Laser Raman Spectra of Long Chain Sulfur Derivatives[1]

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ABSTRACT

Laser Raman spectroscopy is proving to be an important complement to IR absorption spectroscopy in the analysis of derivatives of fatty acids and esters containing sulfur in their structure. Selected esters are being evaluated as extreme presssure lubricants, and information upon the nature of the sulfur linkages in these derivatives should be useful in preparing products with satisfactory performance characteristics. The techniques of laser excited Raman spectroscopy have been applied to elucidate the molecular structure of a series of mercaptans, sulfides, and disulfides, as well as sulfur containing derivatives of long chain fatty acids and esters.

INTRODUCTION

Although predicted as early as 1923 by Smekal (1), the Raman effect was not discovered experimentally until 1928 by Raman and Krishnan (2). Even then, it did not become really useful until the 1960's after the laser had been invented. The technique has not been applied a great deal to long chain compounds or derivatives of fatty acids or esters. However, O'Neill and Falla (3) reported on the Raman spectra of linseed oil, tung oil, and a pentaerythritol-linseed-*o*-phthalic alkyd resin; and Bailey and Horvat (4) used Raman spectroscopy in the determination of *cis*- and *trans*-isomer content of some methyl esters and triglycerides.

In research concerned with the development of potential lubricants suitable for extreme pressures, we synthesized derivatives of oilseed fatty acids and their esters containing various sulfur structures and applied laser excited Raman spectroscopy to assist in the determination of their structures. No Raman spectra of similar sulfur compounds or their analogues appear in the literature. As a preliminary step, we studied the Raman spectra of sulfur compounds of known structure and from this information interpreted the Raman spectra of the fatty acid derivatives.

EXPERIMENTAL PROCEDURES

Raman spectra were measured using a Carson Laboratories model 101 argon-krypton mixed gas laser giving 80-180 mW exciting power at 488.0, 514.5, 568.2, and 647.1 nm. In most samples, the 488.0 nm line was used. Neat samples were irradiated by the laser in 1.0 ± 0.1 mm inside diameter capillary tubes. This Raman spectrometer is a Spex Industries Ramalab model with a 0.5 m double monochrometer of the Czerny-Turner type and also equipped with the optional photomultiplier tube, an ITT FW-130 with extended S-20 response, and a Products for Research model TE-104 thermoelectric refrigerated chamber for cooling. This spectrometer uses the Yokogawa Electric Works type 3041-S14 recorder.

The chemicals studied were either made at the Northern Regional Research Laboratory, Peoria, Ill., or purchased from suppliers and repurified.

Raman spectra of the chemicals were compared with their IR spectra determined with a Beckman model IR-8 spectrophotometer. IR spectra were from neat samples between NaCl windows or from Nujol and Fluorolube mulls.

RESULTS AND DISCUSSION

Raman spectra of three classes of typical long chain sulfur compounds include octadecanethiol, diotadecyl sulfide, and dioctadecyl disulfide (Fig. 1). Locations of the bands found on these spectra are given in Table I. Intensities of the bands discussed are normalized to a photon counting rate of 1 x 10^4 counts/sec.

S-H Vibrations

Bands associated with three vibrations should be ob-

TABLE I

Raman Spectral Bands of Octadecyl Sulfur Compounds ($\Delta\nu$)

Octadecanethiol	Dioctadecyl sulfide	Dioctadecyl disulfide
110	110	100
175	175	175
225	220	225
330		
	355	
	440	
		520
	535	537
640	630	640
		660
740	743	720
840		
890	885	900
1062	1060	1065
1090	1100	1110
1130	1140	1135
1290	1295	1300
1420		
1440	1440	1450
1473	1480	1470
2550		
2710	2720	2720
2840	2850	2860
2880	2885	2880
2920	2910	2910
2960		

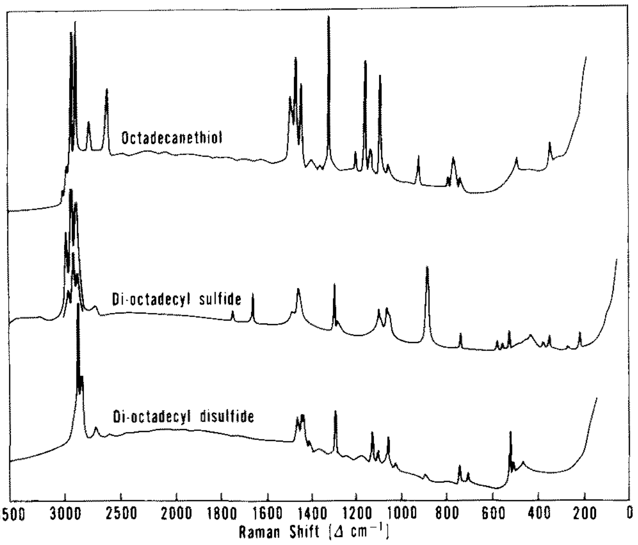

FIG. 1. Laser Raman spectra of octadecanethiol, dioctadecyl sulfide, and dioctadecyl disulfide.

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[2] ARS, USDA.

served in the spectra of alkyl mercaptans. These are the S-H stretching and in-plane and out-of-plane S-H deformations. In 1946, Trotter and Thompson (5) reported on the spectra of ethyl, propyl, and butyl mercaptans; and, in 1950, Sheppard (6) reported on mercaptans ranging from methyl to hexyl. Their findings showed that the S-H stretching band occurs between 2600 and 2550 Δcm^{-1} in both the IR and Raman spectra. The band was usually weak in the IR spectra and strong in the Raman spectra. The S-H in-plane deformation vibration in ethyl mercaptan occurred as a weak Raman band at 832 Δcm^{-1} and was not observed in the IR (7). Out-of-plane S-H deformation of this compound had a Raman band at 332 Δcm^{-1}.

We found that the IR spectra of longer chain mercaptans reveal an S-H stretching vibration as a weak band in the 2571-2564 cm^{-1} region for 1° mercaptans with an $R\text{-}CH_2\text{-}S\text{-}H$ structure, such as dodecanethiol or octadecanethiol. This mode is seen as a moderate band in their Raman spectra in the 2550-2580 Δcm^{-1} region with intensities of 13-14%. With a 2° mercaptan, 2-octanethiol, the S-H stretching mode is observed at 2570 Δcm^{-1} in the Raman spectra with an intensity of 53%, whereas it is found at 2577 cm^{-1} in the IR spectra.

In-plane deformation of the C-S-H bond is observed in the IR spectra of the compounds as a very weak band at 855-858 cm^{-1}. This band is found at 840-850 Δcm^{-1} in the Raman spectra with intensities of 1.5-2% for the primary mercaptans and at 858 Δcm^{-1} for 2-octanethiol with an intensity of 8.

The out-of-plane deformation band is observed in the Raman spectra of octadecanethiol at 330 Δcm^{-1} with an intensity of 2.5, while it shifts to 355 Δcm^{-1} with an intensity of 4.5 for dodecanethiol. With 2-octanethiol, it is observed at 350 Δcm^{-1} with an intensity of 13.

C-S Vibrations

Reportedly (5,6), the C-SH stretching vibration in alkyl mercaptans induces a weak band in the IR between 700 and 600 cm^{-1}. This band is very strong in the Raman spectrum. In 1° mercaptans with an $R\text{-}CH_2\text{-}S\text{-}H$ structure, the C-SH stretching mode occurs in the 640-650 Δcm^{-1} region. In a 2° mercaptan, with an RR′CH-S-H structure, 2-octanethiol, it is found at 620 Δcm^{-1}. The intensity varies greatly: from 19 for 2-octanethiol to 15 for dodecanethiol to two-thirds for octadecanethiol.

Two C-S stretching vibrational bands would be expected in the 600-700 Δcm^{-1} region of the spectrum for dialkyl sulfides, due to the asymmetric and symmetric stretching about the C-S-C bond. Spectra of didodecyl sulfide, dioctadecyl sulfide, and ethyl octadecyl sulfide exhibit the asymmetric C-S-C stretching mode at 735-760 Δcm^{-1} with an intensity of 6-8. The symmetric stretching mode is observed at 630-655 Δcm^{-1} with ethyl octadecyl sulfide having this band at 655 Δcm^{-1}. Didodecyl sulfide and dioctadecyl sulfide exhibit this band at 635 and 630 Δcm^{-1}. Intensities of this band vary from 1 for the symmetric sulfides to 9 for ethyl octadecyl sulfide.

An in-plane deformation is observed in the spectra of the sulfides as a very weak band in the 300-314 Δcm^{-1} region.

There would also be C-S bands in the third type of compounds studied, the disulfides. Dioctadecyl disulfide shows two peaks at 660 and 640 Δcm^{-1} with intensities of 1 and two-thirds, respectively. This band compares with those at 665 and 640 Δcm^{-1} in the spectrum of a short chain compound, dipentyl disulfide.

S-S Vibrations

There are two peaks for disulfides in the S-S stretching vibration region of Raman spectra. For dioctadecyl disulfide, they are observed at 537 and 520 Δcm^{-1} with intensities of 7.5 and 1, respectively. With the di-*n*-pentyl disulfide, the S-S stretching mode is observed at 530 and 515 Δcm^{-1} with intensities of 44 and 61, respectively.

Alkyl Chain Vibrations

A number of vibrations observed in Raman spectra of long chain sulfur compounds are due to the long alkyl chain. They are found as weak bands at 2955-2960 and 2910-2930 Δcm^{-1} and as strong bands at 2880-2900 and 2840-2860 Δcm^{-1} due to the stretching of the C-H bonds of the methyl and methylene units. A weak band is observed at 2710-2730 Δcm^{-1}. In-plane deformation of the methylene chain occurs at 1440-1460 Δcm^{-1} as a strong band, as does the methylene wagging mode at 1290-1300 Δcm^{-1}. Carbon-carbon stretching and bending modes are seen at 1126-1140, 1060-1065, 880-900, 160-175 and 92-110 Δcm^{-1} in Raman spectra of all long chain compounds.

Laser excited Raman spectroscopy aids in determining the molecular structure of sulfur derivatives of oilseed fatty acids. For example, addition of H_2S to methyl linoleate gives a compound that has more Raman bands than methyl linoleate. Those at 2570, 840, and 330 Δcm^{-1} indicate the presence of the mercaptan adduct. The C-S linkage is noted in the presence of bands at 680 and 635 Δcm^{-1}. In addition, a band is seen at 550 Δcm^{-1}, which shows crosslinking since it is due to the S-S linkage. Analytical data from NMR and mass spectrometry confirmed the existence of these structures in the H_2S-methyl linoleate adduct (8).

Raman spectra of several sulfurized oils intended as extreme pressure lubricants were examined to determine the classes of sulfur compounds formed during the sulfurization process. Two commercially prepared sulfurized oils were compared with an oil prepared at the Northern Regional Research Laboratory. All were observed to be esters of long chain fatty acids by their IR spectra. The laser excited Raman spectra of these compounds showed the presence of mercaptans (S-H stretching near 2530 Δcm^{-1}), sulfides (C-S-C stretching bands ca. 740 and 630 Δcm^{-1}), and disulfudes (S-S stretching ca. 450 Δcm^{-1}). There was also evidence of cyclic sulfides in the commercial oils, including a 4 membered cyclic disulfide which is noted by the shifted C-S bonds to near 700 and 650 Δcm^{-1} and the multiple S-S and ring deformation modes near 540 and 430 Δcm^{-1}. Such structures cannot be determined by IR spectroscopy.

Raman and IR spectroscopy are complementary methods of analytical chemistry. Determining the molecular structure of long chain sulfur compounds is a good example of this concept. Absorption bands caused by the S-H bond are very weak in the IR spectra; but, being stronger in the Raman spectra, they are clearly visible. Bands due to C-S and S-S bonds are, not only weak in the IR, but are usually beyond the range of most IR spectrophotometers. These bands are stronger in the Raman spectra and come well within the instrument's range (normally 0-4000 Δcm^{-1}).

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