

Letters to the Editor

On the possibility of purifying substances from admixtures using a free electron laser

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It has been shown previously^{1–4} that infrared multi-photon dissociation (IR MPD) can be carried out and isotopes can be divided upon resonance excitation of ground stretching vibrations of C–H, C=O, and N=O in molecules using a free electron laser (FEL). The possibility of purifying substances in the gas phase by selective IR MPD has been demonstrated⁵ for the first time for a pulse CO₂ laser. In this work, we attempted to reveal whether FEL can be used for purification of carbon tetrachloride mixed with chloroethane. C₂H₅Cl molecules are characterized by absorption bands at ~3 mm (stretching vibrations of C–H), whereas CCl₄ is transparent in this region. Therefore, a FEL with generation frequencies variable over a wide range should have an advantage over a CO₂ laser.

A Mark-III FEL of Duke University (North Carolina, USA) was used in experiments. Its radiation can be varied in a spectral range of 2–9 μm (5000–1100 cm⁻¹) with a width $\Delta\lambda/\lambda = 0.01$ –0.02. The laser radiation consisted of macropulses (repetition frequency 10 Hz; duration 2–4 μs; energy 10–30 mJ), each of which was a sequence of micropulses (duration 1–2 ps, repetition period 350 ps). The laser beam was focused inside a gas cell by a lens with a focus distance of 50 cm. The pressure in the cell was 1 Torr.

According to previous studies,^{6,7} IR MPD of chloroethane occurs *via* the molecular mechanism to form stable products: C₂H₅Cl → C₂H₄ + HCl. The characteristic absorption bands of HCl (2700–2900 cm⁻¹) and C₂H₄ (3000–3200 cm⁻¹) are distinctly seen in

Fig. 1. Since radicals are not generated, the consumption of CCl₄ should not occur chemically. To treat a mixture of gases, the laser was adjusted at $\lambda = 3.4$ μm, which cor-

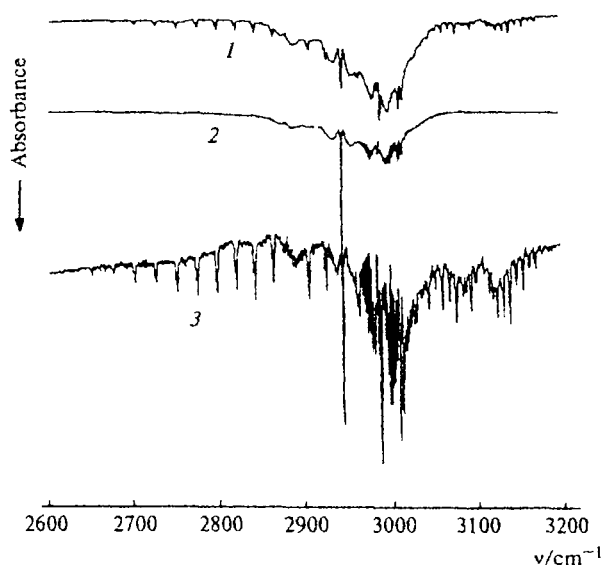


Fig. 1. IR spectrum of the mixture containing products of dissociation of C₂H₅Cl (1); the same spectrum after subtraction of the contribution of the remaining C₂H₅Cl (2) and fivefold extension (3).

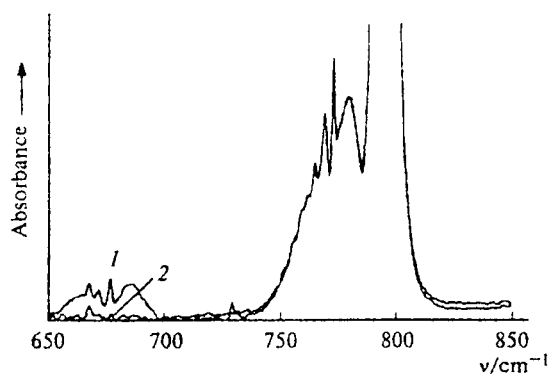


Fig. 2. IR spectra of the $\text{C}_2\text{H}_5\text{Cl}-\text{CCl}_4$ mixture before (1) and after (2) irradiation.

responds to the maximum rate of dissociation of $\text{C}_2\text{H}_5\text{Cl}$. Before gas admission, the cell was evacuated to 10^{-3} Torr. The process was monitored by the change in pressure and variation of IR absorption spectra.

The regions of the IR spectra of the mixture in the area of stretching vibrations of C—Cl of both molecules are presented in Fig. 2. The spectra were detected before (curve 1) and after (curve 2) irradiation for 3 h. It is well seen that the intensity of the band assigned to CCl_4 remained unchanged, while the band characterizing $\text{C}_2\text{H}_5\text{Cl}$ disappeared nearly completely.

Note that the possibility of purification can be unsuitable for substances whose dissociation under laser irradiation gives products capable of entering secondary reactions.

The efficiency of the FEL used is too low for its actual application in the technology of purification of substances or decomposition of toxic waste. However, the possibilities⁸ of increasing the pulse energy by three

orders of magnitude and narrowing by an order of magnitude the width of the generation line of the FEL developed in Novosibirsk make it possible to solve these problems.

The authors thank Prof. J. Madey and Prof. K. Straub for the FEL and for help in the work. This work was financially supported (grant IGSO-97-2.2).

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Received June 26, 1998;
in revised form July 15, 1998