INVERSE RAMAN SPECTRA: INDUCED ABSORPTION AT OPTICAL FREQUENCIES

W. J. Jones* and B. P. Stoicheff[†]

Division of Pure Physics, National Research Council, Ottawa, Canada (Received 15 October 1964)

According to the dispersion theories of Kramers and Heisenberg, and Dirac, the occurrence of incoherent scattering of radiation manifests itself both in <u>emission</u> and in <u>ab-</u> <u>sorption</u>.¹ Up to the present time, all investigations of such processes, including Compton scattering, the normal Raman effect, or the recently discovered stimulated Raman scattering,² have been concerned with the <u>emission</u> of the scattered radiation and its spectrum. We wish to report here spectroscopic evidence for the <u>absorption</u> occurring during incoherent scattering at optical frequencies.

In studies of normal and stimulated Raman scattering, the scattering medium is irradiated with monochromatic light of frequency ν_0 and energy density ρ_0 . This light is absorbed and simultaneously light is emitted spontaneously or by stimulation, at either the Stokes frequency $\nu_0 - \nu_M$ or the anti-Stokes frequency $\nu_0 + \nu_M$, with the atoms or molecules changing their energy states by $\pm h\nu_M$. The probability of absorption of ν_0 and emission of $\nu_1 = \nu_0 \mp \nu_M$ is given by

$$\frac{16\pi^4}{h^4} \int |\mu|^2 \rho_0 \left(\rho_1 + \frac{8\pi h \nu_1^{-3}}{c^3}\right) d\nu_0, \qquad (1)$$

where μ is the well-known matrix element for two-photon processes.¹ The term $\rho_0 \cdot 8\pi h \nu_1^{3/2}$ c^3 leads to normal or spontaneous Raman scattering, and the term $\rho_0\rho_1$ leads to stimulated Raman scattering. The energy density ρ_1 at frequency $\nu_0 \neq \nu_M$ is usually considered to arise from spontaneous scattering; however, it can also build up from light at $\nu_0 \neq \nu_M$, which is incident on the medium together with light at ν_0 .^{1,3}

In our experiments, the scattering medium was irradiated simultaneously with intense <u>monochromatic light</u> of frequency ν_0 and with an intense <u>continuum</u>. Under this excitation the atoms and molecules are stimulated to emit radiation at ν_0 and at the same time to absorb radiation at $\nu_0 + \nu_M$ or $\nu_0 - \nu_M$ from the continuum, the net effect being to change their energy states by $+h\nu_M$ or $-h\nu_M$, respectively. The transitions representing this stimulated scattering process are shown on the energylevel diagram of Fig. 1(a), along with the resulting absorption spectrum. The probability for this process is again given by Eq. (1) when ρ_0 and ρ_1 are interchanged and ν_1 is replaced by ν_0 . We have observed sharp and very strong absorption lines in the spectrum of the continuum after it traverses the medium. These absorption lines appear on the high-frequency side of ν_0 , that is, at $\nu_0 + \nu_M$, and their frequency displacements from ν_0 correspond to known Raman shifts ν_M for the scattering medium. We believe the absorption spectra arise from the stimulated scattering process just discussed and shall call them "inverse Raman spectra."⁴

The experimental arrangement is shown in Fig. 1(b). The exciting source for radiation ν_0 was a giant-pulse ruby maser having at the transmitting end of the cavity a plane-parallel plate (reflectivity ~20%) of Corning 2-58 glass which also served as a mode selector and as a light filter. The radiation was emitted in single bursts of duration ~30 nsec and energy 0.1 joule. Usually the emission occurred at



FIG. 1. (a) Molecular transitions and virtual transitions leading to Raman emission and inverse Raman (absorption) spectra. Incident radiation is represented by solid lines, observed radiation by dashed lines. (b) Experimental arrangement (schematic) for obtaining inverse Raman spectra. Cell A is used to furnish a continuum of suitable frequency range $(\nu_0 + \nu_M \pm \delta)$ which is then incident on cell B simultaneously with maser radiation ν_0 . a single frequency, but sometimes at two or more frequencies within a range <1 cm⁻¹. Earlier spectroscopic studies⁵ of stimulated Raman radiation revealed that when the maser emission was in a single sharp spectral line, all of the Raman emission lines were sharp; whenever the maser emission contained additional components, all of the Raman emission lines, with the exception of the first Stokes line, were considerably broadened, sometimes up to several hundred cm^{-1} . Examples of these two extremes are given in Figs. 2(a) and 2(b)showing the first anti-Stokes line of the 992.0- $\rm cm^{-1}$ vibrational frequency of liquid benzene. This broad anti-Stokes emission was chosen as the source of background continuum for the present experiments. To be sure, its frequency range is somewhat limited, but its advantages are high intensity and synchronization with the maser beam.

Maser radiation was first incident on liquid toluene in cell A placed near the focus of a lens where the beam power density was ~ 100 MW/cm² and produced intense stimulated Ra-



FIG. 2. The anti-Stokes line of liquid benzene at $\nu_0 + 992.0 \text{ cm}^{-1}$. (a) Sharp and (b) broad stimulated Raman emission lines of benzene obtained when maser radiation is emitted in one or two lines, respectively; (b) also shows the sharp absorption line from benzene itself. (c) Inverse Raman spectrum, obtained with a single maser pulse using as a background continuum the broad toluene emission whose center is indicated by the arrow. (d) Inverse Raman line of nitromethane at $\nu_0 + 917.8 \text{ cm}^{-1}$. tion emerging from cell A was then incident on a second liquid, in cell B on Fig. 1(b). The resulting radiation fell on a ground-glass screen which was focused on the slit of a large grating spectrograph having a resolving power of 10^5 and a dispersion of 2.5 Å/mm. With sufficiently intense maser radiation, the toluene "continuum" extends to the region of the benzene anti-Stokes line at $\nu_0 + 992.0 \text{ cm}^{-1}$. When benzene was placed in cell B, the prominent absorption line shown in Fig. 2(c) was observed. Its frequency is the same as that of the Raman emission line. It exhibits almost complete absorption and its width is $\sim 2 \text{ cm}^{-1}$, equal to that of the normal Raman emission line.⁵ Similar absorption spectra were observed with liquid pyridine (at $\nu_0 + 990.2 \text{ cm}^{-1}$) and with liquid nitromethane (at $\nu_0 + 917.8 \text{ cm}^{-1}$) in cell B. The spectrum of nitromethane is shown in Fig. 2(d). In this case, the Raman shift is $\sim 90 \text{ cm}^{-1}$ from that of toluene, and 10 flashes from the maser were necessary to extend the toluene continuum to this region. Even with this weak continuum, the absorption is seen to be very strong (and the linewidth very narrow), an indication that a threshold is not involved in this induced process.

man emission at $\nu_0 \mp 1003$ cm⁻¹. The radia-

Strong absorption within the stimulated Raman anti-Stokes emission line itself has already been reported,⁵ and examples are shown in Figs. 2(b) and 2(c) for benzene and toluene, respectively. We have observed similar absorption in other liquids, including bromoform, carbon disulfide, nitrobenzene, nitromethane, pyridine, and tetrachloroethylene. We suggest that this absorption or "self-reversal" is due to the induced scattering which is discussed here and which is demonstrated more convincingly by the present experiments using two different liquids. It should be stressed that all of the inverse Raman spectra reported here were observed under conditions such that the power losses in cell A were sufficient to reduce the maser radiation incident on cell B below threshold for stimulated Raman emission and to permit higher order processes at $\nu_0 \neq n \nu_M$ to occur, and only the stimulated Raman Stokes and anti-Stokes lines of toluene (i.e., the liquid in cell A) were observed.

From the present discussion and Eq. (1), it is clear that the inverse Raman spectrum is the analog of the stimulated Raman emission spectrum, and, therefore, the available theories^{3,6} of the stimulated Raman effect should apply to both emission and absorption. In principle, one would also expect to find similar characteristics in the two spectra since the same matrix elements are involved in absorption and emission. However, the different methods used in stimulating the scattering, depending on whether emission or absorption is to be observed, lead to significant differences in the corresponding spectra, which should be noted. Since stimulated Raman emission is usually excited with light of one frequency, it exhibits a threshold and, therefore, in the emission spectrum generally only one or two vibrational lines are observed corresponding to the lines of highest intensity per bandwidth in the normal Raman spectrum. In order to observe the inverse Raman spectrum, both the continuum and the monochromatic stimulating radiation are supplied. There is no threshold and therefore the complete Raman-active spectrum should be observable. In addition, since extremely high electric fields are necessary for observing inverse Raman spectra, higher order terms in the polarizability ($\mu = \alpha E + \beta E^3 + \cdots$) may become significant and lead to less restrictive selection rules.

Investigations of inverse Raman spectra are potentially of great importance in molecular spectroscopy. With improvement in the present pulsed technique (particularly in the use of a more suitable broad continuum), or with the development of continuous operation techniques using cw masers, it should be possible to investigate the inverse Raman spectra of gases, liquids, and solids, including rotational and electronic transitions in addition to the vibrational transitions reported here. Highspeed Raman spectroscopy of interest in the study of free radicals and other short-lived species may be possible. On the practical side, inverse Raman spectroscopy may help to avoid the difficult problems of fluorescence emission and the consequent masking of the normal Raman emission spectrum which has plagued the users of Raman emission for analytical purposes. It may also be mentioned that although Raman absorption is weak with ordinary emission sources, it may be of importance in astrophysics. Finally, since the inverse spectrum is so intimately related to the stimulated emission spectrum, its study may help in a quantitative understanding of the stimulated Raman effect which in emission is overlapped by higher order and parametric effects.

One of us (B.P.S.) gratefully acknowledges stimulating discussions with Dr. T. Y. Wu on this subject 12 years ago. At that time attempts to observe the inverse Raman spectrum using powerful mercury lamps and a long multiple-traversal cell were unsuccessful.

†Present address: Department of Physics, University of Toronto, Toronto, Canada.

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^{*}National Research Council (Canada) Postdoctorate Fellow 1962-1964; present address: Trinity College, Cambridge, England.



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