - \Gamma_2\rho_{\pm}(t) \mp \tfrac{1}{2}i\chi(t)[\rho_j(t) - \rho_g(t)], \quad (1a)$$

$$\dot{\rho}_j(t) - \dot{\rho}_g(t) = -i\chi(t)[\rho_+(t) - \rho_-(t)] - i\sum_{k=1}^{n} R_{jk}\rho_k(t), \quad (1b)$$

$$\dot{\rho}_k(t) = -i\sum R_{kk'}\rho_{k'}(t), \qquad k \neq j. \quad (1c)$$

Here $\rho_1(t)\dots\rho_n(t)$ are the populations of the n excited levels, $\rho_g(t)$ is the population of the ground state, while $\rho_+(t)$ and $\rho_-(t)$ represent the off-diagonal elements of the molecular density matrix (i.e. "optical coherences") between $|g\rangle$ and $|j\rangle$, so that $\rho_+(t) \equiv \rho_{gj}(t)$ and $\rho_-(t) \equiv \rho_{jg}(t)$. The off-resonance energy is $\Delta = \omega_0 - \overline{\omega}$ where ω_0 is the resonance frequency of the molecular velo-

city group and $\overline{\omega}$ in the mean frequency of the light pulse. Also, $\chi(t) = \mu_{jg}E_0\varphi(t)$ is the coupling strength, μ_{jg} being the dipole matrix element between $|g\rangle$ and $|j\rangle$ while $\varphi(t)$ is the envelope of the pulse amplitude with maximal field E_0, given the applied electric field $E(t) = E_0\varphi(t)\cos\overline{\omega}t$. Finally, the relaxation processes in eq. (1) are specified in terms of the level-decay matrix R (for T_1 processes) which contains diagonal (level damping) and off-diagonal (intraband relaxation) terms, and by the line width Γ_2 which corresponds to the damping of coherence (T_2 type processes). Γ_2 consists of contributions of population damping (T_1 processes) as well as proper T_2 processes (phase shifts and reorientations).

Eq. (1) is valid for arbitrary intensities of the light pulse. With sufficiently strong fields, the appearance of $\chi(t)$ on the r.h.s. of eq. (1) will lead to saturation effects, which can be studied by a numerical solution of this set of differential equations. We shall now specialize to weak light pulses, whereupon we set in (1a)

$$\rho_g = \rho_g^0; \qquad \rho_j = 0,$$

where ρ_g^0 is the equilibrium population of $|g\rangle$, and we neglect equilibrium populations of the excited manifold. We can now solve eqs. (1a) for $\rho_+(t)$ and $\rho_-(t)$, substituting these solutions into (1b) to obtain the set of equations for the populations $\{\rho_k(t)\}$

$$\dot{\rho}_j(t) = -i\sum_k R_{jk}\rho_k(t) + \eta(t), \quad (2a)$$

$$\dot{\rho}_k(t) = -i\sum_{k'} R_{kk'}\rho_{k'}(t), \qquad k \neq j. \quad (2b)$$

Here

$$\eta(t) \equiv -i\chi(t)[\rho_+(t) - \rho_-(t)]$$

$$= \dot{\rho}_g\chi(t)\,\mathrm{Re}\int_{-\infty}^{t} d\tau\,\varphi(\tau)G_2(t-\tau), \quad (3)$$

where we have defined a 1×1 T_2-type correlation matrix

$$G_2(t) = \Theta(t)\exp[i\Delta t - \Gamma_2 t], \quad (4)$$

and where $\Theta(t)$ is the Heaviside step function.

Eq. (2) may be solved by the Fourier transform method. We define $\widetilde{\rho}_j(E)$ and $\widetilde{\eta}(E)$ as the Fourier transforms of $\rho_j(t)$ and $\eta(t)$, respectively, i.e.,

$$\widetilde{\rho}_k(E) = \int dt \rho_k(t) \exp(iEt),$$

$$\widetilde{\eta}(E) = \int dt \eta(t) \exp(iEt), \tag{5}$$

utilizing the conditions $\rho_k(t) \xrightarrow[t \to \pm\infty]{} 0; k = 1,2 \ldots n$ we get the explicit solution

$$\widetilde{\rho}_k(E) = i[(E\mathsf{I} - \mathsf{R})^{-1}]_{kj}\widetilde{\eta}(E), \tag{6}$$

for all k, where I is the unit $n \times n$ matrix. The inverse transform of (6) is given by

$$\rho_k(t) = -(2\pi i)^{-1}$$
$$\times \int_{-\infty}^{\infty} dE \exp(-iEt)[(E\mathsf{I} - \mathsf{R})^{-1}]_{kj}\widetilde{\eta}(E). \tag{7}$$

Alternatively this result can be recast in terms of a convolution integral

$$\rho_k(t) = \mu_{gj}E_0 \int_{-\infty}^{t} d\tau [\mathsf{G}_1(t - \tau)]_{kj}\eta(\tau), \tag{8}$$

where the $(n \times n)$ T_1-type correlation matrix is defined by

$$\mathsf{G}_1(t) = -(2\pi i)^{-1} \int dE(E\mathsf{I} - \mathsf{R})^{-1} \exp(-iEt). \tag{9}$$

Finally, utilizing the definitions (3) and (4) we obtain

$$\rho_k(t) = \int_{-\infty}^{t} \int_{-\infty}^{t} d\tau d\tau' \varphi(\tau)\varphi(\tau')$$
$$\times [\mathsf{G}_1(t - \tau)]_{kj}G_2(\tau - \tau'). \tag{10}$$

Time-resolved photon scattering monitors the populations $\{\rho_k(t)\}$ each weighed by the radiative decay rate Γ_k^r of the kth level. The photon counting rate $F(\Delta, t)$ from the $\{|k\rangle\}$ manifold is

$$F(\Delta, t) = \sum_k \Gamma_k^r \rho_k(t) \tag{11}$$

and making use of eq. (10) one gets

$$F(\Delta, t) = 2\mathrm{Re}\rho_g^0 |\mu_{gj}E_0|^2 \sum_k \Gamma_k^r$$
$$\times \iint d\tau d\tau' \varphi(\tau)\varphi(\tau')[\mathsf{G}_1(t - \tau)]_{kj}G_2(\tau - \tau'). \tag{12}$$

The experimental photon counting rate $\{F(\Delta, t)\}$ from a gas at thermal equilibrium is obtained by convoluting $F(\Delta, t)$ [eq. (12)] with the Doppler profile

$$f(\Delta) = (\pi\beta^2)^{-1/2} \exp(-\Delta^2/\beta^2), \tag{13}$$

where β is the Doppler width, so that

$$\{F(\Delta, t)\} = \int d\Delta' F(\Delta', t) f(\Delta - \Delta'). \tag{14}$$

This formal solution [eqs. (12) and (14)], was obtained previously [9] by utilizing the Liouville-operator formalism.

To obtain a more tangible result we now introduce a set of simplifying assumptions:

(a) Let the radiative widths Γ_k^r be equal, i.e. $\Gamma_k^r = \Gamma^r$ for all k.

(b) Let the n excited states be characterized by the same damping rates Γ' and cross relaxation terms Γ'' so that

$$\Gamma_{kj} = \Gamma'\delta_{kj} - \Gamma''(1 - \delta_{kj}). \tag{15}$$

In view of assumption (a) we need to evaluate $\Sigma_k(\mathsf{G}_1)_{kj}$ in eqs. (12) and (14). As a result of assumption (b) it follows that $\Sigma_k[\mathsf{G}_1(\tau)]_{kk} = \exp(-\Gamma_1\tau)$, where Γ_1 is an eigenvalue of the Γ matrix, given by

$$\Gamma_1 = \Gamma' - (n - 1)\Gamma''. \tag{16}$$

Eq. (14) can now be written in the form

$$\{F(\Delta, t)\} = \int d\Delta' \int d\Delta'' F^0(\Delta - \Delta', t) L(\Delta' - \Delta'') f(\Delta''), \tag{17}$$

where

$$F^0(\Delta, t) = |\mu_{gj}E_0|^2 \left| \int_{-\infty}^{t} d\tau \varphi(\tau) \exp[-\tfrac{1}{2}\Gamma_1(t - \tau)] \right|^2 \tag{18}$$

is the photon counting rate from a hypothetical "isolated molecule" characterized by the decay time Γ_1 only, and lacking T_2 processes. This counting rate is convoluted with the lorentzian function

$$L(\Delta) = (\hat{\Gamma}/\pi)/(\hat{\Gamma}^2 + \Delta^2), \tag{19}$$

where $\hat{\Gamma} = \Gamma_2 - \tfrac{1}{2}\Gamma_1$ is a line-broadening rate from which the contribution of the decay of the band is omitted.

The photon counting rate from a collisionally perturbed model molecule, assumes the form of a triple convolution of F^0, eq. (18), L, eq. (19), and f, eq. (13). Collisional effects enter into the photon counting rate in two ways. First, they modify Γ_1 via inelastic collisions, e.g. collisional induced predissociation in the case of the $B^3\Pi$ state of I_2. Second, they result in a convo-

lution of the photon counting rate with the lorentzian function $L(\Delta)$, whose width is determined by cross relaxation within the excited manifold and by proper T_2 processes.

In order to account for the recent experimental data we take a simple, physically realistic model for the light-pulse envelope,

$$\varphi(t) = \exp(\tfrac{1}{2}\gamma t), \qquad t < 0;$$
$$= 1, \qquad\qquad 0 < t < T; \qquad (20)$$
$$= \exp(-\tfrac{1}{2}\gamma t), \qquad t > T.$$

The relevant molecular parameters have been determined from various experimental data [6,7,18]. From fluorescence quenching experiments [18] it was found that the levels of I_2 around 5145 Å are subjected to collisionally induced predissociation and that

$$\Gamma_1 = \Gamma_s + 2.264(70/\text{Å}^2)(p/\text{torr})\text{s}^{-1},$$

where $\Gamma_s = 4.2 \times 10^5$ s^{-1} is the inverse lifetime of the collision-free molecule (including contributions of both radiative decay and spontaneous predissociation). From high-resolution spectral measurements [7] we have determined $\hat{\Gamma} = 1.4 \times 10^7 (p/\text{torr})\text{s}^{-1}$. The appropriate

pulse parameters are $T = 10^{-7}$ s, $\gamma = 7.5 \times 10^8$ s^{-1}. The Doppler width is $\beta = 4 \times 10^8$ s^{-1}. In fig. 1 we compare the calculated time-resolved photon counting for I_2 at off-resonance energy difference $\Delta = 1.7 \times 10^9$ Hz with the recent experimental work of Rousseau et al. [7].

We conclude that in this system which is characterized by a long decay time ($\Gamma_s^{-1} \approx 2.5 \ \mu$s), even at the lowest pressure (0.03 torr) studied up to date, collisional perturbations are crucial in determining the time-resolved photon scattering, and these effects are adequately accounted for in terms of our theory.
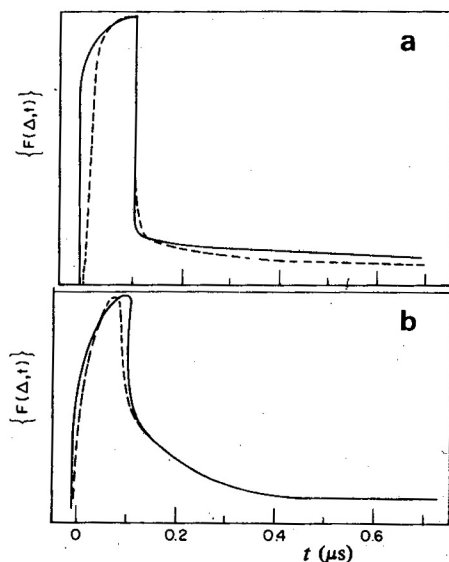

Fig. 1. Comparison of the experimental results of the time-resolved photon scattering in I_2 with our model calculations. $\Delta = 1.7$ GHz, $\beta = 0.4$ GHz, $\hat{\Gamma} = 14$ MHz (p/torr), $\gamma = 0.75$ GHz, $T = 0.1 \ \mu$s. ---- exp., —— calc. (a) $p = 0.03$ torr, $\Gamma_1 = 0.9$ MHz; (b) $p = 0.25$ torr, $\Gamma_1 = 4.5$ MHz.

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