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

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Synopsis. The sensitization effect in the infrared fluorescence spectra for diethyl ether–alkene systems has been examined in terms of the quantity and the kind of alkenes added as sensitizers. The sensitivity seems to be determined by the molar ratios between diethyl ether and alkenes, and the sensitization degree lowers in an orderly fashion as the alkene molecules become larger.

In the previous papers,[1,2] we examined the sensitization effect in the laser-induced infrared fluorescence (IR-F) spectroscopy, which was realized when some alkene compounds were added as second components. The degree of sensitization was examined quantitatively in terms of the concentrations of diethyl ether as an objective sample. In the present investigation, we have examined this sensitization effect for the same sample in view of the influence of the quantity and the kind of alkene compounds as the sensitizer.

Experimental

The experimental arrangement for the measurement of IR-F spectra is the same as that described in the previous papers.[1,2] The samples are vibrationally excited with the irradiation of the 10.6μm lines from a CO_2 laser (output power: 3 W), and the emitted light from samples is spectrally measured. Diethyl ether was used as a sample, and the alkenes such as ethylene, propylene, 1-butene, 1-pentene, and 1-hexene were added as the sensitizing agents. The 8.7 μm band (C–O–C stretching vibration band) of diethyl ether was used as a key band. The measurements were all made for samples in the gaseous state.

Results and Discussion

The Relation between the Degree of Sensitization and the Quantity of a Sensitizing Agent. It was reported in the previous paper[2] that the degree of sensitization increases to a great extent as the concentrations of diethyl ether become lower. It will be reasonable to consider that the sensitivity depends also on the quantity of sensitizing agents. Thus, we have examined the influence of the partial pressure of added alkenes on the sensitized IR-F intensities of the 8.7 μm band of diethyl ether. In Fig.1 are plotted the values of $H_{8.7}/P_E$ ($H_{8.7}$: the peak intensity of the 8.7 μm band of diethyl ether, P_E: the partial pressure of diethyl ether) against the partial pressure of propylene, P_P. $H_{8.7}/P_E$ can be regarded as the intensity per unit concentration of diethyl ether, and therefore, this variable is considered to be a measure of the spectral sensitivity. It is seen that the sensitivity clearly depends on P_P, though the changes of $H_{8.7}/P_E$ with P_P are more gentle than the dependence of $H_{8.7}/P_E$ on P_E.[2] It appears that there is an optimum range of P_P to give the maximum degree of sensitization.

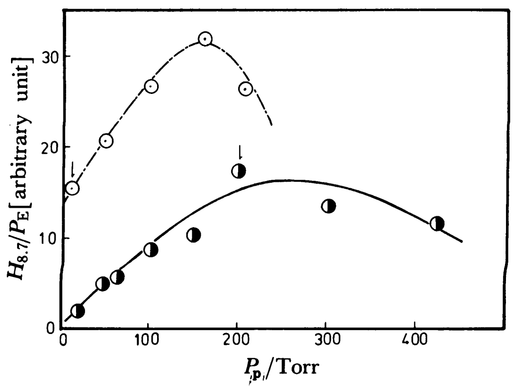

Fig. 1. Plots of values of $H_{8.7}/P_E$ *vs.* P_P on diethyl ether–propylene mixed sample.
$H_{8.7}$: Peak height of 8.7 μm band of diethyl ether, P_E: partial pressure of diethyl ether, P_P: partial pressure of propylene. ◑: P_E=20 Torr, ⊙: P_E=1 Torr. The data marked with arrows correspond to molar ratio of 1:1 (diethyl ether:propylene).

We examined the fashion of the curves in Fig. 1 in view of the kinetics of the energy transfers relating to the infrared emissions in question. We assume that five vibrationally excited energy levels are involved in the kinetics of the energy transfers. One of them is a level of propylene which is responsible for the absorption of the exciting laser light, and the others are those of diethyl ether. Three of the latter four levels yield the infrared emission bands, and the remaining one is representative of all other levels. Moreover, we assume that the sample system is in the stationary state. Under these conditions, the following expression is derived for the population of the emitting energy levels, *i.e.*,

$$X_i = \frac{A_iP_s^5+B_iP_s^4+C_iP_s^3+D_iP_s^2+E_iP_s+F_i}{P_s^5+G_iP_s^4+H_iP_s^3+I_iP_s^2+J_iP_s+K_i}, \tag{1}$$

where X_i is the population of the i-th energy level of the objective sample molecule, resulting from the energy transfers, P_S is the partial pressure of the sensitizer (in this case, P_P), and A_i, B_i, *etc.*, are the constants related to the rate constants for various energy transfers. Formula (1) predicts that when P_S becomes greater, the fashion of the change of X_i (consequently, the fashion of the intensity change of the i-th emission band) becomes gradually flat, converging ultimately to a constant, A_i. This partly explains the fashion of the curves in Fig.1.

Concerning the reason why the sensitivity lowers when P_P becomes greater than a certain magnitude, the following considerations may be possible. The first is the lowering of the effective absorption coefficient of propylene at 10.6μm because of the pressure broadening of rotational lines responsible for the absorption. The second is the weakening of the intensity of the exciting laser light due to the absorption of the added component. The third is that when the number of propylene molecules becomes much larger than that of diethyl ether, the energy first absorbed by propylene molecules may be transferred mainly to the same molecules rather than to diethyl ether. Of course, these are only speculations, and it is highly probable that some other factors play essential roles in the experimental results in question. The problem is related to the mechanism of the

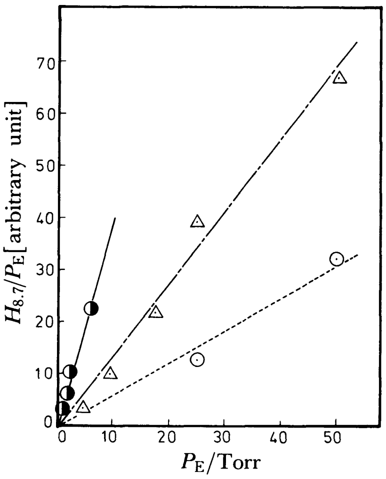

Fig. 2. Effect of molar ratios of diethyl ether to ethylene on the relations between IR-F intensities of 8.7 μm band of diethyl ether and P_E.
◑: 1:100 (diethyl ether:ethylene), △: 1:5, ⊙: 1:1. The points in the case of the molar ratio of 1:1 are only a part of the data up to P_E=100 Torr, which fit well to the straight line shown in the figure.

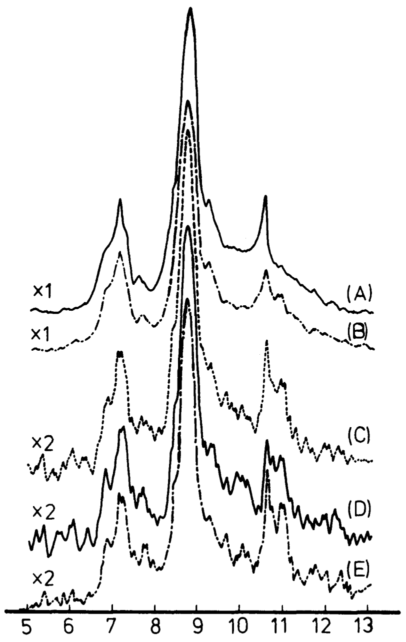

Fig. 3. Effect of the kind of alkenes on IR-F spectra of diethyl ether–alkene mixed samples. (A) ethylene, (B) propylene, (C) 1-butene, (D) 1-pentene, (E) 1-hexene. The instrumental sensitivity for the spectra (C), (D) and (E) is set twice higher than that for (A) and (B).

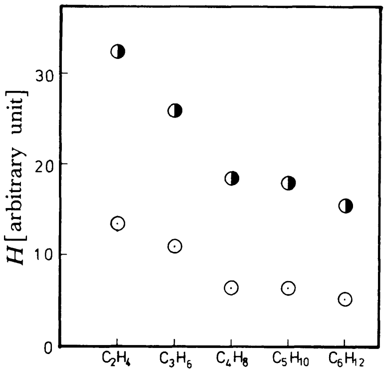

Fig. 4. Effect of the kind of alkenes on IR-F intensities of 8.7 and 7.1 μm bands of diethyl ether.
◑: 8.7 μm band, ⊙: 7.1 μm band.

sensitization effect, and we are not in a position to make further mention of it in the present note.

It is noteworthy that the optimum range of P_p in the case of both P_E=20 Torr (1 Torr≈133.322 Pa.) and P_E=1 Torr seems to be not so different. This fact can be favourably utilized when the effect in question is made use of in analytical applications. Furthermore, it is also noticeable that the values of $H_{8.7}/P_E$ corresponding to the equal molar ratio between diethyl ether and propylene appear to be constant.

Therefore, we have examined the IR-F intensities in terms of the molar ratios between diethyl ether and a sensitizing agent. Figure 2 shows the result for diethyl ether–ethylene system. In this figure are shown the relations between $H_{8.7}$ and P_E for the individual constant molar ratios. From these results, it was proved that the slopes of the straight lines, *i.e.*, $H_{8.7}/P_E$, are kept constant for each of the molar ratios, and that the sensitivity of IR-F becomes rapidly greater when the quantities of ethylene increase relative to those of diethyl ether. The latter result is consistent with the phenomena that $H_{8.7}/P_E$ increases rapidly with lowering P_E under the constant partial pressure of ethylene. To sum up, the IR-F sensitivity changes not only with the quantity of diethyl ether but also with that of sensitizing agents, and the sensitivity is not influenced independently by the two quantities but by the relative magnitudes of them.

The Influence of the Kind of Alkenes on the Degree of Sensitization. We have examined the difference in degree of sensitization due to the kind of alkenes. In Fig. 3 are shown the IR-F spectra for the mixed samples which consist of 50 Torr of diethyl ether and 50 Torr of various alkenes. It is clear that the IR-F intensities of the 8.7 μm band of diethyl ether are markedly different according to the kind of alkenes. Figure 4 shows graphically the dependence of the intensities of the 8.7 and 7.1 μm band of diethyl ether on the kind of sensitizing compounds. It is seen that as the alkene molecules become larger, the sensitized IR-F intensities lower in an orderly fashion. Although any definite interpretation for this result can not be given at present, it can be supposed that the factors which may be related to the phenomenon are the following, *i.e.*, the characteristics and the number of vibrational levels of the alkenes involved, the intensities of the absorption at 10.6 μm and the agreement of the wavelengths of excitation laser lines with the rotational absorption lines of the alkenes, *etc.*

It can be concluded that though there remain many problems unsolved, the present experimental results give useful guide for the analytical and structural applications of the IR-F spectra sensitized by addition of the alkenes.

References

1) S. Higuchi, N. Kihara, H. Waki, and S. Tanaka, *Chem. Lett.*, **1981**, 609.

2) Y. Kagawa, S. Higuchi, and S. Tanaka, *Bull. Chem. Soc. Jpn.*, **55**, 1437 (1982).