May, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***55***, *1437—1440 (1982)* 1437

The Sensitization Effect in the Laser-induced Infrared Fluorescence Spectroscopy by Addition of a Second Component. II

Yasuhiro Kagawa, Seiichiro Higuchi,* and Shigeyuki Tanaka
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

(Received August 3, 1981)

A considerable degree of the sensitization is realized in the laser-induced infrared fluorescence spectra when some of the alkene compounds are mixed with an objective sample in the gas phase. This sensitization effect has been examined quantitatively for diethyl ether when ethylene or propylene is added as a second component. The 8.7 μm band of ether is used as a key band. The degree of sensitization is abruptly enhanced with lowering the concentration of diethyl ether, and at about 0.1 Torr[†] of the sample the intensities per unit concentration become about 150 and 50 times greater for ether–ethylene and ether–propylene systems, respectively compared with that without ethylene or propylene. A possibility of a new vibrational spectroscopy with high sensitivity and its applications to microanalysis are suggested.

Recently we have developed a measurement system for the laser-induced infrared fluorescence (IR-F) spectra, and begun to examine its analytical applications.1) During this investigation, the intensities of IR-F bands of some organic compounds were found to be enhanced remarkably when propylene was added as a second component. In a previous paper,2) we made a preliminary report on the experimental evidence of this sensitization effect. Since this effect comes out as the increase of the intensities per unit concentration, the phenomenon in question is interesting and attractive in view of not only pure scientific aspects but also analytical applications of the IR-F spectroscopy.

The IR-F spectroscopy is a new technique for measurements of vibrational spectra. Experimentally, it is based on the irradiation of a sample by a monocharomatic or quasi-monochromatic laser light. The sample is vibrationally excited to the various vibrational levels through some mechanisms. Thus, the IR-F spectrum which is a kind of infrared emission spectrum, is obtained. 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, though several possible mechanisms are proposed.3,4) The main reason is that the emission mechanism of the IR-F spectrum is not fully explained at present.

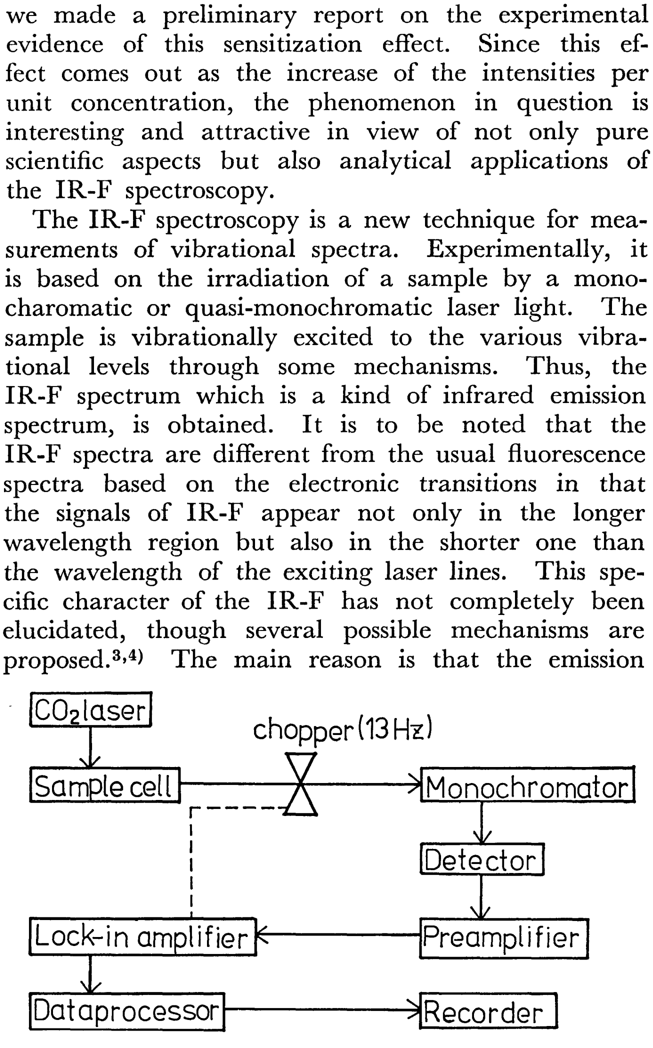

Fig. 1. The block diagram of the measurement system of IR-F spectra.

Under these circumstances, we are not in a position to make a satisfactory explanation about the phenomenon either. Therefore, only the experimental results are presented and they are discussed from the viewpoint of analytical utility. That is, after presenting a preliminary paper,2) we have made a more detailed and quantitative experimental investigation on the sensitization effects of ethylene and propylene as the second component, which will be described in this paper.

Experimental

In Fig. 1 is shown the block diagram of the measurement system for IR-F spectroscopy, developed in our laboratory. The details for the essential elements composing this system were described in the previous paper.1)

In this system, the sample in the sample cell is irradiated with the 10.6 μm lines from a CO_2 laser (output power: about 3 W). 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 spectrophotometers, 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 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. The pressures or the partial pressures of samples were from a few hundred to about 0.1 Torr. The lower limit of sample pressures is determined mainly by the sample preparation apparatus, not by the sensitivity of the instrument. This fact needs to be borne in mind when the sensitivity of the IR-F spectroscopy is discussed in the later section of this paper.

[†] 1 Torr ≈ 133.322 Pa.

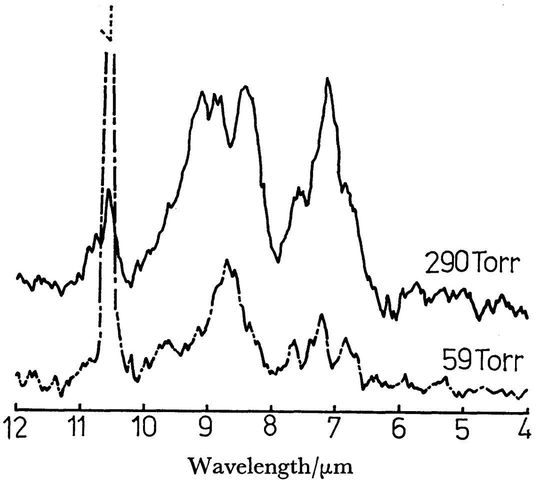

Fig. 2. IR-F spectra of diethyl ether at two different pressure.
——: 290 Torr, - - - -: 59 Torr.
The sharp band at 10.6 μm is considered to be due to the scattering of laser light in the sample cell.

Results and Discussion

The IR-F Spectra of the Sample Compound and the Sensitizing Agents. In the present investigation, we have selected diethyl ether as an objective sample, and the IR-F spectra for the mixed samples consisting of diethyl ether and some of the alkene compounds have been examined.

In Fig. 2 are shown the spectra of diethyl ether alone at the two different pressures. As is seen from this figure, the spectral patterns of ether in the 8—9 μm region are different for each pressure. That is, the 8.7 μm band, which can be assigned to the C–O–C stretching vibration, splits apparently into two peaks for the higher pressure, while the spectrum for the lower pressure exhibits only one band. This is considered to be due to the self-absorption.[1,5] Such phenomenon often occurs in the IR-F spectra when the pressures of gaseous samples are relatively high. This type of the band splitting is considered to be realized when the absorptions of samples are strong and the widths of the absorption bands are comparatively narrower than those of the corresponding IR-F bands.

In Figs. 3 and 4 are shown the IR-F spectra of ethylene and propylene, which are used as the main sensitizing agents in the present study. As can be seen from these figures, the IR-F spectra of these compounds exhibit no marked signal in the 7—9 μm region. Therefore, the influence of the presence of ethylene or propylene can be favorably examined, using the 8.7 μm band of diethyl ether as a key band. Thus, we deal with the intensity changes of this band in the range of the partial pressures of diethyl ether where no influence of the self-absorption appears.

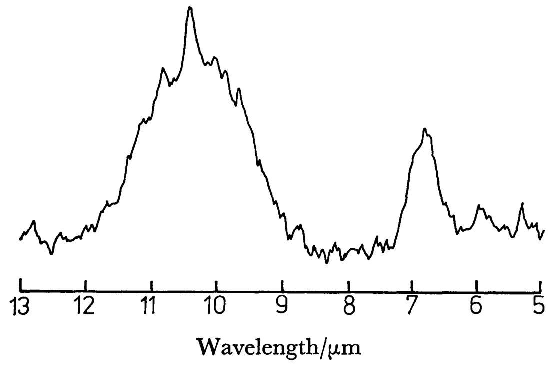

Fig. 3. IR-F spectra of ethylene (191 Torr).

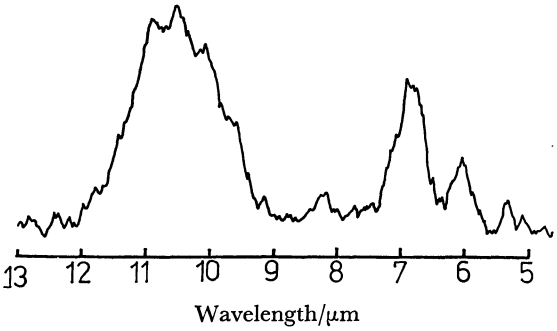

Fig. 4. IR-F spectra of propylene (260 Torr).

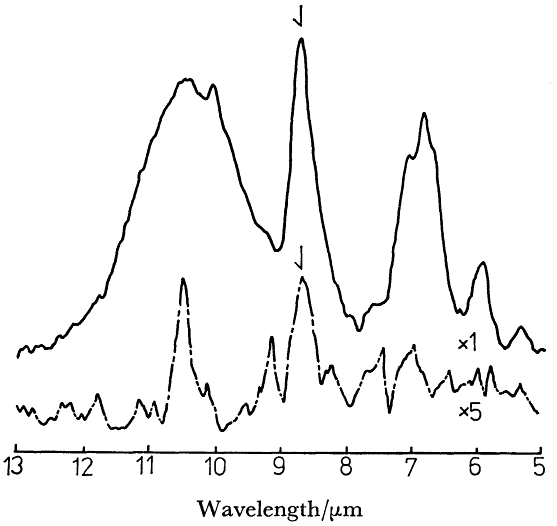

Fig. 5. IR-F spectra of diethyl ether only (19.2 Torr) and of diethyl ether (19.9 Torr)–propylene (425 Torr) mixed sample.
——: Mixed sample, - - - -: diethyl ether only.
Arrows show the 8.7 μm band of diethyl ether.

The IR-F Spectra of Mixed Samples. Next we show the spectral evidence of the sensitization effect observed when some alkene compounds are added as the second component. The examples are shown in Figs. 5—7. Obviously the intensities of the 8.7 μm band of diethyl ether are enhanced considerably for the mixed samples, compared with those without a second component. All of the alkene compounds examined in the present study, *i.e.*, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, have been found to induce the sensitization effect, though its degree is different among them.

We will examine the experimental results more quantitatively. Figure 5 shows the IR-F spectrum of diethyl ether alone (19.2 Torr) and that of a mixture of diethyl ether (19.9 Torr)–propylene (425 Torr).

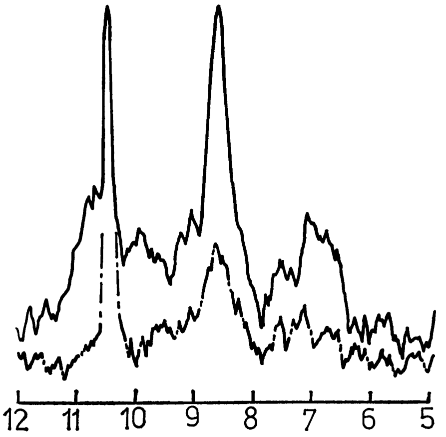

Fig. 6. IR-F spectra of diethyl ether only (59 Torr) and of diethyl ether (20 Torr)-1-butene (100 Torr) mixed sample.
——: Mixed sample, - - - -: diethyl ether only.

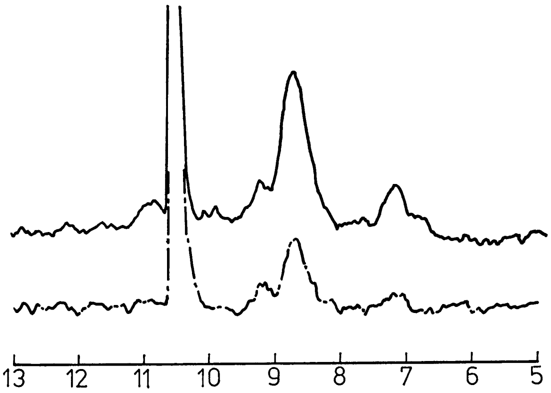

Fig. 7. IR-F spectra of diethyl ether only (37 Torr) and of diethyl ether (37 Torr)-1-hexene (37 Torr) mixed sample.
——: Mixed sample, - - - -: diethyl ether only.

The spectrum of ether alone has been measured with the instrumental sensitivity set five times higher than for the mixed sample. The sensitization of about one order of magnitude is realized in this particular case.

The Relation between the Degrees of the Sensitization and the Partial Pressures of Diethyl Ether. As was mentioned briefly in the previous paper,[2] the degrees of the sensitization were found to increase when the partial pressures of objective sample became smaller. In the present investigation, we have examined this phenomenon in more detail and quantitatively.

Theoretically, the experimental fact in question can be explained qualitatively in terms of the absorption of the laser light by ethylene, propylene or other sensitizing components, which is followed by inter- and intramolecular energy transfer, though the details of such mechanism remain obscure. In view of such mechanism, the above-mentioned experimental fact seems to be natural, since the probability of the intermolecular energy transfer between the sensitizing agent and diethyl ether is considered to increase when the concentration of the sensitizer relative to that of ether becomes greater. From such viewpoint, we have examined experimentally the changes of the sensitization degree with the concentrations of ether. Since the effect in question comes out as the increase of the intensities, such results have direct relation to the microanalytical utility of the IR-F spectroscopy.

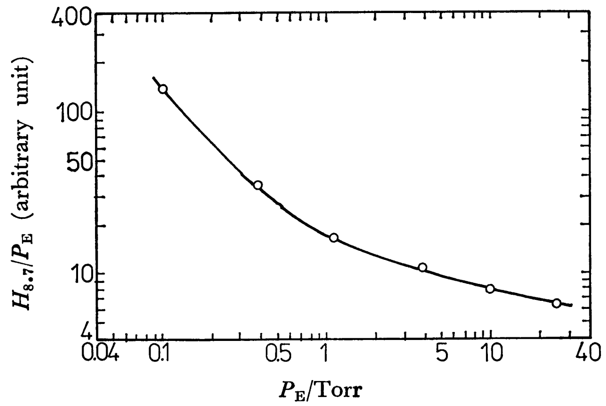

Fig. 8. Plots of value of $H_{8.7}/P_E$ *vs.* P_E on diethyl ether–ethylene mixed sample.
$H_{8.7}$: Peak height of 8.7 μm band of diethyl ether, P_E: partial pressure of diethyl ether.

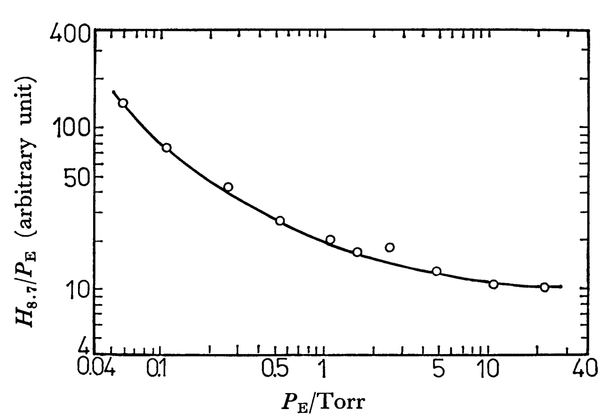

Fig. 9. Plots of value of $H_{8.7}/P_E$ *vs.* P_E on diethyl ether–propylene mixed sample.

In the examinations described in the following, we have fixed the partial pressure of the sensitizing components at 100 Torr rather arbitrarily, and the effect of the concentrations of diethyl ether on the degrees of the sensitization has been examined for ethylene and propylene as the second components. The results are shown in Figs. 8 and 9. In these figures, we have plotted the values of $H_{8.7}/P_E$ ($H_{8.7}$: the peak height of the 8.7 μm band of diethyl ether, P_E: its partial pressure) against P_E. The value $H_{8.7}/P_E$ 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 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 these figures, the intensity per unit concentration is enhanced to a great extent for both of the sample systems when the partial pressures of diethyl ether become lower. For ethylene as a second component the values of $H_{8.7}/P_E$ become about

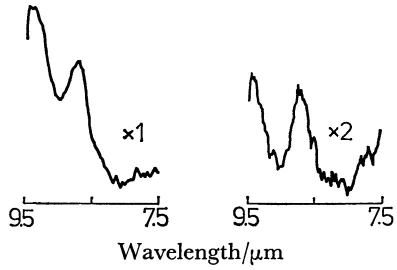

Fig. 10. The 8.7 μm bands of diethyl ether for the lowest concentrations.
Left side: diethyl ether (0.1 Torr)–ethylene (100 Torr) mixed sample, right side: diethyl ether (0.06 Torr)–propylene (100 Torr) mixed sample.

22 times greater when the pressures of ether change from 20 to 0.1 Torr. Since the intensity of the 8.7 μm band increases about 7 times when 100 Torr of ethylene is added to 20 Torr of diethyl ether, the sensitivity becomes about 150 times greater at 0.1 Torr of ether compared with that without ethylene. The value of 150 is to be considered the minimum, since this is estimated on the assumption that the relation between the pressures of diethyl ether and the peak heights is linear. In IR-F spectroscopy the relation is not always linear, but the one such as $H=\mathrm{const}\times P^{X}$ ($X\geqq 1.0$) is often observed.[1,6] Thus, the sensitivity increase becomes greater than 150 when X is larger than unity.

For propylene as a sensitizing agent the same tendency of the changes of intensity per unit concentration of diethyl ether is realized. However, the types of the curves shown in Figs. 8 and 9 are obviously different. Quantitatively, for propylene, $H_{8.7}/P_{\mathrm{E}}$ increases about 7 times when the pressure of ether changes from 20 to 0.1 Torr. Since the intensity of the 8.7 μm band is enhanced also about 7 times at the sample pressure of 20 Torr when 100 Torr of propylene is added, the minimum sensitivity enhancement is about 50 times, about one third of the value for ethylene. This fact indicates that the effectiveness of the alkenes as sensitizers is widely different among them.

In Fig. 10 are shown the 8.7 μm bands of diethyl ether for the lowest concentrations so far studied. At present, the lower limit of concentration is determined by the apparatus used for the sample preparation rather than by the sensitivity of the measurement system. The spectrum on the right side of this figure has been measured with the instrumental sensitivity set twice higher than that on the left. Considering the sensitivity changes shown in Figs. 8 and 9, and that the spectra for the lower concentrations were not measured, we cannot estimate the detection limits in the strict sense of the word from the spectra shown in Fig. 10. However, as a measure of the detection limits, we have estimated the concentrations at S/N=2 from these spectra. The results are the same for both spectra and 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 under the presence of some alkene compounds. The experimental results prove that the alkene compounds generally induce the enhancement of the IR-F intensities for the bands of samples. The quantitative discussions about the degrees of sensitization have been given for the diethyl ether–ethylene and diethyl ether–propylene systems in terms of the concentrations of ether.

The authors realize that there remain some important problems left unsolved. The first of them is the details of the mechanism of the phenomenon presented here. The second is where is the extremes of the improvement of the sensitivity, including the sensitizers other than ethylene and propylene. 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.[1] 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. The fourth is a rather important one, that is, the influence of the quantities of sensitizing agents, which is now under the examination as the next step of this investigation.

For all the above-mentioned problems left unsolved, we believe that the results obtained here suggest that the presented method greatly improves the sensitivity of the IR-F, and there is a possibility that the IR-F spectroscopy becomes an useful tool of microanalysis based on the vibrational spectra. The further examination in line with this purpose is proceeding in our laboratory.

The present work was supported by a Grant-in-Aid for Scientific Research No. 443014 from the Ministry of Education, Science and Culture.

References

1) S. Higuchi, N. Kihara, H. Waki, S. Tanaka, and N. Sakayanagi, *Bunko Kenkyu*, **30**, 250 (1981).
2) S. Higuchi, N. Kihara, H. Waki, and S. Tanaka, *Chem. Lett.*, **1981**, 609.
3) J. W. Robinson and J. D. Dake, *Anal. Chim. Acta*, **71**, 277 (1974).
4) J. W. Robinson, D. Nettles, and L. H. Jowett, *Anal. Chim. Acta*, **92**, 13 (1977).
5) D. M. Hailey, H. M. Barnes, and J. W. Robinson, *Anal. Chim. Acta*, **56**, 175 (1971).
6) J. W. Robinson and J. D. Dake, *Spectrosc. Lett.*, **6**, 685 (1973).