THE SENSITIZATION EFFECT IN THE LASER INDUCED INFRARED FLUORESCENCE SPECTROSCOPY BY ADDITION OF A SECOND COMPONENT

Seiichiro HIGUCHI, Noriaki KIHARA, Hiroshi WAKI and Shigeyuki TANAKA

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

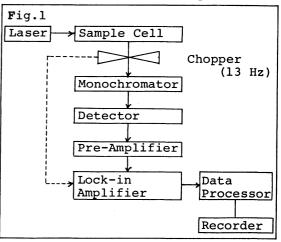
The laser induced infrared fluorescence spectra of gaseous samples were measured, adding propylene as a second component. It was shown that the marked intensity enhancement was realized for the bands of the objective components in such mixed samples. This effect seemed to become larger with smaller concentrations of the components.

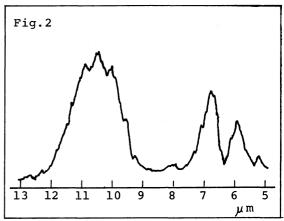
Recently, we developed a measurement system for the laser induced infrared fluorescence spectra (IR-F spectra) and succeeded in the measurements of IR-F spectra of some organic compounds in the gaseous state 1). In the process of the subsequent investigation, it has been found that there occurs the remarkable intensity enhance-

ment for the IR-F bands of some compounds under the coexistence of propylene. The purpose of this note is to present a preliminary report on the experimental results about this new sensitization effect in the IR-F spectroscopy.

In Fig.1 is shown the block diagram of the developed measurement system. The details for this system were reported in the previous paper 1). In this system, IR-F spectra are excited with the 10.6 μ m lines of a CO₂ laser. The output power of the laser is about 3 W. All of the spectra were measured for the samples in the gaseous state.

The IR-F spectrum of propylene is shown in Fig. 2. As is seen from this figure, propylene has no distinct band in the 7.5-9.0 μ m region, and this indicates that the influence of the coexistence of propylene on the spectra of the objective samples is conveniently examined for the bands appearing in this wavelength region. Fig. 3 shows the obtained spectra for ethyl ether -propylene mixed sample and for ethyl ether only As can be seen from this figure, in the case of the mixed sample consisting of ca. 50 torr of

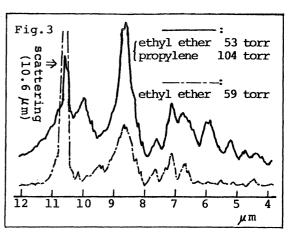


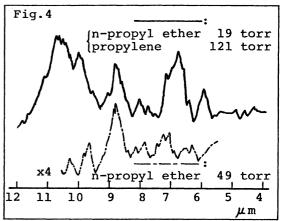


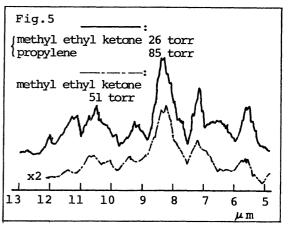
ethyl ether and ca. 100 torr of propylene, the sensitization effect is obviously observed for the band of ethyl ether at 8.7 μ m. That is, the intensity of this band increases about 2.5 times at this partial pressure of the ether, when compared with the case of adding no propylene.

Theoretically, this experimental fact can be attributed to the effect of the absorption of the laser light by propylene, followed by the interand intra-molecular energy transfer. Apart from such theoretical problems, it is considered to be significant that the effect has been exhibited as a distinct spectral evidence. Since the effect comes out as the increase of the IR-F band intensity, this experimental result is interesting especially in view of analytical applications of the IR-F spectrometry. About the interference effect of the coexisting components, Robinson et al. 2) examined for the IR-F bands of ethylene and they reported that no marked effect was observed for the sample systems treated. This is probably due to the fact that they paid attention to the bands of ethylene, which has a strong absorption band at 10.6 μ m just like propylene.

In Figs.4 and 5 are shown the similar results for n-propyl ether-propylene and methyl ethyl ketone-propylene systems. It is made clear from these results that the 8.8 μ m band of n-propyl ether is enhanced in the intensity about 8 times at 19 torr and the 8.4 μ m band of methyl ethyl ketone, about 6 times at 26 torr, if the linearity can be assumed for the relation between the pressures of samples and the intensities when propylene does not exist. The similar phenomena were also observed for n-propyl formate and







propionaldehyde. Moreover, the interesting fact is that the degrees of sensitization seem to increase remarkably when the partial pressures of the sample become smaller. For example, in the ethyl ether-propylene system, the degree of sensitization becomes about 7 times larger when the pressure of the ether changes from 50 to 5 torr.

All of the above-mentioned experimental results are interesting and attractive in view of realizing the high sensitivity of this spectroscopy and developing it to become a new tool of microanalysis. The more detailed and quantitative investigation about the phenomena is required and now proceeding in our laboratory.

Reference

1)S.Higuchi, N.Kihara, H.Waki, S.Tanaka and N.Sakayanagi, submitted to Bunko Kenkyu. 2)J.W.Robinson and J.D.Dake, Anal. Chim. Acta, 71, 277(1974).