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Resonant Raman Scattering or Resonance Fluorescence in I_2 Vapor?

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An examination of the foreign-gas pressure dependence of the intensity and spectrum of the signal from I_2 vapor under off-resonance monochromatic excitation indicates that the re-emission process is not resonance Raman scattering as recently reported by Fouche and Chang.

Raman scattering enhanced by proximity of the exciting line to resonance, often called resonance Raman scattering (RRS), has received considerable attention in the last few years,[1-3] in part because of its potential utility as a quantitative remote probe of gas systems. In a recent paper[4] Fouche and Chang (FC) reported the observation of strong RRS from I_2 vapor in air, excited by monochromatic light slightly (~ 0.0016 nm) off resonance with two effectively coincident absorption lines of I_2. These lines are located within the 514.5-nm gain curve of an argon laser, which is single moded and tuned within the gain curve by a tilted etalon. The report of FC is stimulating additional interest in the use of RRS for gas probing. However, whereas we share this interest, we have been unable to confirm either the quantitative results of FC or their interpretation of the re-emission as RRS.

In their paper FC first describe a measurement of the re-emission within a 34-cm^{-1}-wide spectrometer channel centered on the first vibrational Stokes band, which is shifted by ~ 213 cm^{-1} from the exciting line. The intensity of this re-emission was observed as the argon laser was tuned over the 514.5-nm gain curve. They observed a strong emission peak with excitation wavelength near one edge of the gain curve, and a weak peak with excitation near the center. Between these wavelengths they found a minimum signal wavelength, which they identified as point *B* on their Fig. 1. Using excitation at this wavelength they observed the sharp line re-emission which they identified as RRS.

There is as yet no universally accepted criterion for distinguishing between fluorescence and RRS. However, Raman scattering is usually described as an intrinsically "instantaneous" process,[5] and thereby insensitive to collision-induced quenching, and redistribution of excitation energy.[1] It is relevant that these properties establish the advantage of Raman scattering over fluorescence as a probe of gas systems. In the FC paper, sharp line re-emission observed with near-resonance excitation is attributed to RRS on the basis of its apparent lack of quenching.

We have attempted to duplicate the results of FC and have investigated in detail the effects of adding a foreign gas (N_2). We find (1) that the sharp line re-emission observed by FC does quench significantly; and (2) that the spectrum of the scattering changes as a result of collisional redistribution of the energy among the rotational sublevels of the excited electronic-vibrational manifold. These results support the conclusion that the sharp line re-emission is not RRS.

Our apparatus is very similar to theirs. We used a Spex 1400 double monochromator, RCA C31000E photomultiplier, photon counting elec-

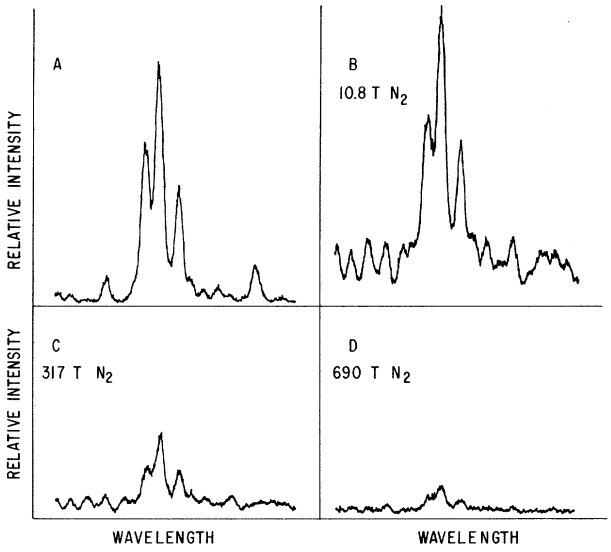

FIG. 1. Spectrum of the first Stokes signal from monochromatically excited I_2 vapor with (a) no N_2 added and (b),(c),(d) with N_2 added at various pressures. The total scan width is 34 cm^{-1}, while the monochromator spectral slit width (full width at half-maximum) is 1 cm^{-1}. The relative intensity scales are the same.

tronics, and Coherent Radiation model 52B argon laser with over 500 mW single mode available. The wavelength of this laser is stable to better than 100 MHz ($<10^{-4}$ nm) over periods of several hours. Using a 34-cm^{-1} slit width we found the signal minimum to fall approximately 1750–1800 MHz from the maximum. In Fouche and Chang's Fig. 1 this separation is shown as 17 modes or 1950 MHz. The difference is probably due to their reported wavelength drift.

In Fig. 1 we show the evolution of the detailed spectrum of the light scattered in the 34-cm^{-1}-wide channel as the foreign gas pressure is increased with the incident wavelength at the minimum signal point. These measurements were taken with a triangular slit function of width 1 cm^{-1}. In Fig. 1(a) the spectrum consists principally of the two doublets, overlapping to form a triplet, which result from excitation of the nearly coincident $43 \leftarrow 0$ $P(12)$ and $R(14)$ lines. In Fig. 1(b), with 10.8 Torr of N_2 added to the cell, a background consisting of many small peaks has appeared. These peaks are fluorescence from molecules whose rotational states have been changed by collisions. Since rotational-state changes are more probable than vibrational or electronic de-excitation, collisions redistribute the fluorescence among the rotational lines of a given electronic-vibrational manifold more rapidly than they quench to another vibrational state. The occurrence of these lines in the spectrum is evidence that the signal is not RRS, since the I_2 molecules must remain excited long enough to undergo collisions. These lines in I_2 fluorescence spectra have been used, for example, to study molecular collision kinetics[6] and to measure excited-state molecular parameters.[7]

Figures 1(c) and 1(d) show that as more N_2 is added the re-emission spectrum approaches a continuum. The original sharp line re-emission is quenched by an order of magnitude, and thus is not RRS.

We are not aware of any measurements of collisional broadening of I_2 absorption lines by N_2. However, the quenching coefficients for other foreign gases measured by Kurzel and Steinfeld,[8] combined with their value of 1 μsec for the natural lifetime, yield collision-broadened linewidths in the range from 3000 to 5000 MHz in the presence of 760 Torr of a foreign gas. Since our separation from the resonance center is only ~1800 MHz, it is not surprising that the re-emission is fluorescence and can be quenched.[9]

The results reported by FC are significant in that they call attention to the possibility of strongly enhanced re-emission which is less sensitive to foreign gas pressure than usual fluorescence. However, our results indicate that the insensitivity to quenching they report is misleading and that their interpretation of the re-emission as RRS is incorrect.

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[9]There are also hyperfine components of these two absorption lines spread over an interval of 1200 MHz. See M. S. Sorem and A. L. Schawlow, Opt. Commun. 5, 148 (1972).