Resonance Raman Scattering and Collision-Induced Redistribution Scattering in I_2

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We report the first experimental observation of broad-banded re-emission resulting from quasi-elastic collisional transfer processes. The data may be interpreted by the general theory of scattering of monochromatic light in gases. The connection between this theory and one derived for solids is discussed.

Resonance scattering of monochromatic light from gases has been relatively well understood theoretically for many years although several aspects of the theories have not been confirmed experimentally. According to the general theories[1,2] under appropriate conditions there should be two contributions to resonance and near-resonance light scattering. For the first contribution the re-emitted light appears at the frequency of the excitation energy and the linewidth of the re-emitted light is limited only by the linewidth of the incident excitation (Heitler phenomenon).[3] The second contribution to the scattering results from a redistribution term in which, through an excited-state collisional relaxation process, the re-emitted light appears at the natural frequency of the oscillator, independent of the excitation frequency. In addition it displays the full width of the excited state involved. This Letter reports the first experimental observation of this collisionally induced broad-banded re-emission in high-resolution spectral measurements, and the observation of its temporal behavior in time-decay measurements. These measurements were made on the Raman-shifted re-emitted light where complications due to scattering of unwanted spurious incident light are greatly reduced.

The theory of re-emission of light following monochromatic excitation has been derived by Huber[1] and by Omont, Smith, and Cooper.[2] The collisional processes were treated in the impact approximation, and although the calculations apply only to Rayleigh scattering, the results are readily extended to Raman scattering. The energy levels for this process are depicted in Fig. 1. Here we are considering a Raman transition from g to f via intermediate state i. With neglect of Doppler broadening the differential scattering cross section is given by[1,2]

$$\frac{d^2\sigma}{d\omega_s\,d\Omega_s}=\frac{\omega_l\omega_s^3|\langle f|\vec{\mathrm{P}}\cdot\vec{\mathrm{A}}|i\rangle|^2|\langle i|\vec{\mathrm{P}}\cdot\vec{\mathrm{A}}|g\rangle|^2}{\hbar^2c^4[(\omega_l-\omega_{ig})^2+(\gamma_N+\gamma_I+\gamma_E)^2]}\left\{\delta(\omega_l-\omega_s-\omega_{fg})+\frac{\gamma_E(\gamma_N+\gamma_I+\gamma_E)}{\pi(\gamma_N+\gamma_I)[(\omega_s-\omega_{if})^2+(\gamma_N+\gamma_I+\gamma_E)^2]}\right\}. \tag{1}$$

The intermediate-state linewidth consists of three Lorentzian contributions: γ_N corresponds to the natural radiative lifetime; γ_I is the broadening resulting from a shorter lifetime caused by inelastic collisions, i.e., those collisions in which the molecule is knocked into a different quantum state; and γ_E is the contribution from quasi-elastic collisions, i.e., those collisions in which the phase of the oscillator is interrupted but it remains in the same quantum state.

In the limit of a very low-pressure gas γ_E and γ_I are zero so that the second term in the curly brackets in Eq. (1) vanishes. In this low-pressure limit, and where only one intermediate state is contributing to the scattering amplitude, the first term in Eq. (1) fully characterizes the light scattering. There is a phase memory between the incident and scattered radiation, and for an individual molecule the scattering process is coherent regardless of whether or not the incident frequency coincides with the center frequency of the transition. When the incident frequency is moved away from resonance the intensity of the scattered light varies in a Lorentzian manner as defined by Eq. (1). Therefore under these conditions one may not legitimately classify the re-emission resulting from on- and off-resonance

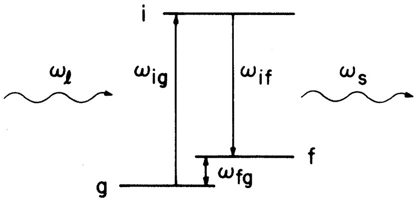

FIG. 1. Schematic three-level energy diagram. ω_{ig}, ω_{if}, and ω_{fg} are the designated transition energies between the ground, g, intermediate, i, and final, f, states. ω_l and ω_s are the incident and scattered photons, respectively.

excitation as being the product of two physically distinct processes. Attempts so to classify the on- and off-resonance scattering as resonance fluorescence and resonance Raman scattering, respectively, are artificial and misleading. For this reason we consistently label all the scattering resulting from the first term in Eq. (1) as Raman scattering (resonance Raman scattering for exact resonance).

As the gas pressure is increased, the second term in the curly brackets in Eq. (1) becomes important. This term represents a physically distinguishable process, resulting from a disturbance in the excited state such that the phase is randomized. In contrast to the Raman term this term corresponds to *independent* absorption and emission processes. The emission resulting from the second term in Eq. (1) is redistributed over the full width of the pressure-broadened excited state, is centered at the resonant energy independent of excitation energy, and has a lifetime $1/(\gamma_N + \gamma_I)$. Obviously this may occur only if the line-broadening mechanism includes a relaxation process which can take up or remove energy. In gases this occurs through quasi-elastic collisional broadening where during a collision the phase of the oscillator is interrupted but the molecule remains in the same quantum state. Because this term results in a redistribution of the incident energy, to maintain generality we shall refer to it as the redistribution term. We emphasize that the redistribution scattering requires the presence of some excited-state relaxation process. In the absence of such a process only the Raman scattering remains, even for exactly resonant excitation. Simple energy-conservation arguments then require the re-emission linewidth to be independent of the excited-state linewidth.

We have made lifetime and spectral measurements of both of the contributions of Eq. (1) in the

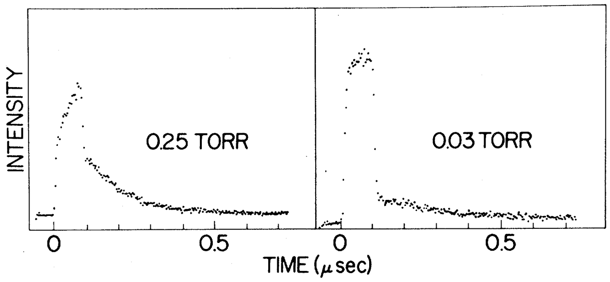

FIG. 2. Time response of 214-cm^{-1} Stokes re-emission at 0.25 Torr and 0.03 Torr of I_2. The excitation pulse was 100 nsec long, and shifted from exact resonance by ~1.7 GHz.

re-emission from molecular iodine with 5145-Å excitation. In the 5145-Å excitation region the iodine Raman re-emission, shifted by about 214 cm^{-1}, has a triplet structure (O, Q, and S branches) because of the simultaneous excitation of two transitions [$P(13)$ and $R(15)$].[4] Measurements were made on and off resonance with these transitions by varying the frequency of the single-mode argon-ion laser over its Doppler-gain band.

The lifetime measurements were made by a delayed-coincidence technique on an apparatus described previously.[5,6] The scattered light was dispersed by passing it through a double-grating spectrometer set to observe the overlapping Q-branch emission from the $P(13)$ and $R(15)$ transitions.

In Fig. 2, we present the time-decay data obtained at two different I_2 pressures. Each spectrum was obtained with 100-nsec-duration excitation about 1.7 GHz away from the maximum of the resonant transitions. The measurements were made off resonance, where the time response of the Raman contribution follows the laser pulse,[5] since on resonance each of the contributions in Eq. (1) have the same lifetime. At 0.25 Torr of I_2 there are two prominent components to the scattering. One has a fast rise and decay (it follows the excitation pulse) and therefore results from the Raman contribution to the scattering. The other contribution has an exponential rise and decay and we attribute it to the redistribution term. It has a lifetime of about 300 nsec, substantially shorter than the natural lifetime (about 2 μsec) as expected since at these pressures the lifetime is given by $1/(\gamma_N + \gamma_I)$.

As the I_2 pressure is lowered γ_E decreases so that the intensity of the redistribution term relative to that of the Raman term also decreases. Consequently, as seen in Fig. 2 at 0.03 Torr of

I_2, the long-lived contribution is greatly reduced with respect to the short-lived component. The lifetime for the slow component is longer than that of the redistribution term at the higher pressure although not as long as expected on the basis of the natural lifetime because of the spatial resolution imposed by the narrow spectrometer slits used in the experiment.

High-resolution spectral measurements were made by directing the scattered light through an interference filter centered at the Stokes frequency shift (~ 214 cm^{-1}) and into a piezoelectrically scanned Fabry-Perot interferometer with a 10-GHz free spectral range. The measurements were made in a near-forward-scattering geometry to reduce the effects of Doppler broadening,[7] and, as in the lifetime measurements, the excitation frequency was shifted 1.7 GHz away from the center of the resonant transitions. The resulting spectrum is depicted by the points in Fig. 3. The sharp features in the spectrum result from Raman scattering from the S, Q, and O branches (in different orders of the interferometer) and the laser line which leaked through the narrow-band filter. We attribute the broad underlying structure to redistribution scattering.

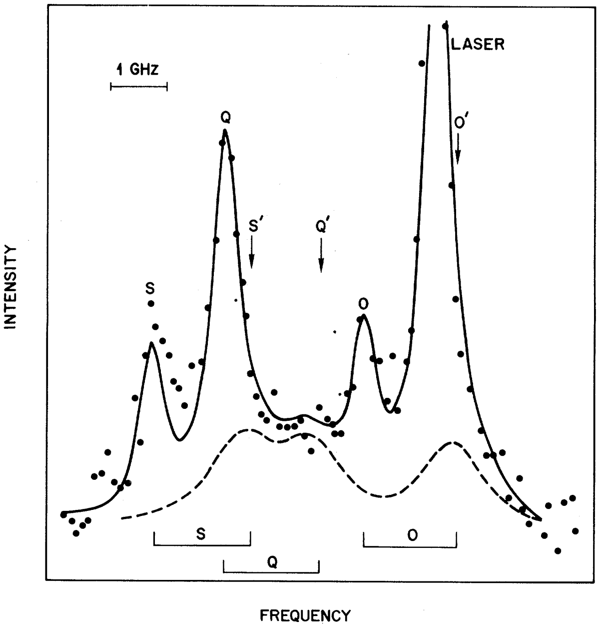

FIG. 3. High-resolution frequency spectrum of 214-cm^{-1} Stokes re-emission of I_2 obtained with 1.7-GHz off-resonance excitation. S', Q', and O' correspond to the positions of the rotational branches obtained with resonant excitation. The points are the experimental data. The solid line is a theoretical curve, and the dashed line is the redistribution-scattering contribution. The bars at the bottom indicate the 1.7-GHz shift between each Raman-redistribution pair.

The solid curve in Fig. 3 is a calculation of the spectrum obtained in the following manner. The frequencies of the sharp S, Q, and O Raman lines were fitted to coincide with the experimental frequencies and were assigned the expected 1:2:1 relative-intensity ratios. Shifted 1.7 GHz away from each of the sharp Raman lines a redistribution band is located. Its shape was determined from the second term in Eq. (1) and its intensity corrected for an accidental absorption at the Q-branch resonance frequency. The resulting spectrum was then folded into a Lorentzian interferometer-response function and a best fit to the data was obtained by adjusting the relative intensity of the total Raman contribution to the total redistribution contribution. The redistribution contribution to the total intensity after convolution with the slit function is depicted by the dashed curve in Fig. 3. We found that the redistribution term had an integrated intensity of about 0.8 that of the Raman contribution. We believe that the minor remaining discrepancies between the observed and the calculated spectra result primarily from additional low-intensity bands resulting from *inelastic* collisional transfer processes.[8]

It should be noted that in solids similar questions concerning the equivalence of and distinction between resonance Raman scattering and hot luminescence (absorption followed by luminescence) have arisen[9,10] and theoretical results equivalent to those presented here have been derived by Shen.[10] In his density-matrix derivation, Shen[10] has accounted for the relaxation of the system by including a completely general damping term. With use of Eqs. (3) and (6) of Ref. 10 the cross section for the total steady-state scattering may be written in a form similar to Eq. (1) as follows:

$$\frac{d^2\sigma}{d\omega_s\,d\Omega}=\frac{\omega_l\omega_s{}^3|\langle f|\vec{P}\cdot\vec{A}|i\rangle|^2|\langle i|\vec{P}\cdot\vec{A}|g\rangle|^2}{\hbar^2\pi c^4[(\omega_l-\omega_{ig})^2+\Gamma_{ig}{}^2]}\left\{\frac{\Gamma_{fg}}{(\omega_l-\omega_s-\omega_{fg})^2+\Gamma_{fg}{}^2}+\frac{[2\Gamma_{ig}T_i-1]\Gamma_{if}}{(\omega_s-\omega_{if})^2+\Gamma_{if}{}^2}\right\}. \tag{2}$$

Here the Γ's correspond to the linewidths for the transitions indicated in Fig. 1, and T_i is the lifetime of state i. When the relaxation is dominated by lifetime broadening $2\Gamma_{ig}T_i$ equals 1 and the second term in the curly braces vanishes, leaving only the first. Because Shen[10] has included a finite ground-state linewidth, this term is represented by the line-shape function with finite width rather than the δ function. This term then corresponds to a Raman re-emission just as does the first term in Eq. (1). If the relaxation mechanism is not limited to lifetime broadening and the excited state is randomized by the broadening mechanism, then $2\Gamma_{ig}T_i$ is not equal to 1 and re-emission obeying the second term in curly braces in Eq. (2) may take place. In analogy to the gas-phase case and as pointed out by Shen,[10] scattering (hot luminescence) by this mechanism may be broad since its width is dependent on the width of the excited state and it is of course a physically distinguishable process. Observation of both terms to the scattering have been seen[11] in CdS where resonance Raman scattering and luminescence from bound excitons occur simultaneously.

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K-Shell Fluorescence Yield of Multiply Ionized Ne

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The K fluorescence yields $\bar{\omega}^i$ of Ne ions with 0–6 L-shell vacancies (charge states KL^i) have been calculated by computing term transition rates for initial multiplet states and statistically averaging individual multiplet fluorescence yields. We find $\bar{\omega}^i = 0.0159$, 0.0176, 0.0199, 0.0248, 0.0390, 0.0862, and 0.229 for $i=0, \ldots, 6$. Existing measurements are critically reviewed and found to agree with present theoretical results once proper account is taken of the ^4P (KL^6) intensity contained in the KL^5 x-ray peak.

In this Letter we report results of a new calculation of the K-shell fluorescence yields of Ne in the presence of i L-shell vacancies (charge states KL^i, $i=0, \ldots, 6$) and make comparison with recent measurements. Term transition rates were computed[1,2] and fluorescence yields were calculated for the individual multiplets LS that arise in a configuration n:

$$\omega(LS,n)=\frac{\Gamma_R(LS,n)}{\Gamma_R(LS,n)+\Gamma_A(LS,n)}\,. \tag{1}$$

Here, Γ_R is the radiative width and Γ_A, the radiationless width of the state.

The effective fluorescence yield of a configuration is

$$\bar{\omega}(n)=\sum_{L,S} C_n(LS)\omega(LS,n), \tag{2}$$

where the $C_n(LS)$ are the population probabilities of multiplet states LS in the configuration n. If the multiplets are populated statistically, we have

$$\bar{\omega}(n)=\Big[\sum_{L,S}(2L+1)(2S+1)\omega(LS,n)\Big]\times\Big[\sum_{L,S}(2L+1)(2S+1)\Big]^{-1}. \tag{3}$$

The effective fluorescence yield of a charge state