

Table I. Rayleigh scattering cross sections and losses.  $\alpha_a$  and  $\alpha_s$  are the extinction coefficients for absorption and scattering, respectively.  $\delta_t$  is the total Rayleigh cross section.

	$\alpha_a$ ( $\text{cm}^{-1}$ )	$\alpha_s$ ( $\text{cm}^{-1}$ )	$10^{28}\delta_t$ ( $\text{cm}^2$ )
$\text{CCl}_4$	$2.3 \times 10^{-4}$	$0.52 \times 10^{-4}$	83
Benzene	$4.3 \times 10^{-4}$	$1.40 \times 10^{-4}$	210
Toluene	$4.7 \times 10^{-4}$	$1.47 \times 10^{-4}$	260

measured earlier being 0.435 and 0.528 for benzene and toluene, respectively. Again, no deviations due to coherence are noticeable.

Recently Leite, Moore, and Whinnery<sup>6</sup> made available precise measurements of absorptancies in "transparent liquids" where absorption is too low to be measured by current photometric techniques. Knowledge of the angular dependence of scattered intensity permits calculation of the Rayleigh cross section and the extinction coefficient due to scattering. We can now compare losses due to absorption with

losses due to scattering at  $6328 \text{ \AA}$  in highly transparent liquids. Table I summarizes these results for  $\text{CCl}_4$ , toluene, and benzene.

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\*On leave of absence from the Instituto Tecnológico de Aeronautica, Brazil.

<sup>1</sup>T. V. George, L. Slama, M. Yokoyama and L. Goldstein, *Phys. Rev. Letters* **11**, 403 (1963).

<sup>2</sup>T. V. George and L. Goldstein, Air Force Cambridge Research Laboratories Scientific Report No. AFCRL 63-549, 1963 (unpublished).

<sup>3</sup>See, for instance, G. Placzek, *Handbuch der Radiologie* (Akademie Verlagsgesellschaft, Leipzig, Germany, 1934), Vol. VI, Part 2, p. 209.

<sup>4</sup>R. C. C. Leite, R. S. Moore, and S. P. S. Porto, *J. Chem. Phys.* **40**, 3471 (1964).

<sup>5</sup>George *et al.* did not make the volume correction (private communication).

<sup>6</sup>R. C. C. Leite, R. S. Moore, and J. R. Whinnery, *Appl. Phys. Letters* **5**, 188 (1964).

### ANGULAR DEPENDENCE OF THE RAMAN SCATTERING FROM BENZENE EXCITED BY THE He-Ne cw LASER

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The angular dependence of Raman scattering has never been studied before due to the difficulty in obtaining well-collimated exciting beams maintaining both a well-defined frequency and a strong enough intensity. The discovery of the laser provided for light sources for which all the above requirements are accomplished. Knowledge of the angular dependence of Raman-scattered radiation would provide for identification of point-group symmetries of molecular transitions. Leite and Porto<sup>1</sup> showed recently that a He-Ne gas laser was suitable for easy photoelectric recording of the Raman scattering from molecular liquids.

We report in this Letter preliminary results on the angular dependence of some Raman emission lines from benzene. Figure 1 is a diagram of the experimental arrangement used for such studies. The Raman frequencies were isolated by a Bausch and Lomb model 33-86-25 grating monochromator, mounted on a rotating arm centered at the geometrical center of the

sample cell. Due to internal scattering inside the monochromator, a Corning Glass 2-64 filter was used in front of the entrance slit

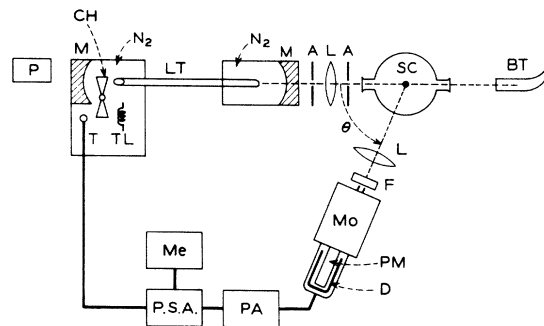


FIG. 1. Diagram of experimental arrangement. LT=laser tube, M=mirrors, CH=chopper, L=lens, D=Dewar, T=solar cell, TL=tungsten lamp, P=power monitor, A=aperture, SC=sample cell, Me=meter, Mo=monochromator, N<sub>2</sub>=nitrogen atmosphere, BT=light trap, F=filter, PM=photo-multiplier (S-20), P.S.A.=phase synchronous amplifier, and P.A.=preamplifier.

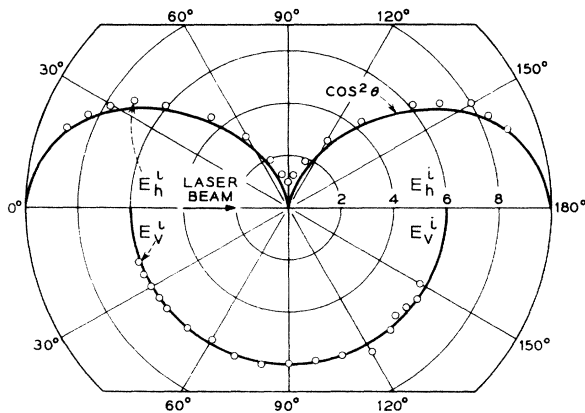


FIG. 2. Angular dependence of the Raman-scattered  $992\text{-cm}^{-1}$  line from benzene. ( $E_h^i$  is normalized to 10 at  $180^\circ$  and  $E_v^i$  to 6.)

to reduce the background due to the exciting frequency. The acceptance angle was about  $5^\circ$ . The remainder of the instrumentation is similar to the one described earlier by Leite and Porto<sup>1</sup> and Leite, Moore, and Porto.<sup>2</sup>

Figure 2 shows the angular distribution of the  $992\text{-cm}^{-1}$  vibrational frequency of benzene that has  $A_{1g}$  symmetry.<sup>3</sup> Both polarizations of the incident beam are presented. For the incident electric field vector perpendicular to the plane of observation ( $E_v^i$ ) the intensity distribution is constant with the observation angle  $\theta$ . (Volume correction is included here as well as for Figs. 3 and 4.) For the electric field vector parallel to the observation plane ( $E_h^i$ ) the intensity distribution follows a  $\cos^2\theta$  law. This behavior was theoretically predicted by Placzek<sup>4</sup> for isotropic Raman-scattered radiation. Theoretical curves are included in Fig. 2 for comparison. Deviations from

the theoretical curves in all data are probably due to the relatively large solid angle used for light collection, the extended source, and the departure of the  $(\sin\theta)^{-1}$  volume correction.

Figure 3 shows the angular dependence of the  $1585\text{-}1606\text{-cm}^{-1}$  doublet. Since both have the same symmetry ( $e_{2g}$ ),<sup>3</sup> it is not necessary to resolve one from the other. Here again, both polarizations of the exciting beam are included. For a quadrupole type of scatterer the intensity angular distribution is analytically expressed by  $1 + (\cos^2\theta)/13$ ,<sup>4</sup> the contribution due to  $E_v^i$  being constant and that due to  $E_h^i$  being given by  $1 + (\cos^2\theta)/13$ . Good agreement with Placzek's theoretical predictions for a quadrupole scatterer is obtained.

A more involved case is furnished by the  $3049\text{-}3062\text{-cm}^{-1}$  doublet whose frequencies have different vibrational symmetries ( $e_{2g}$ ,  $a_{1g}$ , respectively).<sup>3</sup> For the incident electric field vector parallel to the observation plane, the experimental points fit a theoretical expression of the form  $1 + \frac{1}{3}\cos^2\theta + b\cos^2\theta$  when  $b = 1.8$ . This is a combination of a quadrupole with an isotropic type of scattering. This is consistent with the observations described in Figs. 2 and 3, since those lines have similar symmetries to each of the lines contained in the  $3049\text{-}3062\text{-cm}^{-1}$  doublet. When the incident electric field vector is perpendicular to the observation plane, the angular distribution is again constant as expected for such a combination of scatterers as described above.

The angular dependence of the Rayleigh scattering and the Rayleigh cross section for benzene was recently measured by Leite *et al.*<sup>5</sup>

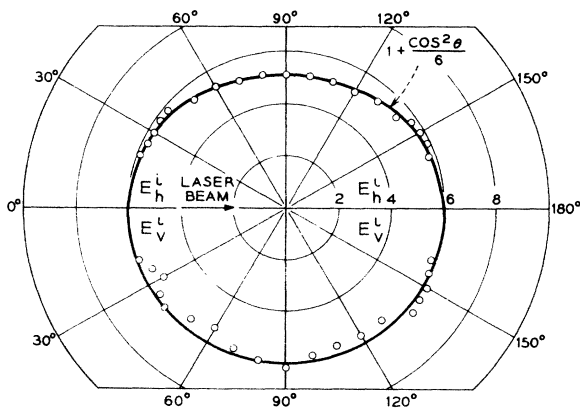


FIG. 3. Angular dependence of the Raman-scattered  $1583\text{-}1606\text{-cm}^{-1}$  doublet from benzene. ( $E_h^i$  and  $E_v^i$  are normalized to 6 at  $180^\circ$ .)

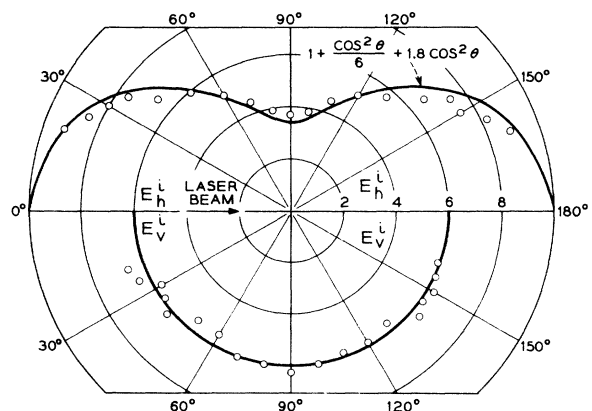


FIG. 4. Angular dependence of the Raman-scattered  $3049\text{-}3062\text{-cm}^{-1}$  doublet from benzene. ( $E_h^i$  is normalized to 10 at  $180^\circ$  and  $E_v^i$  to 6 at  $180^\circ$ .)

Table I. Rayleigh-to-Raman cross-section ratios and absolute Raman cross sections from benzene at 6328 Å.  $\Delta\nu$  = wave number displacement,  $\delta_0$  = absolute Rayleigh cross section,  $\delta_R$  = absolute Raman cross section.

$\Delta\nu$ ( $\text{cm}^{-1}$ )	$\delta_0/\delta_R$	$10^{28}\delta_R$ ( $\text{cm}^2$ )
992	220	0.56
1583-1606	1980	0.062
3049-3062	250	0.50

Together with the present measurements this allows for precise calculation of both Raman-to-Rayleigh cross-section ratios and absolute Raman cross sections. Results are summarized in Table I for the aforementioned benzene Raman frequencies; the values of the total cross sections carry an uncertainty of about

20%. We are presently improving the apparatus for extensive measurements on other molecular liquids.

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<sup>1</sup>R. C. C. Leite and S. P. S. Porto, *J. Opt. Soc. Am.* **54**, 981 (1964).

<sup>2</sup>R. C. C. Leite, R. S. Moore, and S. P. S. Porto, *J. Chem. Phys.* **40**, 3741 (1964).

<sup>3</sup>G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1949), 4th ed.

<sup>4</sup>G. Placzek, *Handbuch der Radiologie* (Akademische Verlagsgesellschaft, Leipzig, Germany, 1934), Vol. VI, Part 2, pp. 205-274.

<sup>5</sup>R. C. C. Leite, R. S. Moore, S. P. S. Porto, and J. E. Ripper, preceding Letter [*Phys. Rev. Letters* **14**, 7 (1965)].

## NEGATIVE IONS IN LIQUID HELIUM II †

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This Letter presents a calculation which supports the conjecture that negative ions in liquid helium II are self-trapped electrons.<sup>1,2</sup> The mechanism responsible for this trapping is the electron-helium interaction produced by the requirement that the electron wave function be orthogonal to the 1s core states of a helium atom and modified by the long-range attraction due to polarization. A self-trapped electron occupies a cavity or bubble whose surface is a shell of polarized helium atoms. To test the validity of this model one must know how effectively an electron repels helium from a volume in the liquid. A measure of this ability is the energy of repulsion between electrons and helium atoms which is calculated here.

To investigate the properties of such an electron moving in liquid helium, the model of an electron propagating in a periodic lattice is used for calculation from first principles. In replacing the liquid structure by a solid structure, one hopes to estimate the behavior of an electron in a dense fluid. Only for certain energies will an electron be able to move through this periodic array without attenuation. The lowest energy satisfying this condition will be the

kinetic energy required for an electron to penetrate into liquid helium. Such an energy barrier has been found experimentally by Sommer.<sup>3</sup>

The wave equation is written down for the scattering of a particle of energy  $k^2$  by a lattice of Fermi pseudopotentials<sup>4</sup> representing the electron-helium interaction (units of  $\hbar = 1$ ,  $2m = 1$  are used). Only the S-wave, low-energy term of the pseudopotential is retained:

$$(\nabla^2 + k^2)\psi(\vec{r}) = 4\pi l \sum_{\vec{a}} \delta(\vec{r}-\vec{a}) \frac{\partial}{\partial |\vec{r}-\vec{a}|} [|\vec{r}-\vec{a}| \psi(\vec{r})], \quad (1)$$

where  $l$  is the scattering length. Now write

$$\psi(\vec{r}) = \sum_{\vec{b}} \varphi_{\vec{b}} e^{i\vec{b} \cdot \vec{r}}, \quad (2)$$

where the  $\vec{b}$  are  $2\pi$  times the reciprocal lattice vectors generated by the lattice  $\vec{a}$ . Thus,

$$\psi(\vec{r}) = -\frac{16\pi^2 l}{\Delta} \sum_{\vec{b}} \frac{e^{i\vec{b} \cdot \vec{r}}}{b^2 - k^2}, \quad (3)$$

where  $\Delta$  is the volume of the unit cell of the lattice  $\vec{a}$ . An integral representation for the