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P. Robrish, H. J. Rosen and O. Chamberlain

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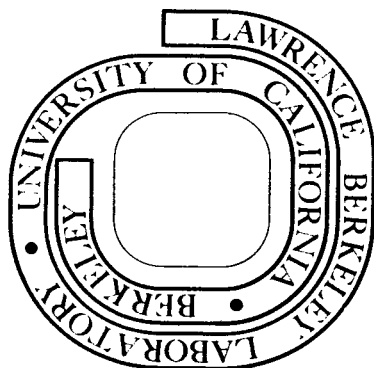
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Observation of a Continuous Transition from
Resonance Raman Scattering to Fluorescence*

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ABSTRACT

We have measured resonance Raman scattering in I_2 vapor near several rotational lines of the 0-25 vibrational band of the B-X electronic transition with a narrow-band tunable dye laser. Our measurements of the scattering cross-section versus nitrogen buffer gas pressure for laser frequencies near the 0-25 P(47) rotational line support the view that there is no fundamental distinction between fluorescence and resonance Raman scattering in gases.

There has been considerable debate on the distinction between resonance Raman scattering and fluorescence in gases.^{1,2,3} It has been suggested that they are two separate quantum mechanical processes. Recently, Williams et al.,³ have argued that fundamentally there is only one process involved which has different properties on and off resonance and that these properties change in a continuous fashion as the exciting source is tuned across an absorption line in a gas. In this letter, we shall present measurements which support this point of view.⁴

Most of the controversy has centered on measurements near the 0-43 P(12), R(14) levels of the B-X electronic transition in I₂ vapor using an argon laser operating at 5145Å as an exciting source. These experiments have been very interesting but there have been significant quantitative disagreements^{1,2} and the measurements were limited to some extent by the fact that one can not tune more than .06 cm⁻¹ away from the resonance without overlapping the 0-45 P(64) transition. We have investigated resonance Raman scattering in I₂ vapor for several of the strongest rotational absorption lines in the 0-25 vibrational band of the B-X electronic transition with a narrow-band pulsed dye laser. We chose to investigate this band because the product of the matrix elements for absorption and inelastic reemission is the largest of the B-X system.⁵ Our effort has concentrated on the 0-25 P(47) rotational line which is relatively isolated from other absorption lines. For this line we have measured the resonance Raman cross-section versus nitrogen buffer gas pressure for various laser frequencies.

The experimental arrangement consisted of the usual 90° scattering geometry, a Jarell Ashe double monochromator and a gated electrometer which integrated the charge from a RCA 8575 photomultiplier tube. The exciting source was a nitrogen-laser-pumped dye laser similar to that of Hänsch⁶ using a 5×10^{-3} molar solution of Fluorescein Disodium Salt in ethanol. The bandwidth of the laser was narrowed by using a beam expanding telescope and a 1 cm^{-1} air spaced etalon in series with a grating blazed at 61° and operated in fifth order. In this configuration, the laser had a linewidth of $.037 \pm .007 \text{ cm}^{-1}$ and an average power of .2 mW. The etalon and the grating were enclosed in a vacuum tight chamber so that fine tuning could be accomplished by varying the pressure within the chamber. The advantage of pressure tuning is that the bandpass of the etalon remains centered on that of the grating without the mechanical manipulation of either the grating or the etalon. Using pressure tuning we have been able to tune over an interval of 3 cm^{-1} in steps of $.01 \text{ cm}^{-1}$ in a stable and reproducible manner.

In Fig. 1 we show a plot of the integrated intensity of the first Raman mode of I_2 versus laser frequency. The spectrum was taken by centering the spectrometer bandpass (75 cm^{-1}) on the Stokes Raman mode at $\sim 213 \text{ cm}^{-1}$ and then pressure tuning the laser. The sample cell contained I_2 at its room temperature vapor pressure (.65 mm) with no buffer gas present. The laser beam was attenuated and defocussed sufficiently to avoid saturation and heating effects. The peaks in the scattered intensity correspond within experimental error to peaks in the absorption spectrum.⁷ As one approaches an absorption line, the cross-section increases dramatically.

For example, at the peak of the 0-25 P(47) transition, the differential scattering cross-section, $\frac{d\sigma}{d\Omega}$, was measured to be 3.6×10^{-21} cm²/ster which is ten orders of magnitude larger than the Raman cross-section for nitrogen at 5460A.⁸ The cross-sections presented in this paper were calculated by using the cross-section for the 992 cm⁻¹ mode of benzene⁹ as a standard and making small corrections for absorption and spectral efficiency.

We have investigated the quenching of the scattering cross-section by nitrogen near the 0-25 P(47) transition. This transition, in contrast to the 0-43 P(12), R(14) transitions investigated by previous authors,^{1,2,3} has very little structure within .4 cm⁻¹ of its high frequency side (see Fig. 1). In Fig. 2 we show a plot of the resonance Raman cross-section versus nitrogen pressure for several different laser frequencies. For these measurements, both the incident laser beam and the scattered light accepted by the spectrometer were polarized perpendicular to its entrance slit. The bandpass of the spectrometer was set to 75 cm⁻¹. With the laser set on resonance, the cross-section is quenched by over a factor of 1000 for a change in N₂ pressure from 2 mm to 730 mm. As one tunes off resonance, the quenching becomes progressively smaller until at .2 cm⁻¹ away from the absorption line there is virtually no quenching.

We may understand the results of this experiment qualitatively by invoking the uncertainty principle, which implies that the time spent by the molecule in the intermediate state is never greater than the order of $(\omega - \omega_{Res})^{-1}$ where ω is the (angular) frequency of the incident light. Since the lifetime of the intermediate state reached by the B-X electronic

transition is known to be about 1 μsec ^{10,3} and the collision time at one atmosphere of N_2 is roughly .1 ns,¹¹ we expect that the scattering should be quenched considerably near the center of the resonance line. On the other hand, as we tune away from resonance the re-emission process should occur more rapidly so that the effects of collisions become progressively less. For example, when the incident light is off resonance by $\Delta\nu = 0.1 \text{ cm}^{-1}$ ($\Delta\omega = 2 \times 10^{10}/\text{sec}$) the quenching should be rather slight. Recently Williams et al.,³ have measured the time dependence of resonance Raman scattering as they tuned across an absorption line and their results are consistent with an explanation based on the uncertainty principle.

We can also make a quantitative comparison of our data to theory, but the analysis is complicated by the doppler and hyperfine broadening of the absorption line and the linewidth of the laser. Near an isolated absorption line, the resonance Raman cross-section can be written as:^{12,13}

$$\frac{d\sigma}{d\Omega} \propto \frac{\Gamma_T}{\Gamma_T - \Gamma_e} \int_0^\infty S(\nu_\ell - \nu_\ell^0) d\nu_\ell \int_0^\infty \frac{G(\nu_r - \nu_r^0) d\nu_r}{(\nu_\ell - \nu_r)^2 + \Gamma_T^2}$$

where $G(\nu_r - \nu_r^0)$ is the line shape of the resonance due to doppler and hyperfine broadening centered at ν_r^0 and $S(\nu_\ell - \nu_\ell^0)$ is the line shape of the laser centered at ν_ℓ^0 . Γ_T is the linewidth due to collisions and natural damping and Γ_e is the contribution to the linewidth from elastic collisions. In order to evaluate the dependence of $\frac{d\sigma}{d\Omega}$ on pressure, P, and $\Delta\nu = \nu_\ell^0 - \nu_r^0$ we assume that G and S are gaussians and use fourier transforms to reduce the double integral to a single integral. We then neglect natural damping, assume the Γ 's vary linearly with P, and evaluate the integral numerically as a function of $\Delta\nu$ and P. The results of such a

calculation are shown as the curves in Fig. 2, where we have assumed that $\Gamma_T = (1.4 \times 10^{-4} \text{ cm}^{-1}/\text{mm}) * P$ and that the convoluted gaussian half width (at 1/e) of the laser and the resonance is $.024 \text{ cm}^{-1}$. Overall normalization was set by a best fit to the $\Delta\nu = 0$ data. It is clear that this model calculation adequately represents the data as a function of $(\Delta\nu)$ and P , further supporting the view that there is no distinction between resonance Raman scattering and fluorescence in gases.

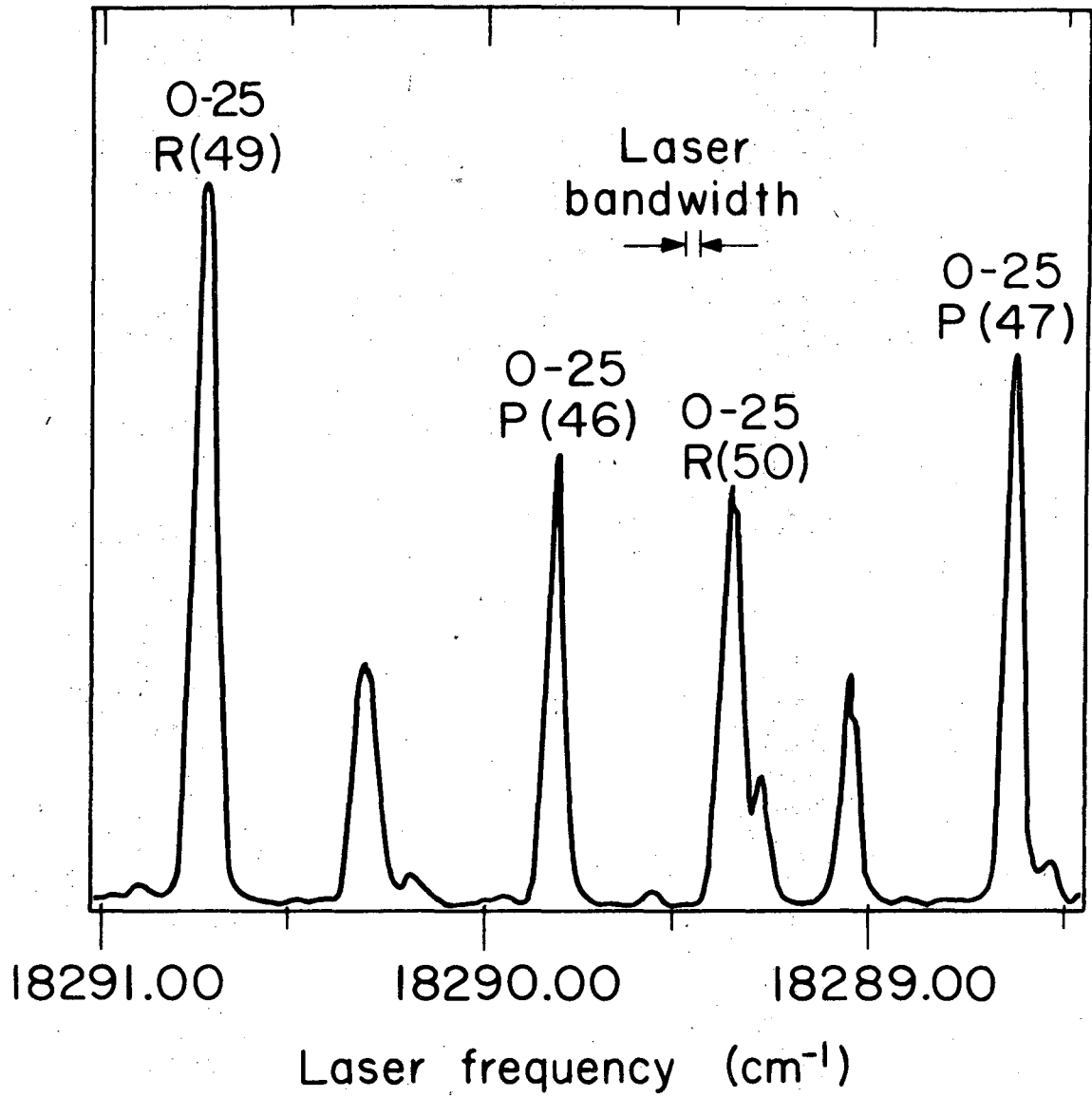
Our measurements of large scattering cross-sections for I_2 in nitrogen at atmospheric pressure are also of practical interest for the possible use of laser backscattering for remote detection of pollutant levels in the atmosphere. The cross-sections we have measured should allow the detection of less than 1 ppm of I_2 at several kilometers.

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- * Research supported by National Science Foundation, RANN Division and U.S. Atomic Energy Commission.
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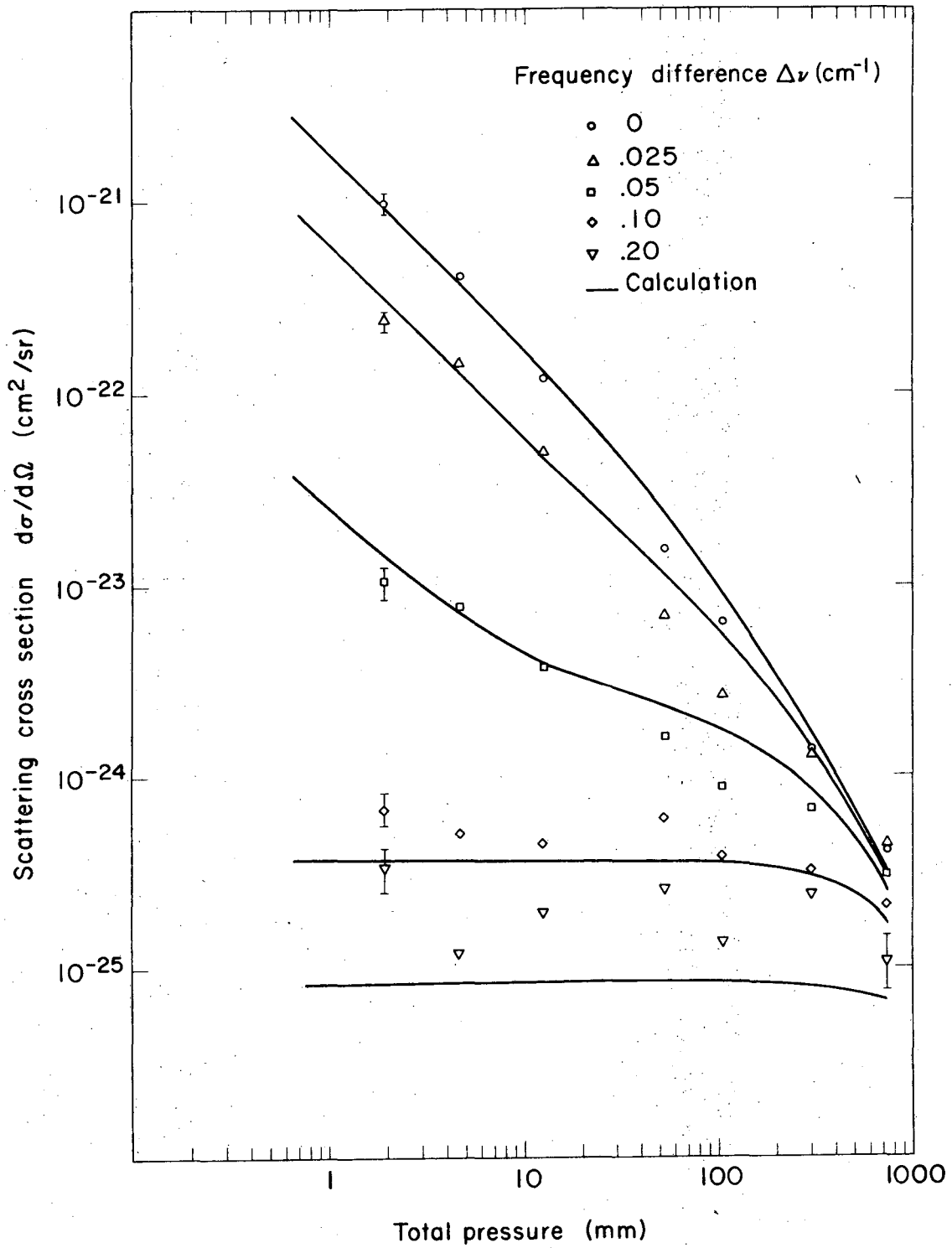
Figure Captions

- 1) Scattered intensity of Raman mode located at $\sim 213 \text{ cm}^{-1}$ vs. laser frequency for I_2 vapor at a pressure of .65 mm with no buffer gas present.
- 2) Plot of the differential Resonant Raman scattering cross-section for the Raman mode located at $\sim 213 \text{ cm}^{-1}$ vs. nitrogen buffer gas pressure for laser frequencies separated from the center of the 0-25 P(47) rotational line by 0, .025, .05, .1 and .2 cm^{-1} .



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Fig. 1



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Fig. 2

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