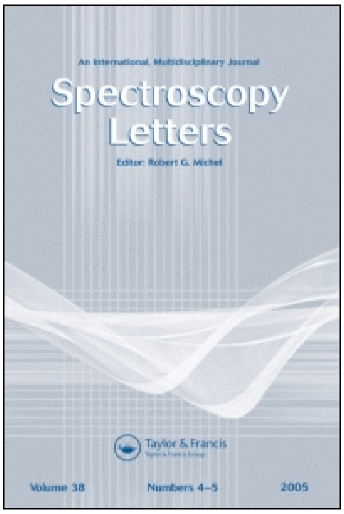

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The Sensitization Effect in the Laser-Induced Infrared Fluorescence Spectroscopy by Addition of SF_6

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THE SENSITIZATION EFFECT IN THE LASER-INDUCED INFRARED FLUORESCENCE SPECTROSCOPY BY ADDITION OF SF_6

Key Words : Infrared fluorescence, Infrared laser, Sensitization effect, Sulfur hexafluoride

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ABSTRACT

A considerable degree of the sensitization is realized in the laser-induced infrared fluorescence spectra when sulfur hexafluoride (SF_6) is mixed with objective samples in the gas phase. It is shown that the marked intensity enhancement occurs though the quantity of added SF_6 is very small relative to those of samples. The sensitization degree has been examined in terms of the concentration of an objective sample

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and it is shown that the degree of sensitization is abruptly enhanced with lowering its concentration. A possibility of a new vibrational spectroscopy with high sensitivity by use of this effect of SF_6 and its applications to microanalysis are suggested.

INTRODUCTION

The laser-induced infrared fluorescence (IR-F) spectroscopy is one of the new techniques for measurements of vibrational spectra, using infrared lasers. Experimentally, it is based on the irradiation of a sample by a monochromatic or quasi-monochromatic laser light. The sample is vibrationally excited to the various vibrational levels through a certain mechanism. It is to be noted that the IR-F spectra are different from the usual fluorescence spectra based on the electronic transitions in that the signals of IR-F appear not only in the longer wavelength region but also in the shorter one than the wavelength of the exciting laser lines. This specific character of the IR-F has not completely been elucidated. Thus, the IR-F spectroscopy presents the problems, which are interesting but has not yet been solved completely, in the field of the studies on vibrational excitation and relaxation, intra- and intermolecular energy transfer, etc.

Apart from the physicochemical aspects such as the above-mentioned, the IR-F spectroscopy has the possibility of becoming a new analytical method based on vibrational spectra. At present, however, we can find as such investigations only a series of the works by Robinson and his coworkers.1-10) They examined experimentally the various aspects of the IR-F spectroscopy with the intention of applying it to the remote sensing for air pollutants.

Recently, we have developed a measurement system for the IR-F spectra, and begun to examine its analytical applications. During this investigation, the intensities of IR-F bands of some organic compounds were found to be enhanced remarkably when the alkenes such as ethylene, propylene etc., were added as the second component.11) In the subsequent examinations, it has been found that the addition of sulfur hexafluoride (SF_6) induces also the great enhancement of IR-F intensities, and that the effect of SF_6 is different from that of alkenes in that only a small amount of SF_6 causes the sufficient sensitization. The purpose of this note is to present a preliminary report on the experimental results about the effect of this sensitizing agent and to demonstrate the possible analytical utility of the IR-F spectroscopy sensitized by SF_6.

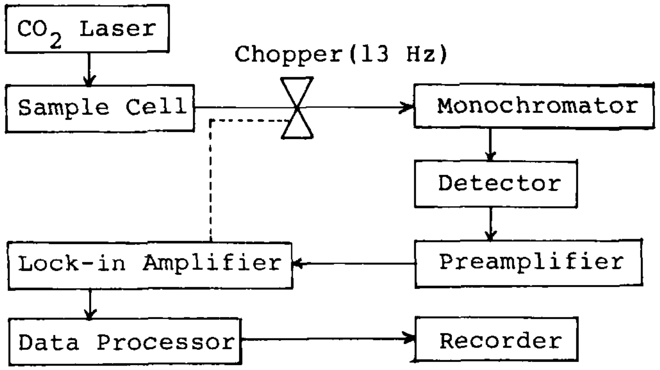

FIG.1 The block diagram of the measurement system of IR-F spectra.

EXPERIMENTAL

In FIG.1 is shown the block diagram of the measurement system for the IR-F spectroscopy, developed in our laboratory. In this system, the sample in the sample cell(path length of the laser beam:about 5 cm, window:Irtran-2) is irradiated with the 10.6 μm lines from a CO_2 laser(output power:about 3 W, beam diameter: 4 mm). Then, the vibrationally excited sample emits the fluorescence light, and a part of this light going out from the cell in the direction perpendicular to that of the laser beam is modulated with a chopper of the frequency of 13 Hz. This frequency, which is adopted in commonly used infrared spectrophotometer, is selected rather arbitrarily and it is not certain whether it is optimal or not. This problem is left to be examined in the future. This chopped emission is sent into a monochromator and spectrally measured. The signals from a detector (MCT semiconductor detector) are discriminated and amplified with a lock-in amplifier. Finally, the signals are processed with a data processor containing a microcomputer, and then, they are recorded out. The IR-F spectra are all measured with the mechanical slit width fixed at 3.0 mm (the full width for the monochromator used). The resolutions are 0.05, 0.06, 0.07, 0.08, and 0.08 μm at the wavelengths, 12.0, 10.0, 8.0, 6.0, and 5.0 μm, respectively. The scanning speed was about 5 μm/min, and the number of the repetitive scans was 16 or 32.

All of the spectra were measured for the samples in the gaseous state.

RESULTS AND DISCUSSION

Now, we will go on to examine the obtained experimental results. SF_6 is the compound studied extensively in the infrared laser photochemistry. It has a very strong absorption at 10.6 μm (ν_3 band at 10.4 μm), and is considered to be easily promoted to the highly excited vibrational states by irradiation of the 10.6 μm lines of a CO_2 laser.[12] Since the sensitization effect in question is considered to be caused by the intermolecular energy transfer between the sensitizing molecules in the vibrationally excited states and the samples, the above-mentioned

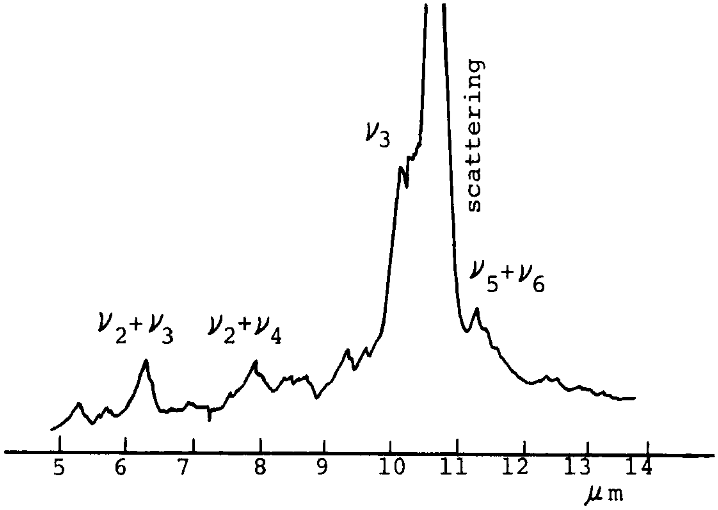

FIG.2 The IR-F spectrum of SF_6 (15 Torr).

characteristics of SF_6 in photochemistry are inferred to be favourable for the sensitization in IR-F.

In FIG.2 is shown the IR-F spectrum of SF_6. As is seen from this figure, SF_6 exhibits only very weak combination bands in the almost whole wavelength region except for the 10 μm region where the ν_3 band of SF_6 and the strong scattering signal coming from the exciting laser lines appear. The circumstances are very convenient for the observation of sensitized IR-F spectra of samples over the wide wavelength region. It will be worth mentioning that in the case of using the alkenes as sensitizers, only the bands of samples in the limited wavelength region of 7.5-9.0 μm can be observed due to the appearance of bands of the alkenes.

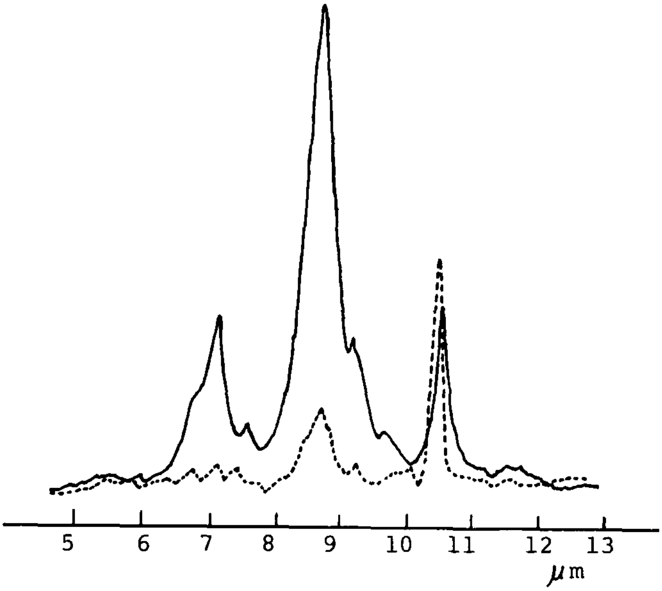

FIG.3 The IR-F spectra of diethyl ether alone (40 Torr) and of diethyl ether (40 Torr) - SF_6 (1 Torr) mixed sample.
———————:mixed sample,
-----------:diethyl ether alone.

FIG.3 shows the IR-F spectra of diethyl ether-SF_6 mixed sample and diethyl ether alone. It is seen that the considerable sensitization is realized by adding only 1 Torr of SF_6 to 40 Torr of ether. For example, the 8.7 μm band of diethyl ether is enhanced about 6 times when compared with the case of adding no SF_6. In FIG.4 is shown the similar result when 200 Torr of propylene is added as the second component. It was found in our laboratory that the addition of 150-200 Torr of propylene causes the maximum sensitization. The intensity enhancement in this case is 3.5 times.

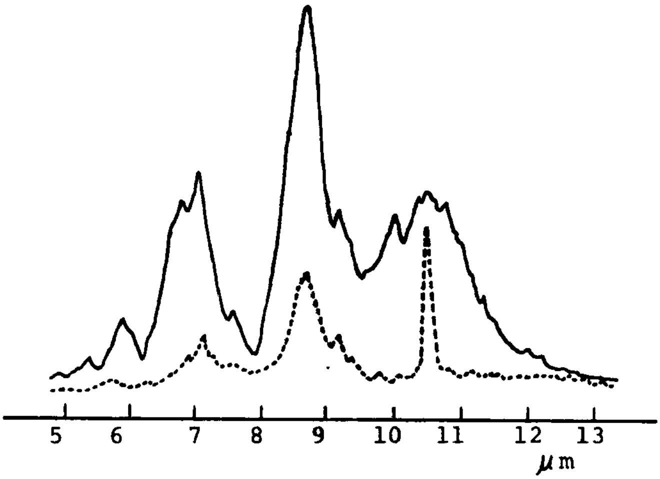

FIG.4 The IR-F spectra of diethyl ether alone (50 Torr) and of diethyl ether (50 Torr) - propylene (200 Torr) mixed sample.
———————:mixed sample,
-----------:diethyl ether alone.

Thus, only 1 Torr of SF_6 causes the sensitization comparable to, or, exceeding that induced by 200 Torr of propylene. Apart from the physicochemical aspects of the phenomenon, it can be said that the above-mentioned fact is favourable for the application of this sensitized IR-F spectroscopy as a method of measurements of vibrational spectra because of the almost complete lack of background signals.

FIG.5 is the result for acetone. It is proved that also in this case, the marked intensity enhancement is realized by only 2 Torr of SF_6. It is to be noted that the band of the C=O stretching vibration at 5.7 μm, which can not be observed in the case of acetone

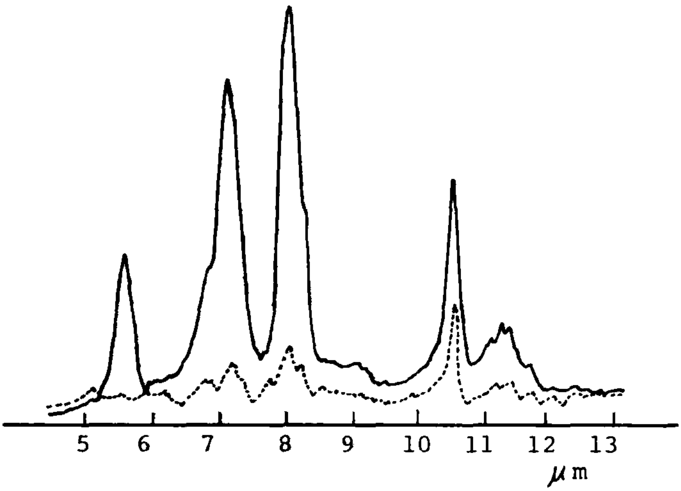

FIG.5 The IR-F spectra of acetone alone (40 Torr) and of acetone (40 Torr) - SF_6 (2 Torr) mixed sample.
————:mixed sample,
-----------:acetone alone.

alone with the instrumental sensitivity for this measurement, appears clearly under the coexistence of SF_6. Moreover, this result suggests that the degree of sensitization differs according to the kind of molecular vibrations.

In FIG.6 are shown the IR-F spectra for methanol samples. The spectrum of methanol alone has been measured with the instrumental sensitivity twice higher than for methanol-SF_6 mixed sample. In general, the IR-F intensity for alcohols are weak, and it is rather difficult to obtain the clear spectra with the output power of the laser used in this study. However, it is seen that the very strong bands of methanol are

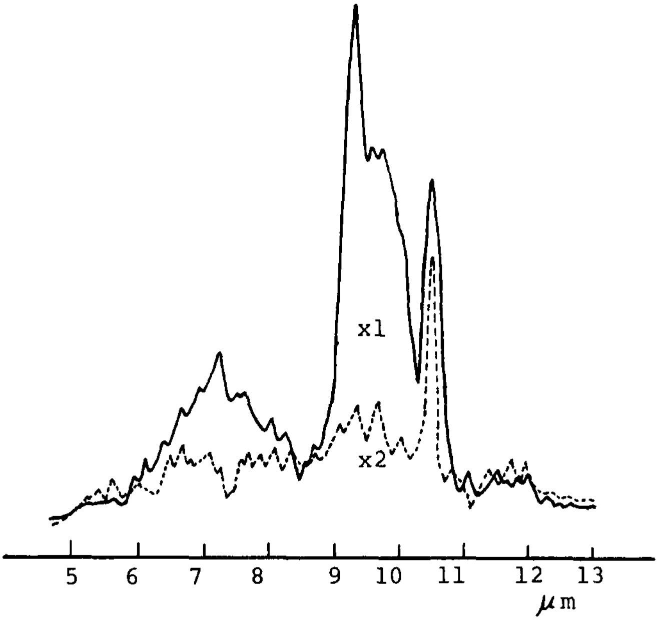

FIG.6 The IR-F spectra of methanol alone (70 Torr) and of methanol (70 Torr) - SF_6 (2 Torr) mixed sample.
————:mixed sample,
-----------:methanol alone.

observed by use of the sensitization effect caused by the addition of SF_6. Especially, it is noticeable that the sensitization of about 14 times is realized for the C-O stretching band at 9.3 μm, though the partial pressure of methanol is as high as 70 Torr relative to only 2 Torr of SF_6. According to the previous experimental results, the degree of sensitization decreases with the increase of the quantities of samples relative to those of sensitizing agents.[11)] It can be inferred from the previous examinations that the sensitization degree is at most 2-3 times at about 70 Torr of the sample pressure when the alkenes are used as sensitizing agents. This great intensity enhancement in question here may have some relation to the fact that the 9.3 μm band of methanol lies near the wavelength of the excitation laser lines or the 10.4 μm band of SF_6. However, this is only a speculation and is not based on any definite theoretical foundations. The discussions about such a problem shall be left to be examined in the near future.

The interesting fact is that the degree of sensitization increases remarkably when the partial pressures of a sample become smaller. Therefore, in the next, we have examined this phenomenon quantitatively for diethyl ether-SF_6 mixed samples. In this examination, we have fixed the partial pressure of SF_6 at 2 Torr rather arbitrarily, and the effect of the concentrations of diethyl ether on the degrees of the sensitization has been examined, using the 8.7 μm band of diethyl ether as a key band. The result is shown in FIG.7. In this figure, we have plotted the values of $H_{8.7}/P$ ($H_{8.7}$:the peak height of the 8.7 μm band of diethyl ether, P:its partial pressure) against P. The value $H_{8.7}/P$ is considered to be the peak intensity per unit concentration of ether. Thus, this variable can be regarded as a measure of the degree of

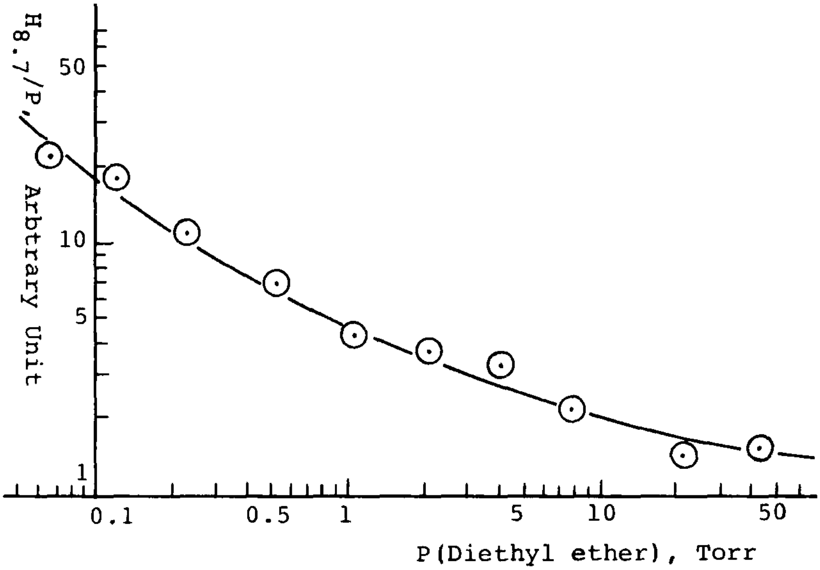

FIG.7 The plots of the value of $H_{8.7}/P$ vs. P on diethyl ether-SF_6 mixed sample.
$H_{8.7}$:Peak height of the 8.7 μm band of diethyl ether,
P:Partial pressure of diethyl ether.

the sensitization effect. Moreover, the data are plotted in a logarithmic scale. This is not based on any theoretical consideration, but we have done it to show the sensitization changes more distinctly.

As is seen from this figure, the intensity per unit concentration is enhanced to a great extent when the partial pressure of diethyl ether becomes lower. The value of $H_{8.7}/P$ becomes about 12 times greater when the pressure of ether changes from 40 to 0.1 Torr. Since the intensity of the 8.7 μm band increases about 8 times when 2 Torr of SF_6 is added to 40 Torr of diethyl ether, the sensitivity becomes about 100 times greater at 0.1 Torr of ether when compared with that without SF_6.

Theoretically, the experimental fact in question can be explained qualitatively in terms of the absorption of the laser light by SF_6, which is followed by inter- and intramolecular energy transfer, though the details of such a mechanism remain obscure. In view of such a mechanism, the experimental phenomenon in question seems to be natural, since the probability of the intermolecular energy transfer between SF_6 and diethyl ether is considered to increase when the concentration of the sensitizer relative to that of ether becomes greater.

Considering the sensitivity change shown in FIG.7, we can not estimate the detection limit in the strict sense of the word from the spectrum for the lowest concentration. However, as a measure of the detection limit, we have estimated the concentration at S/N=2 from the spectrum of the diethyl ether-SF_6 mixed sample for which the partial pressure of diethyl ether is 0.065 Torr, the lowest concentration treated in the present study. The result is about 0.01 Torr. This value corresponds to the concentration of about 12 ppm (1.2×10^{-5} ml/ml). It should be emphasized that we can say at most from this result that the detection limit is lower than 12 ppm for the sample system treated here.

CONCLUSION

In the present investigation, we have examined the sensitization effect observed in the IR-F spectra of some organic compounds under the coexistence of SF_6. The experimental results prove that a very small amount of SF_6 generally induces the marked enhancement of the IR-F intensities for the bands of samples. The quantitative discussion about the degree of sensitization has been given for the diethyl ether-SF_6 system in terms of the concentrations of ether.

In relation to the effect in question, Robinson et al.[2)] once made very suggestive remarks about the behaviour of the IR-F intensities of the band of nitromethane for nitromethane alone and nitromethane-propane mixed sample, though the details of the experimental results are not described in their paper. In fact, the present investigation was stimulated by their paper, and in a sense, it can be regarded as a development of their findings.

The authors realize that there remain some important problems left unsolved. The first of them is the details of the mechanism for the phenomena presented here. The second is where is the extremes of the improvement of the sensitivity by addition of SF_6 as a second component. The third is related to the second problem. That is, from the viewpoint of the instrumental aspects, much of the emissions from samples is not effectively utilized in the present sample cell. Thus, we are going to examine the sensitivity by use of a sample cell which contains the mirror system focusing the emitted light as much as possible into the detection system.3)

For all the above-mentioned problems left unsolved, we believe that the results presented here suggest that the IR-F spectroscopy sensitized by addition of SF_6 becomes an useful tool of microanalysis based on the vibrational spectra. The further examination in line with this purpose is now proceeding in our laboratory from the experimental and the theoretical viewpoint.

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