CHEMISTRY LETTERS, pp. 935-938, 1986.

RAMAN SPECTRUM AND THE S-I STRETCHING FREQUENCY OF BENZOYLSULFENYL IODIDE

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The Raman spectrum of benzoylsulfenyl iodide in ether has been observed for the first time using a high-speed multi-channel Raman spectrometer. The S-I stretching frequency is found to be 387 cm^{-1}, which is useful for the characterization of organosulfur compounds involving the S-I linkage.

Sulfenyl iodides (RSI) are among the most attractive organosulfur compounds from biological and chemical points of view, since they probably play decisive roles as reaction intermediates both in iodination reaction in the thyroid gland[1)] and in I_2-oxidation reaction.[2)] However, because of their instability, information concerning such compounds is very scant. Recently we succeeded in the first isolation of some simple sulfenyl iodides.[3-5)] In addition, the synthetic methods of aromatic acylsulfenyl chloride[6)] and bromide,[7)] which enable the systematic study on the S-halogen stretching frequency, have also been developed in this laboratory. With a series of these compounds in hand, we undertook a study to determine the S-I stretching fequency which has been unknown so far. In this letter we report preliminary results on the first Raman spectrum and the S-I stretching frequency of benzoylsulfenyl iodide.

Benzoylsulfenyl chloride,[6a)] bromide,[7)] and iodide[3)] were synthesized according to the reported procedure and purified by recrystallization from n-hexane.

Raman spectra were recorded on a multi-channel Raman spectrometer (Spex 1877 triple polychromator, EG & PAR OMA-2, DEC MINC-11) using a He-Ne Laser (NEC GLG-108, 632.8 nm, 20 mW at sample) as the exciting light source. All spectra were

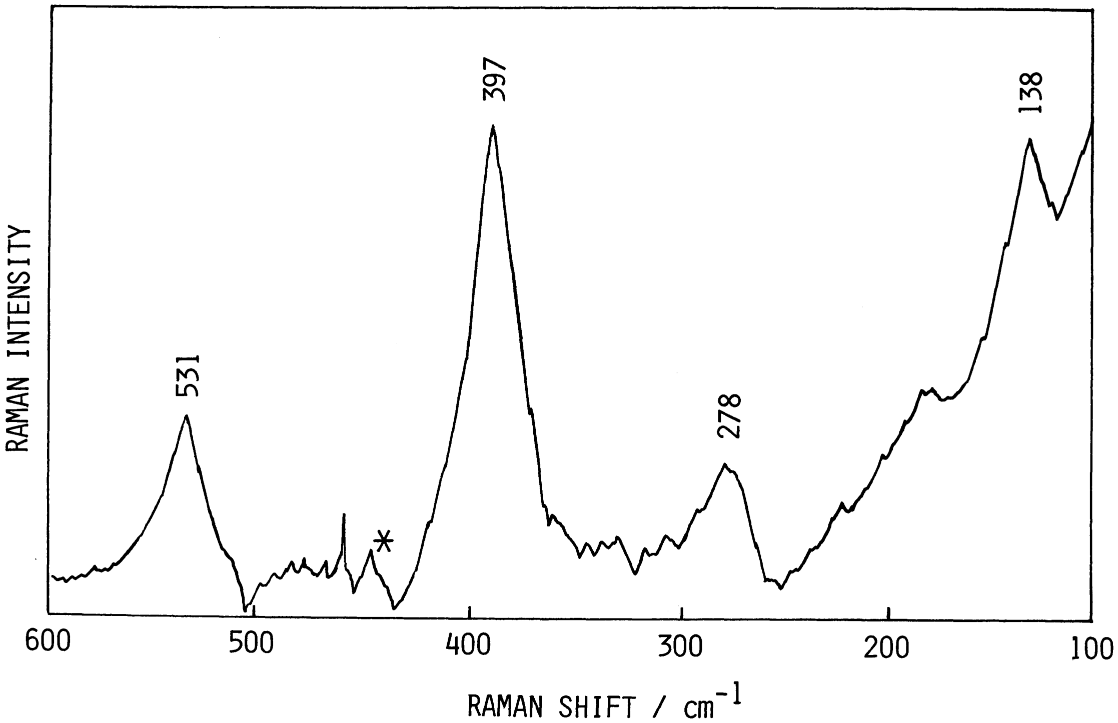

Fig. 1. Raman spectrum of benzoylsulfenyl iodide in ether (0.38 M). The asterisk marks the region overlapped by a solvent band which is already subtracted.

Table 1. Raman spectra of benzoylsulfenyl halides

	$C_6H_5C(O)SX$ / cm^{-1}			
X=	Cl	Br	I	Assignment
	190	153	138	δC-S-X
	276	276	278	
	522	446	397	νS-X
	565	543	531	

measured from freshly-prepared solutions (ca. 0.38 M in dry ether) within a few minutes of the preparation. Typical exposure time was 200 second. Prolonged exposure deteriorated the spectral purity which was seriously affected by the decomposition of the sample.

The low-frequency region of the Raman spectrum of benzoylsulfenyl iodide is shown in Fig. 1. Four peaks are observed at 531, 397, and 278, and 138 cm^{-1}. The assignment of these frequencies can be made by referring to the spectra of the chloride and bromide analogs given in Table 1. Upon substituting iodine with bromine, the 397 cm^{-1} band shifts to 446 cm^{-1} whereas the other three bands exhibit much less frequency changes. These two bands are therefore assigned to the S-I and S-Br stretches, respectively. The assignment of the 397 cm^{-1} band to the S-I stretch is consistent with the Raman intensity pattern; in many organohalogen compounds, the halogen stretching mode gives the highest Raman intensity. The intensity of the 397 cm^{-1} band may also be enhanced by a preresonance effect from the electronic absorption at 464 nm, which causes the orange color of benzoylsulfenyl iodide. It should also be noted that this is, to the best of our knowledge, the first assignment of S-Br frequency for organosulfur compounds.

In going from the bromide to the chloride, the 446 cm^{-1} band shifts further to the higher frequency. Two bands with comparable intensities are observed at 552 cm^{-1} and 565 cm^{-1} in the chloride. We tentatively assign the 522 cm^{-1} band to the S-Cl stretch, for the reported S-Cl stretching frequency is 509 cm^{-1} in CH_3SCl[8)] and 530 cm^{-1} in $(EtO)_2P(S)SCl$.[9)] The 531 cm^{-1} band of the iodide, the 543 cm^{-1} band of the bromide, and the 565 cm^{-1} band of the chloride must correspond to one of the O-C-S and Ph-C-S bending modes or to a mixture of them. There is a possibility of significant mode mixing in the chloride between the S-Cl stretch and these two bending modes.

The lowest frequency bands, 138, 153, and 190 cm^{-1} are assigned to the C-S-X bend, for the frequency increases with the reciprocal of the mass of the halogen atom. The 278 cm^{-1} band, which does not change upon the halogen substitution, must be assigned to a mode localized to the Ph-C-O part.

In this way, the Raman spectra of benzoylsufenyl halides are reasonably assigned and the S-I stretching frequency is established as 397 cm^{-1} in benzoylsulfenyl iodide. We believe that the present result will be useful in the vibrational characterization of the S-I linkage involved in biologically and chemically important sulfenyl iodides.

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4) As far as we are aware, the only other isolated sulfenyl iodide in literature is $ISMe_2CH(NHCbz)CONHPh-Cl-4$ (Cbz = carbobenzo).5) Preparation of two simple organic sulfenyl iodides, $(CH_3)_3CSI$ and $(C_6H_5)_3CSI$, without spectral and elemental analysis data, were also reported by Rheinboldt and Motozuk [Chem. Ber., 72b, 657 (1939)] and Ciuffarin and Guaraldi [J. Org. Chem., 35, 2006 (1974)], respectively. However, we were unable to isolate these sulfenyl iodides, because of their extreme instability.

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(Received March 17, 1986)