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"Study of Various Aspects of Raman Scattering Using C. W. Optical Masers"

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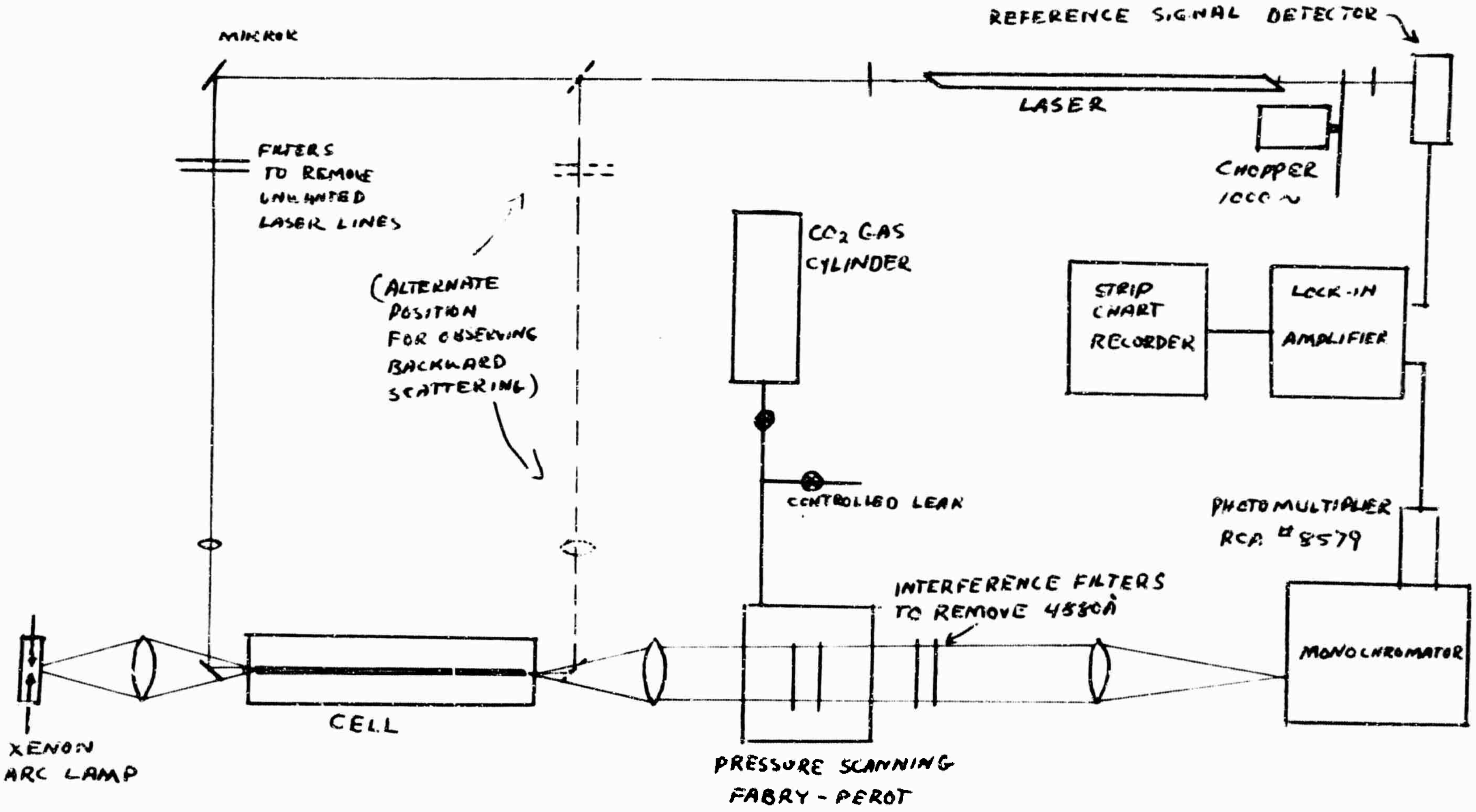
The research program has been based upon an attempt to apply the high intensity Argon laser to problems associated with the Raman effect and related phenomena. A spectrometer which is particularly well suited for study of Raman scattering in the forward and backward direction in liquids and gases has been developed. This apparatus is shown in figure 1.

The sample cell shown in a 20cm. length of quartz capillary tubing with an inside diameter of 0. 5 mm. When filled with a liquid with index of refraction greater than that of quartz the column of liquid acts as a light pipe. A ray of light propagating in the pipe at less than a certain critical angle to the axis of the pipe (about 20 degrees for CS_2) is trapped in the column by total internal reflection, and emerges at the end of the pipe with the original angle of inclination to the axis perserved. This design has two advantages: the usable scattering volume is greatly increased without increasing the cross-sectional area of that volume, which is desirable for maintaining a high intensity together with high resolution in the Fabry-Perot and spectrometer, (without losing any information which may be contained in the scattering angle) and, when the xenon arc lamp is used, a much larger effective solid angle is subtended by the sample than can be realized with other arrangements, thus increasing the intensity. The pressure scanned Fabry-Perot interferometer is designed to operate over a pressure range of 15 to 100 p. s. i. a. rather than the more common 0-15 psi design; the larger scanning range is desirable for interferometers of large interorder spacing. The remainder of the apparatus is conventional.



SKETCH OF THE SPECTROMETER (fig. 1)

I. Linewidth of Raman Scattering--J. R. Murray, A. P. Sheng, J. D. Ducuing

It is, by now, fairly well established that the anomalous behavior of the on-set of stimulated Raman effect observed with a Q-switched Ruby laser beam arises because of the effect of self trapping of the high intensity beam. In the presence of a self trapped beam, however, it is difficult to extract quantitative information on the Raman process itself. Accordingly, it is desirable to examine the size of various parameters involved in the process of the Raman effect free from complications arising from the self-trapping effect. To this end, we have studied with high precision the Raman linewidth of a number of liquids using the C. W. Argon laser system described above. The liquids studied in these experiments were those commonly used in the studies of stimulated Raman effect with a Ruby laser. In fact, we have discussed that the linewidth for carbon disulfite is somewhat lower than those reported previously. (See below.) This experiment at the same time, has enabled us to test the performances of our spectrometer system which utilizes a number of elements not commonly used by other workers in the past.

For the 992 benzene and 1345 nitrobenzene lines the widths were, respectively, 3 and 9 wave numbers. On the carbon disulfide lines at 656, the width of the most intense component was measured to be .64 ± .10 wave numbers, where the error brackets given represent rms error of all measurements made, some under widely varying conditions. Instrumental width (measured separately for each run) was approximately .7 cm^{-1} and has been subtracted from the measurements above. The widths measured for benzene and nitrobenzene agree with those in the literature[1] but the CS_2 width measured is about a factor of two ower than previously reported[2]. The details determining the exact magnitude of his linewidth is not as yet understood. We are presently examining whether similar measurements should be carried out on other molecular species with structures similar to CS_2.

The effect of dilution on the linewidth of CS_2 was briefly investigated to determine the feasibility of studying molecular interactions with this apparatus. The results of a series of measurement are given below:

Vol% CS_2 in Benzene	CS_2 Raman linewidth(656 cm^{-1})
100	.53 (±.07)
80	.53
60	.53
20	.50
10	.75
5	.94

Vol% CS_2 in Styrene	
10	.88
5	1.8

In passing, it might be noted that the signal to noise ratio seen in these measurements was typically 50 to 100:1 on the CS_2 line with .7 wave number resolution and a 1 second time constant. A large part of the residual noise is due to laser flicker, and some effort is being made to reduce it. With the Fabry-Perot removed, a signal to noise ratio of about 50:1 can be obtained on the nitrobenzene 1345 anistokes line with 25 wave numbers resolution and 1 second time constant. Laser power in both cases was approximately 150 mw. at 4880A.

II. Stimulated Raman Absorption in Liquids--J. R. Murray, A. P. Sheng, J. D. Ducuing

Stimulated Raman scattering can be observed as an absorption of light at the Raman antistokes frequency.[3] A continuum background was provided by the xenon arc and absorption at the antistokes frequencies of the benzene 992, nitrobenzene 1345, and carbon disulfide 656 lines was sought. The effect was not observed. This is a reasonable result, as the minimum detectable absorption with the apparatus was roughly one part in 10^5, which is the same order of magnitude as the expected effect with the 300 milliwatt laser power at 4880A available at the time. The largest remaining source of noise in the apparatus after some refinements was flickering of the xenon arc; hence not much improvement in noise can be expected and any future attempt to see the effect must rely on higher laser intensity, a smaller cross-section of the tubing, or an increase in length of the cell. An increase in length is not practical for nitrobenzene (which shows the greatest predicted gain) because of absorption at the antistokes frequency. Smaller cross-sections become difficult experimentally and cut down on the intensity of xenon background available; also nitrobenzene tends to boil in them from heating due to a slight absorption at 4880Å.

III. Two Photon Absorption Processes--J. R. Murray, A. P. Sheng, A. Javan

In a process similar in principle to Raman scattering it is possible that a substance transparent at frequency and opaque at frequency can absorb two quanta of frequency and make a transition to an excited level. The subsequent decay of this excitation may be observed as, for example fluorescence.[4]

We have observed this effect in anthracene using the apparatus of figure 1. The cell and the Fabry-Perot are removed and the laser is focussed into a crystal sample. Transmitted, scattered radiation is imaged on the spectrometer slit. The antracene show a blue fluorescence band at 4500Å. The intensity of which, over the range of intensities used in the experiment, varies as the 1.25 power of the laser intensity. A double photon absorption implies a quadratic power dependence. It is evident that appreciable double photon absorption exists, but is nearly masked by a linear component the origin of which has not been explained; it may be a light leak in the monochromator. These results are very preliminary. Possible experiments using the effect are being considered.

It should be noted that a quantitative understanding of the nature of double quantum transitions is of particular interest at this time. There are reasons to believe that a double quantum transition may introduce sufficient non-linearities to contribute in some cases to the effect of self trapping of a light beam as well as stabilizing a self trapped beam.

IV. Raman Scattering in Gases--Linewidth Phenomena--J. R. Murray, A.P. Sheng, A. Javan

The quadrupole rotation and vibration transitions of the hydrogen molecule have been shown to have very narrow linewidth and, furthermore, no measurable pressure broadening with the instrumental resolution available (.05cm^{-1})[5]. It has been shown that under such conditions a pressure narrowing effect might be expected when the mean free path of the hydrogen molecules becomes comparable to the wavelength associated with the transition.[6] Detailed study of this effect has not been possible in the past without the use of a laser. This effect is of considerable spectroscopic importance. And, at the same time, it may shed additional information on important behaviors of stimulated Raman processes. It is proposed to search for this effect in the Raman scattering from these levels.

It may be shown for forward scattering at small angles and a narrow band exciting source that the linewidth of the Raman scattered light reproduces the width of the quadrupole transitions for both Doppler and inhomogeneous broadening.

A modification of the cell is required for this experiment. The laser must be collimated to pass down the center of the quartz tubing, or at worse to strike the quartz wall at grazing incidence. The Raman scattered light will be trapped in the body of the quartz tubing by total internal reflection. Such a cell for pressures up to 3000 psi is presently under construction. Considerable efforts will be directed towards study of this effect during the forthcoming months.

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