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STIMULATED RAMAN SCATTERING IN HYDROGEN: A MEASUREMENT OF THE VIBRATIONAL LIFETIME*

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The study of vibrational relaxation in H_2 gas has been heretofore limited to the very high temperatures at which the vibrational degree of freedom makes a measurable contribution to the specific heat.^{1,2} We report in this Letter an experiment in which the direct observation of the excess population produced in the first vibrationally excited state by stimulated Raman scattering has allowed, for the first time, a measurement of vibrational relaxation in H_2 at ambient temperature.

Stimulated Raman scattering in H_2 gas³ has been shown to yield sizable transfer of energy from the exciting to Stokes frequencies. To the large (typically 10^{16}) number of Stokes photons produced by a Q -switched focused laser beam, there must correspond an equal number of vibrational excitations located in the focal region. Thus an excess population is created in a very short time (20 nsec) in the first vibrationally excited state. Once the excitation is over, the population distribution relaxes, through molecular collisions, to its thermal equilibrium value with a characteristic time equal to the lifetime of the vibrational state. Although an observation of the stimulated Raman spectrum shows that this excitation selects the $v=1, J=1$ level, it should be noted that ro-

tational thermalization is very fast and that the observed population is spread among the odd rotational levels. The time evolution of this process is obtained from the observation of spontaneous Raman anti-Stokes scattering of a probing beam by the excited medium. The scattered intensity, negligible under conditions of thermal equilibrium, is strictly proportional to the number of molecules in the excited state.

The experimental arrangement is shown in Fig. 1. A Q -switched ruby laser beam is focused through lens L into a cell containing (research grade) gaseous H_2 under pressure where it produces stimulated Raman scattering. The laser power is kept low enough (typically 2 MW for a pulse duration of 20 nsec) so that the fraction of excited molecules is of the order of 1% or less. An ordinary (non- Q -switched) ruby laser provides the probing source. Its output is a train of spikes lasting for about 500 μ sec, the peak power of which is well below threshold for stimulated scattering. Thus the excitations due to the probing beam would come only from spontaneous scattering and are completely negligible. Adequate synchronization is provided between the laser signals. The two beams, accurately overlapped through the use of a 50%

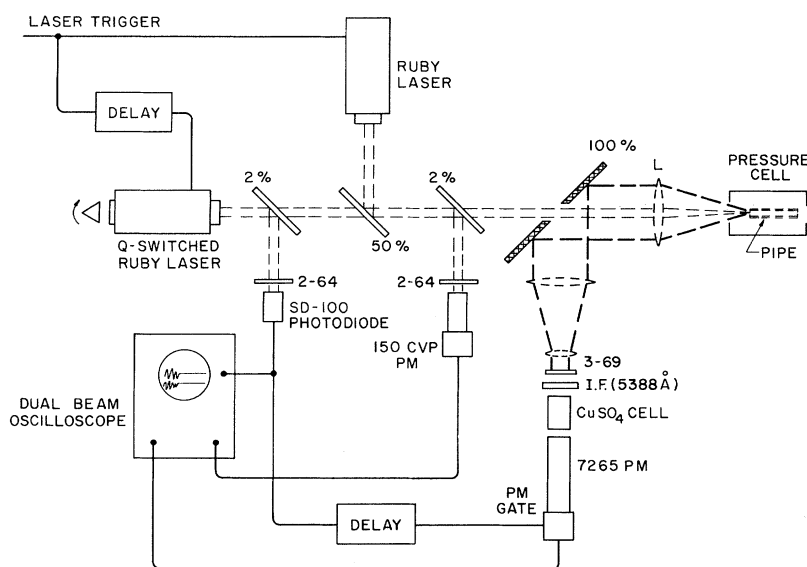


FIG. 1. A schematic diagram of the experimental arrangement (see text).

beam splitter, have a common focus in the cell where a reflecting pipe provides efficient collection by the lens L of the spontaneous anti-Stokes scattering from the excited medium. The spontaneously scattered light is detected by a fast, sensitive, 14-stage photomultiplier (RCA 7265).

Appropriate filtering ensures that only radiation at the anti-Stokes frequency reaches the photocathode. Although observations of backward rather than forward scattering avoids direct exposure of the photomultiplier to the high anti-Stokes intensity of the stimulated scattering, provision was made to switch off the photomultiplier during the exciting laser pulse.

The probing source was monitored by a 150-CVP photomultiplier and the outside signals of the two detectors were displayed on the screen of a dual-beam oscilloscope. Suitable averaging was needed to eliminate fluctuations associated with the filamentary structure of the beams. After this operation, comparison of the probing and scattered intensities showed a nearly perfect exponential decay of the excited-state population as shown in Fig. 2. This excludes any influence of molecular diffusion on the results. We have measured the lifetime $\tau_{\text{H}_2-\text{H}_2}$ of the $v=1$ state for various pressures P in the interval 20-60 kg/cm². Results are shown in Fig. 3. As expected for the two-body collisions (which ought to be dominant at these

pressures), the product $P\tau_{\text{H}_2-\text{H}_2}$ is seen to be constant within the experimental uncertainty. We estimate its value at 300°K to be $P\tau_{\text{H}_2-\text{H}_2} = (1060 \pm 100) \times 10^{-6}$ atm sec. It should be pointed out that this value implies that saturation

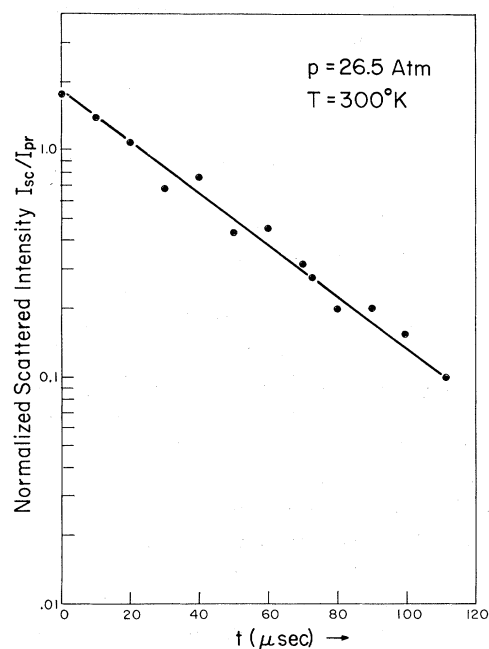


FIG. 2. Time dependence of the ratio (I_{sc}/I_{pr}) of the intensity I_{sc} of anti-Stokes scattering from the excited medium to that, I_{pr} , of the probing beam. Excitation by stimulated scattering occurs at $t=0$.

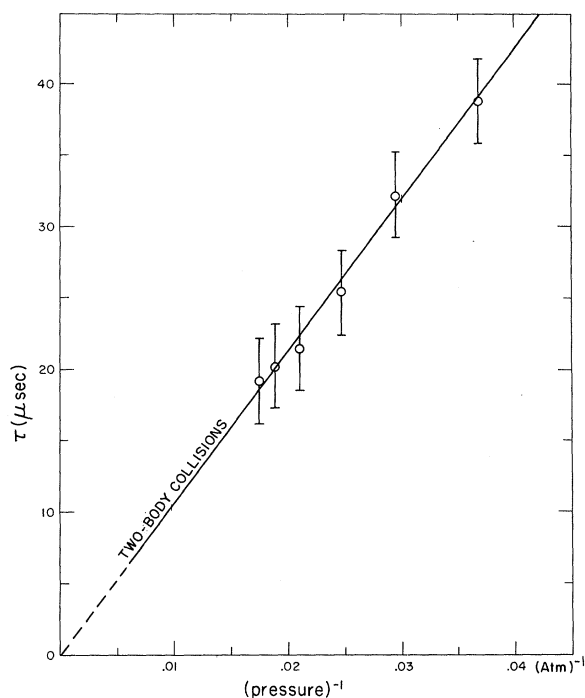


FIG. 3. The vibrational lifetime $\tau_{\text{H}_2-\text{H}_2}$ as a function of pressure at $T = 300^\circ\text{K}$. Experimental points are shown with their associated error flags.

of the Raman transition should easily occur for stimulated Raman scattering in hydrogen.

Kiefer and Lutz² using shock-tube techniques have obtained values of $\tau_{\text{H}_2-\text{H}_2}$ in the temperature range 1100–2700°K. They noted that their results were in excellent agreement with a Landau-Teller law, $\ln(P\tau_{\text{H}_2-\text{H}_2}) = A + BT^{-1/3}$. Although the Landau-Teller expression is not expected to hold strictly for hydrogen at ambient temperature, it is interesting to notice that an extrapolation of their results gives a value only slightly higher than ours. The correction term proposed by Schwartz, Slawsky, and Herzfeld^{4,1} is found to be in error by several orders of magnitude; this is not surprising, as the approximation involved in the mathematical treatment can be shown to lead in the present case to a gross overestimate of the transition probability. It would be of interest to extend the theoretical calculations of Salkoff

and Bauer⁵ to this low temperature range.

The use of stimulated Raman scattering to produce an excited-state population has a definite advantage in the case of the hydrogen molecule, where the large vibrational quantum makes the corresponding specific heat so small that observation of acoustical relaxation is impossible below 1000°K. It also has the more general advantage over acoustical measurements that it allows the study of a definite mode of vibration. Our method can be considered as complementary to that proposed by Gorelik⁶ which uses the acousto-optic effect and applies only to infrared-active vibrations. It can be extended to other gases in which stimulated Raman scattering has been observed,^{3,7} particularly nitrogen for which room-temperature data are still missing. Further details will be published in a subsequent paper.⁸

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