

Table I. Matrix Infrared Spectra of $\text{Re}_2(\text{CO})_{10}$ and $\text{Re}(\text{CO})_5$ in Solid Argon

Re/CO/Ar reaction (10°K)	Matrix isolated $\text{Re}_2(\text{CO})_{10}$ in Ar (10°K)
1995 s	2070 w
1977 w	2018 vs 1976 mw

ture. The observed 4:1 relative intensity pattern is consistent with a square pyramidal pentacarbonyl, rather than a trigonal bipyramidal pentacarbonyl, as the latter would be expected to display a 2:3 intensity pattern.¹⁴ The A_1 equatorial CO stretching mode was too weak to observe, which is to be expected for a square pyramidal pentacarbonyl with a $C_{\text{ap}}\text{-Re-C}_{\text{equ}}$ angle close to 90° .^{13,14}

The experiments were repeated using $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O} \approx 1/1$ and $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}/\text{Ar} \approx 1/1/20$ isotopic mixtures, a typical infrared spectrum being shown in Figure 1B.

The pattern of observed isotope lines is characteristic of a pentacarbonyl containing a unique CO ligand (apical) and a group of four equivalent (equatorial) CO ligands coordinated to a rhenium atom. The apical (A_1) $^{12}\text{C}^{16}\text{O}$ absorption originally at 1977 cm^{-1} produces a *single* $^{13}\text{C}^{16}\text{O}$ counterpart line at 1933 cm^{-1} while the equatorial (E) $^{12}\text{C}^{16}\text{O}$ absorption originally at 1995.5 cm^{-1} produces *six* new isotope lines, *four* in the $^{13}\text{C}^{16}\text{O}$ stretching region 1951.0 , 1957.5 , 1969.5 , and 1988.0 cm^{-1} and *two* observable lines in the $^{12}\text{C}^{16}\text{O}$ stretching region at 2005.0 and 2024.0 cm^{-1} (the commercially available $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$ mixtures contain some $^{13}\text{C}^{17}\text{O}$ (2064.8 cm^{-1}) and $^{13}\text{C}^{18}\text{O}$ (2040.2 cm^{-1}), marked with an asterisk in Figure 1B, which could obscure one of the isotope lines in the $^{12}\text{C}^{16}\text{O}$ stretching region). This is the pattern of lines qualitatively predicted for square pyramidal $\text{Re}(^{12}\text{C}^{16}\text{O})_n(^{13}\text{C}^{16}\text{O})_{5-n}$ (where $n = 0-5$).

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Circularly Polarized Raman Scattering. A Direct Approach to the Determination of Vibrational Symmetries

Sir:

The Raman scattering of circularly polarized laser radiation has been the subject of a number of recent reports.¹ These studies have concentrated on optically active molecules in order to obtain information on mo-

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lecular dissymmetry from differential scattering of left and right circularly polarized radiation. In this communication we demonstrate that Raman vibrations stimulated by circularly polarized laser radiation radiate circularly polarized light. This phenomenon is general and not restricted to optically active molecules. The sign and magnitude of circular polarization may be used in assigning the symmetries of Raman-active vibrations.

This study continues a current program to investigate the interaction of polarized radiation with molecular systems which has emphasized the importance of circularly polarized light in studies of resonant and non-resonant emission processes.²⁻⁴ This is particularly the case for molecules under the influence of an external magnetic field. However, the unique selection rules of circularly polarized radiation also lead to new information in zero-field experiments.²

The results presented here were obtained using apparatus similar to that described recently.⁵ Argon laser radiation is circularly polarized by a quarter wave plate and the stimulated radiation analyzed by means of a photoelastic modulator.⁶ The circular intensity difference ($I_+ - I_-$) is displayed as a function of frequency and we define a circular polarization ratio as $(I_+ - I_-)/(I_+ + I_-)$. This definition differs from the reversal coefficients given by Chiu for example⁷ but is consistent with polarization ratios defined in related experiments.² Raman active vibrations are termed polarized or depolarized according to the ratio of linear polarization of the scattered radiation in directions perpendicular to the propagation vector. The measurement of depolarization ratios consists of rotating a polarizer placed before the monochromator and recording the light level for two mutually perpendicular orientations. Unless precautions are taken to depolarize the light before it enters the monochromator, spurious effects may dominate. This problem is avoided in the experiments described herein since the orientation of the final polarizer is fixed. The main advantage of our method, however, is that modulation techniques increase the sensitivity of polarization measurements by at least two orders of magnitude, and thus our polarization ratios are high in sensitivity and precision.

The spectra shown in Figures 1-4 are of a number of simple molecules in the liquid state and they illustrate clearly the power of the technique. The upper trace shows the Raman spectrum excited by circularly polarized light recorded with no polarization analysis of the scattered radiation; *i.e.*, it records $(I_+ + I_-)$. The lower curve is the circular polarization, and the polarization of the input radiation is shown on each figure. The most striking feature of the spectrum is that the circular polarization curves have *sign* as well as magnitude. In CCl_4 for example one band has the same sign polarization as the incident laser radiation while the others have opposite sign. This phenomenon involves the electric dipole-electric dipole or even parity Raman

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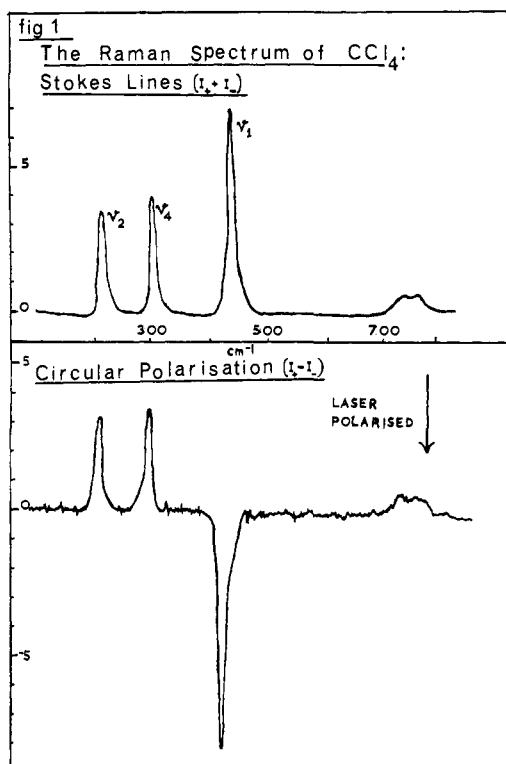


Figure 1. The Raman spectrum of carbon tetrachloride (top curve) and its circular polarization (lower curve). The intensities are in arbitrary units and the scales are related such that the polarization ratio (defined in the text as $(I_+ - I_-)/(I_+ + I_-)$) of $\nu_1 = 0.95$.

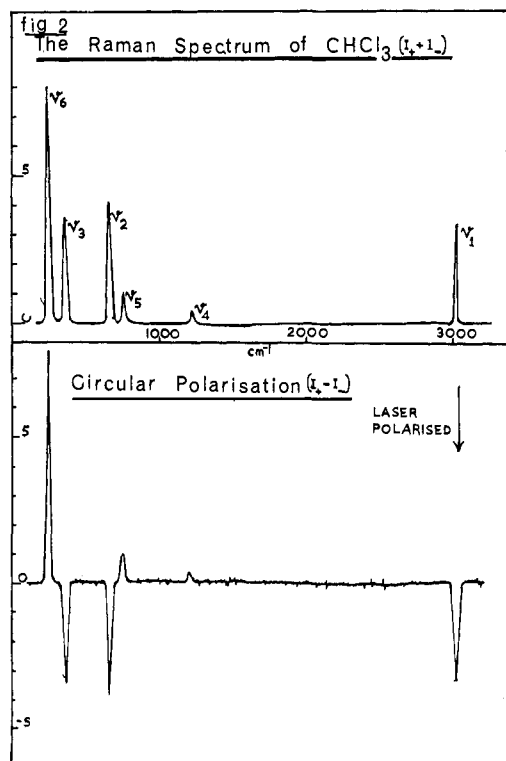


Figure 2. The Raman spectrum (top curve) and circular polarization of chloroform.

process. The much smaller, odd parity processes,⁷ electric dipole–electric quadrupole and electric dipole

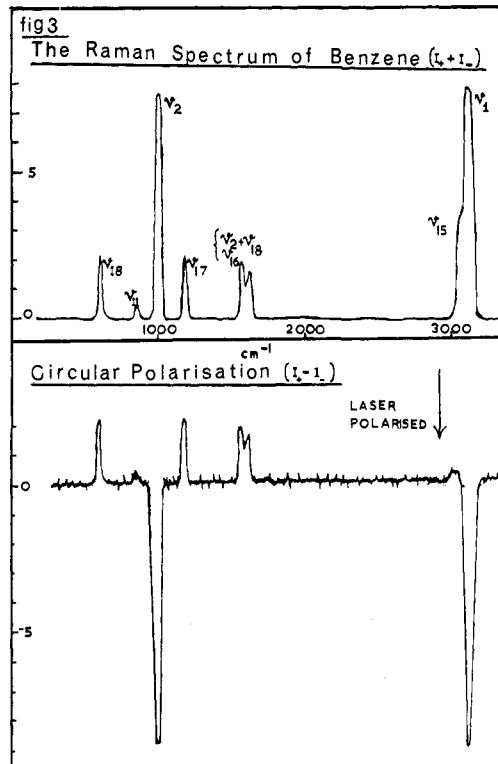


Figure 3. The Raman spectrum and circular polarization of benzene.

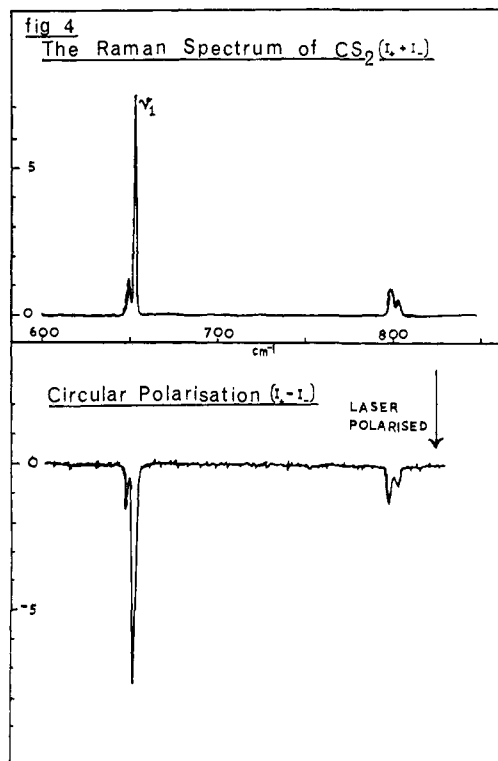


Figure 4. The Raman spectrum and circular polarization of carbon disulfide.

magnetic dipole, which are nonzero for optically active molecules, are not involved.

In order to discuss the effect of circularly polarized stimulating radiation, it is convenient to introduce a new formalism for the scattering tensor. This requires a

complex tensor having elements α_{ij} where $i, j = \pm 1$ and 0 , and the new coordinates are obtained from Cartesian coordinates according to the definition $\pm 1 = 2^{-1/2}(\mp ix + y)$, $0 = iz$. The new tensor has the form

$$\begin{array}{ccc} \alpha_{11} & \alpha_{1-1} & \alpha_{10} \\ \alpha_{-11} & \alpha_{-1-1} & \alpha_{-10} \\ \alpha_{01} & \alpha_{0-1} & \alpha_{00} \end{array} \quad (1)$$

and it is straightforward to express any Cartesian tensor in this notation by means of a unitary transformation. The advantage of using the complex tensor is evident since ± 1 components correspond to left and right circularly polarized light. It is straightforward to show, in the case of CCl_4 for example, that the totally symmetric mode will retain the sign of polarization of the incident radiation since only the diagonal elements of \mathbf{l} are nonzero. This will be a feature of the a_1 symmetry vibrational modes of molecules belonging to the majority of the symmetry groups and may therefore be used to identify such modes. For nontotally symmetric modes it is generally the case that the off-diagonal elements α_{1-1} , α_{-11} give the major contribution and thus the sign of circular polarization is reversed (*i.e.*, the mode acts as a half-wave plate⁸). Again this rule applies to the nontotally symmetric vibrations of molecules belonging to the majority of the point groups. Figures 1–4 illustrate how the a_1 modes may be identified immediately from the circular polarization for the range of molecules in this study. In CCl_4 (Figure 1) vibrational modes ν_2 and ν_4 have symmetry t_2 and e , respectively, and these reverse the sign of circular polarization. ν_1 on the other hand has a a_1 symmetry and consequently has the same sign circular polarization as the laser radiation. This pattern is repeated for the anti-Stokes lines. Chloroform, of lower symmetry, consequently has more a_1 modes than CCl_4 and from Figure 2 it is clear that ν_1 , ν_2 , and ν_3 have a_1 symmetry and the remainder are nontotally symmetric. The spectrum of benzene exhibits two a_1 modes, ν_1 and ν_2 , and a number of modes of e_{2g} symmetry including a combination band. These latter all reverse the sign of polarization. Finally, the linear CS_2 molecule shows a strong ν_1 of a_1 symmetry, the remaining structure arising from hot bands and combinations.

These results indicate clearly the power of this technique as a diagnostic tool in structural analysis since the totally symmetric vibrations may be identified immediately. This rule may not apply to molecules of very low symmetry, C_1 , C_2 , C_i or C_s for instance, in which the α_{xy}, α_{yz} , polarizability components may transform in the same way as α_{xx}, α_{yy} . This restriction also applies to conventional measurements of depolarization ratios. The circular polarization ratios obtained in our experiment are determined by squares of scattering tensor elements for the vibration concerned (or sums of these for degenerate vibrations) averaged over all molecular orientations and thus we obtain information on the $\alpha_{\rho\sigma}$ polarizability components where $\rho, \sigma = x$ or y . Linear differential intensities measured perpendicular to the exciting beam give access to the components in which $\alpha_{\rho, \sigma}$ contains the z coordinate. Together with the tensor components from circularly polarized scattering, these provide data which characterizes the complete

(8) We are indebted to Professor S. F. Mason for this analogy.

Raman spectrum, and results of these more extensive studies will shortly be reported.

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Direct Observation of the Optical Absorption Spectra of Reactive Free Radicals at Room Temperature

Sir:

The preparation of reactive free radicals in concentrations high enough for their direct observation by optical spectroscopy has until recently depended on the use of special experimental techniques such as low temperature matrix isolation^{1,2} and flash photolysis.³ Experiments of this type usually rely on rather elaborate instrumentation for their execution and do not in most cases lead to positive assignments of the species responsible for the observed spectra. In this communication, we wish to report the development of a new method for obtaining the optical absorption and emission spectra of free radicals which not only overcomes the disadvantages of previous techniques but also permits the observation of their spectra at relatively high temperatures and under steady-state conditions.

Our approach makes use of the fact that high concentrations of free radicals can be produced by X-ray and/or uv irradiation of suitable precursors in an adamantane matrix.⁴ Thus, for example, X-irradiation of carefully purified adamantane containing a small amount of 2-methylpentane yields the 1,1-dimethylbutyl radical whose epr spectrum shows six equivalent β -protons at 23.4 G and a temperature-dependent β -methylene proton hfs of 14.9 G at 293°K.⁵ If two pressed disks of adamantane (10 mm o.d., ~1 mm thick) containing the parent hydrocarbon are placed in the sample and reference beams of a Cary 14 spectrophotometer, no absorption is observed down to 200 nm unless the disk in the sample beam has been previously X-irradiated. In that event, one observes a strong absorption feature at 218 nm which decays with a lifetime ($1/e$) of ~0.5 hr at room temperature. Furthermore, it is found that the lines in the epr spectrum of this radical in the *same sample* decay with the *same lifetime* at this temperature. Thus, the band at 218 nm can be assigned unequivocally to the lowest energy electronic transition of 1,1-dimethylbutyl which involves the promotion of the unpaired electron from the nonbonding orbital of π character to the lowest σ^* orbital of the radical.

As further examples of the application of this tech-

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