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PRESSURE-INDUCED LINE SHIFT AND COLLISIONAL NARROWING IN HYDROGEN GAS DETERMINED BY STIMULATED RAMAN EMISSION*

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Comparison of the frequency of stimulated Raman scattering in hydrogen at different pressures yields the shift of the $Q[1]$ frequency. Amplification measurements in the backward direction enable us to measure the linewidth of the $Q[1]$ line to verify the theories on collisional narrowing.

The stimulated Raman effect in gases was first reported by Minck, Terhune, and Rado.[1] At room temperature the $Q[1]$ vibrational transition is dominant in the stimulated Raman effect in H_2. A variation in the vibrational frequency with pressure was observed in the spontaneous Raman spectrum.[2] Since the stimulated emission spectrum can display much narrower and more intense lines, this shift may be determined more accurately by utilizing Raman laser oscillators.[3,4] The Stokes (or anti-Stokes) frequencies of two H_2 Raman lasers are compared. One laser operates at a variable pressure; the other is kept at a constant low pressure and has a fixed frequency constant within 10^{-2} cm^{-1}, the Doppler width for Raman scattering in the forward direction. No splitting was observed when both forward and backward Stokes frequencies were combined, so we concluded that their frequencies were the same within the resolution of our Fabry-Perot.

This measurement has been carried out in the geometry sketched on Fig. 1. The beam of a Q-switched ruby laser is divided into two beams which pass through two high-pressure cells 1 and 2. The double Raman emission is recorded using a Fabry-Perot etalon. Identification of the frequency from each cell is achieved with a half-wave plate in one of the laser beams and two crossed polarizers each covering half of the film. A filter prevents spurious reflections of Raman light by the laser mirrors. Our data for Stokes and anti-Stokes lines are also shown in Fig. 1. We measure a shift of 3.2×10^{-3} cm^{-1}/amagat, which agrees with the shift measured by May et al.[2] in spontaneous emission.

The interest of these results is threefold: (a) As predicted by theory, the stimulated emission occurs at the center of the spontaneous Raman line. (b) There is no important shift due to anomalous dispersion in the Raman susceptibility. (c) As a consequence, this method may be used more confidently to measure the variation of Raman frequencies with pressure, temperature, foreign gas admixture, or other physical processes, and to obtain precisely tuned Raman generators.

The second spectroscopic measurement by means of stimulated Raman emission reported here concerns the verification of collisional narrowing. The experimental line shape may be determined accurately by means of a low-gain Raman amplifier cell.[5] The output-to-input ratio of a low-gain stable amplifier

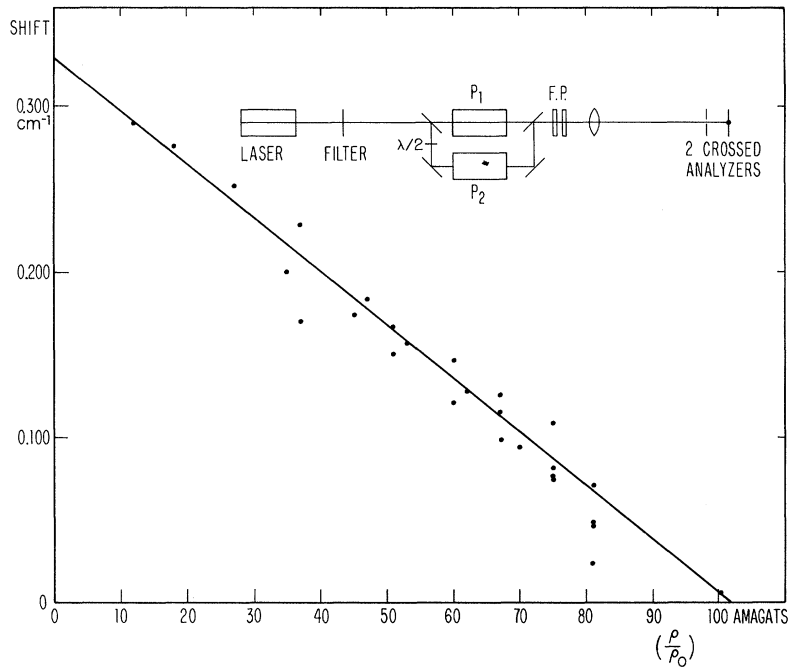

FIG. 1. Experimental setup and results for the frequency shift of the $Q[1]$ vibrational Raman line in H_2 as a function of pressure.

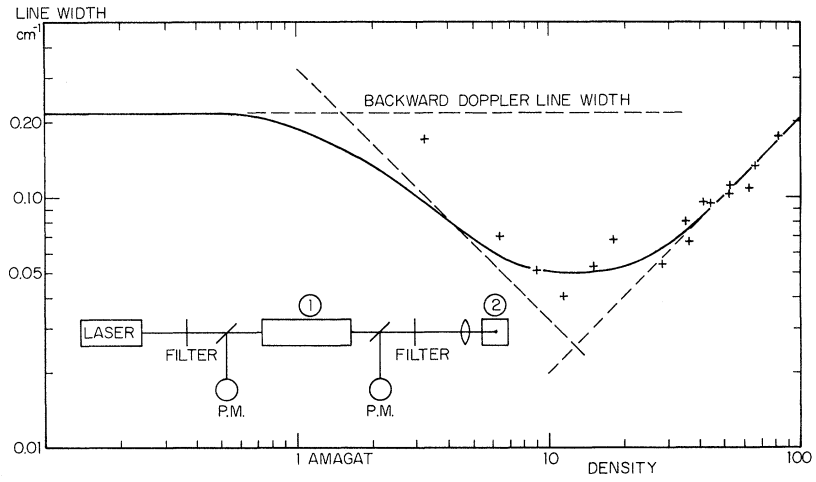

FIG. 2. Determination of the width of the $Q[1]$ vibrational line of H_2 as a function of pressure by means of a Raman amplifier cell for backward Stokes light. The experimental points are compared with the drawn theoretical curve.[7,8]

is given by

$$\ln[g_s^{\text{out}}(\omega)/g_s^{\text{in}}(\omega)] = 8\pi\lambda_s^{-1}|E_L|^2|\chi_s''(\omega)|,$$

where χ_s'' is the imaginary part of the Raman susceptibility. We have measured the gain for back-scattered Stokes light, because the Doppler broadening (full width at half-maximum) in this case is larger,

$$(\Delta\nu_D)_{\text{back}} = (\nu_L + \nu_s)(8kT\ln 2/mc)^{1/2}.$$

The regime of collisional narrowing is therefore more pronounced than in the forward direction.[6] The solid theoretical curve in Fig. 2 is computed by the method of Galatry.[7] At high pressures the linewidth is proportional to the

pressure; at very low pressures the width is constant, equal to the Doppler width. The width is inversely proportional to the pressure in the intermediate region.[8]

In the experimental arrangement a collimated laser beam passes through a cell 1, 30 cm long, with a variable pressure of H_2. The laser power and the pressure are always low enough that no stimulated Raman oscillation occurs in cell 1. Its experimental gain varied from about 1.2 to 30. Most data were obtained with a gain less than e^2. The laser is then focused in a second cell 2 where a strong Raman emission occurs. The backward Stokes light is used with an attenuation of 10-50 dB to test the Raman gain in cell 1 with the help of two photomultipliers. Note that the geometry of the laser beam is undisturbed in the amplifier cell. In the Raman oscillator the laser beam is depleted and perhaps otherwise deformed. Another attenuator prevents the backward Stokes light from reentering the system after reflection on the laser mirrors. Sufficient isolation is an important factor for reliable quantitative measurements.

By varying the pressure in cell 2, the Raman gain in the backward direction can be recorded versus Raman frequency.[9] The process is repeated for several pressures in cell 1. At high pressures, we have been able to scan the complete width of the Raman line. At low pressures, we have scanned one-half of the width only. Below 10 amagat, the maximum gain drops faster than the density, implying that the linewidth increases. The linewidth at 3 amagat was calculated from the value of the maximum gain. Our linewidth measurements are reported on Fig. 2 as a function of pressure. They agree very well with the theoretical curve. Below 110 amagat the measured linewidth is smaller than the Doppler linewidth and presents the expected collisional narrowing region which is clearly demonstrated.

The gains measured in these experiments are comparable to the theoretical gain computed with the known value of the Raman polarizability of the hydrogen molecule and the nominal intensity of the incident laser beam. The amplifier cell, under the conditions reported here, showed no anomalies or sharp changes in the gain as have been observed by others, who have reported sharp thresholds in the stimulated emission.[3,4]

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[8]The first evidence for motional narrowing in a gas came from the proton magnetic resonance in hydrogen gas [E. M. Purcell, R. V. Pound, and N. Bloembergen, Phys. Rev. 70, 986 (1946)]. The narrowing of the Doppler width by collisions in a gas was first discussed by R. H. Dicke, Phys. Rev. 89, 472 (1953). This effect of a buffer gas has been used extensively in microwave spectroscopy. When excited optical levels are involved, the motional narrowing of optical lines will usually not be observable, because each collision process effectively limits the lifetime of the optical level. For Raman scattering, however, where only vibrational-rotational states of the electronic ground state of the H_2 molecule are involved, motional narrowing should be observable, as pointed out in Refs. 4 and 6. We believe Fig. 2 presents the first experimental evidence for this motional narrowing in an optical process.

[9]A technique of a related type has been used by P. D. Maker and R. W. Terhune, Phys. Rev. 137, A801 (1965), to measure the parametric generation of anti-Stokes light in liquids.