

## IR multiphoton dissociation of CF<sub>3</sub>I. Pressure effect with inert and reactive gases

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**Abstract.** The IR multiphoton dissociation of CF<sub>3</sub>I has been studied in the presence of isobutane and with isobutane and Ar and CO<sub>2</sub> as inert gases. The dependence of the reaction probability  $P(\Phi)$  with fluence ( $\phi$ ) is confirmed. Modeling of the experimental results shows that for the energy transfer processes the average energy transferred per collision  $\langle \Delta E \rangle_d$  varies with ( $\phi$ ).

**Keywords.** IRMPD-CF<sub>3</sub>I; isobutane; inert gases; energy transfer.

### 1. Introduction

Studies of the primary characteristics of the multiple IR photon excitation and dissociation of CF<sub>3</sub>I have been done previously by Bagratashvili *et al* (1979), Quack and Seyfang (1982) and Rossi *et al* (1982). In the present work, the IR multiphoton decomposition of CF<sub>3</sub>I has been investigated in the presence of isobutane which acts as a collider deactivating the excited CF<sub>3</sub>I molecules and also as a scavenger of the product of the primary decomposition, CF<sub>3</sub>, by reaction. The influence of collisions with buffer gas molecules such as Ar and CO<sub>2</sub> on the evaluation of the energy transferred is analysed in terms of the nature of the collider. The following reactions are relevant in this system:



with  $\text{M} = \text{Ar}, \text{CO}_2, \text{C}_4\text{H}_{10}$ .

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## 2. Experimental

The experiments were carried out using a pulsed TEA CO<sub>2</sub> laser as irradiation source operated at the 9R 14 line of the 001–020 transition at 9.6 μm. A cylindrical pyrex glass reaction cell (length 15 cm) fitted at both ends with NaCl windows was used. In experiments with variation of fluence the excitation beam was focused with an appropriate optical arrangement. The CF<sub>3</sub>I pressure was held constant at 100 mTorr and that of isobutane was varied between 0.5 and 5 Torr. In those runs with added Ar or CO<sub>2</sub>, mixtures of 100 mTorr of CF<sub>3</sub>I, 1 Torr of isobutane and pressures up to 40 Torr of the inert gases were measured with capacitance manometers. In all cases, measurements were carried out at room temperature and in the dark.

Relative product yields were measured by gas chromatography using a flame ionization detector on a 2 m long Porapak T column operated at 110°C.

Several experiments were performed at two different fluences, 0.6 and 1.2 J/cm<sup>2</sup> in order to analyse its dependence with the average energy transferred per collision,  $\langle \Delta E \rangle_d$ .

## 3. Results

The reaction probability  $P(\Phi)$  was analysed with respect to the incident fluence and the data are displayed in figure 1. These results may be compared to those of Rossi *et al* (1979) and there is very good agreement between both sets of results.

In figure 2 we have represented the reaction probability  $P(\Phi)$  as a function of isobutane pressure at two different fluences, 0.6 and 1.2 J/cm<sup>2</sup>. As can be observed

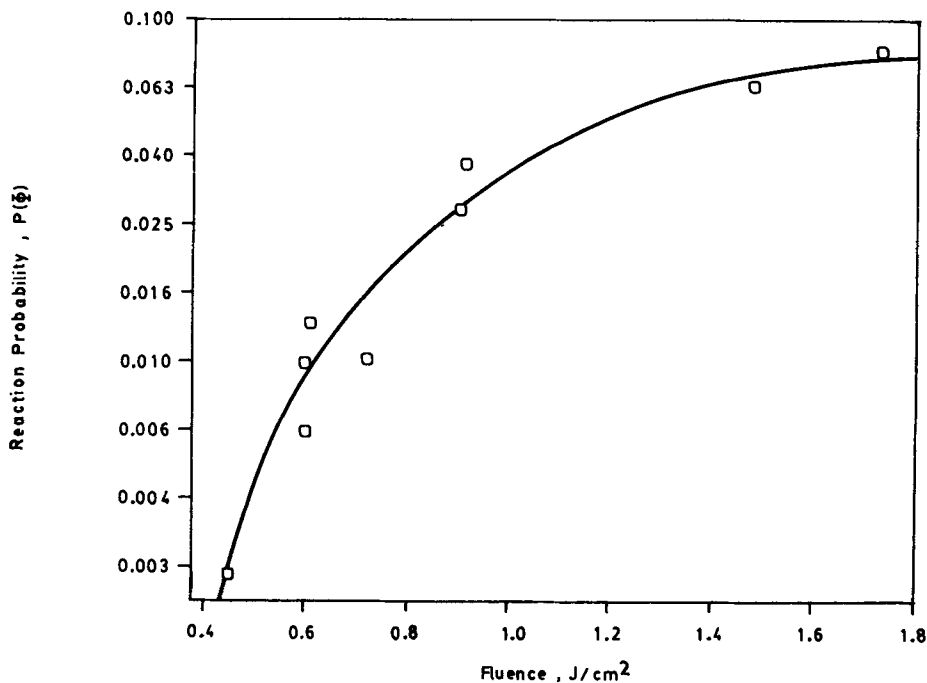


Figure 1. Dependence of reaction probability  $P(\Phi)$  of 0.1 Torr CF<sub>3</sub>I on fluence.

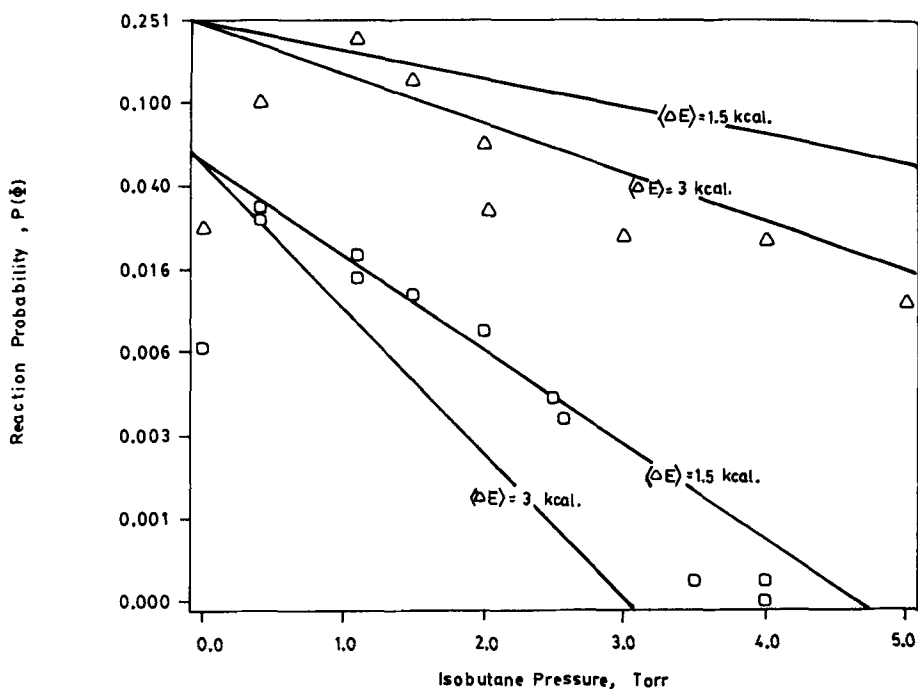


Figure 2. Reaction probability,  $P(\Phi)$  versus pressure of isobutane at two different fluences. ( $\square$ ) refers to fluence  $0.6 \text{ J/cm}^2$ , ( $\triangle$ ) refers to fluence  $1.2 \text{ J/cm}^2$ .

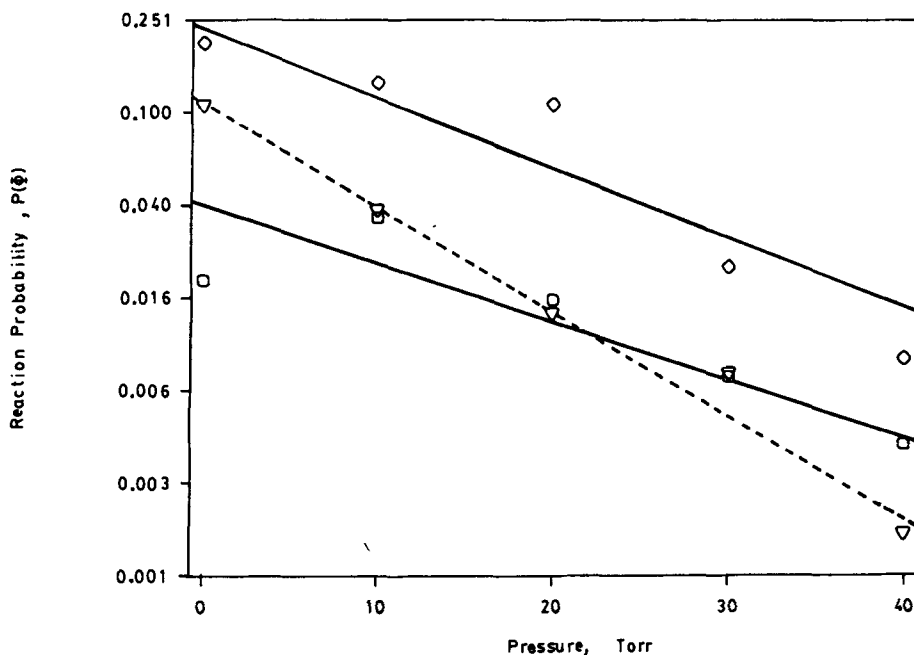


Figure 3. Reaction probability,  $P(\Phi)$  versus pressure of buffer gases. ( $\square$ ) with Ar at  $0.6 \text{ J/cm}^2$  fluence, ( $\diamond$ ) with Ar at  $1.2 \text{ J/cm}^2$  fluence and ( $\nabla$ ) with  $CO_2$  at  $1.2 \text{ J/cm}^2$  fluence.

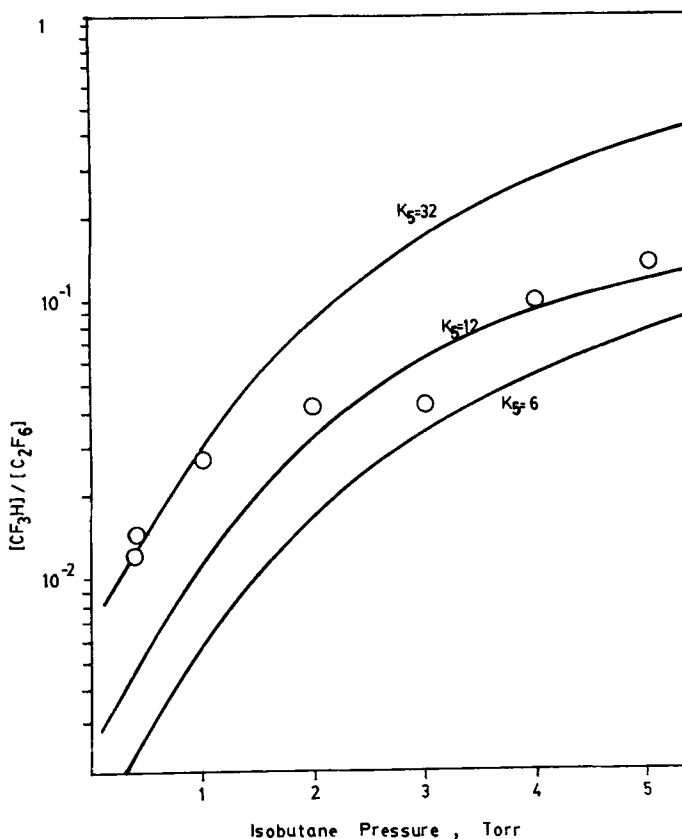


Figure 4. Fractional product yields  $[CF_3H]/[C_2F_6]$  as a function of pressure of isobutane at a fluence of  $1.2 J/cm^2$ . Solid lines are model calculations with the rate constants for H-abstraction as indicated (units of Torr/s).

there is a maximum at 1 Torr pressure of isobutane for  $\phi = 1.2 J/cm^2$  and this maximum shifts to the left at 0.5 Torr when the fluence is  $0.6 J/cm^2$ . In addition the slope of the line beyond the maximum is greater for the lower fluence.

The pressure dependence of the reaction probability by added inert gases is shown in figure 3. In this case it is not possible to observe a maximum over the pressure range of our experiments whereas the slope changes when the fluence is increased for the case of Ar. At a fluence of  $1.2 J/cm^2$ ,  $CO_2$  shows a steeper slope compared to Ar at the same fluence. In figures 4 and 5 we have plotted the fractional product yields,  $[CF_3H]/[C_2F_6]$ , as a function of the pressure of isobutane at the two fluences studied. It can be seen that the product ratio increases with pressure. However, with added Ar or  $CO_2$  no  $CF_3H$  formation was observed at any of the two fluences and for the case of  $CO_2$  at  $0.6 J/cm^2$  no reaction was detected.

#### 4. Discussion

The IR multiphoton decomposition of  $CF_3I$  shows the general behaviour of "small molecules", that is, a maximum in the reaction probability as a function of pressure

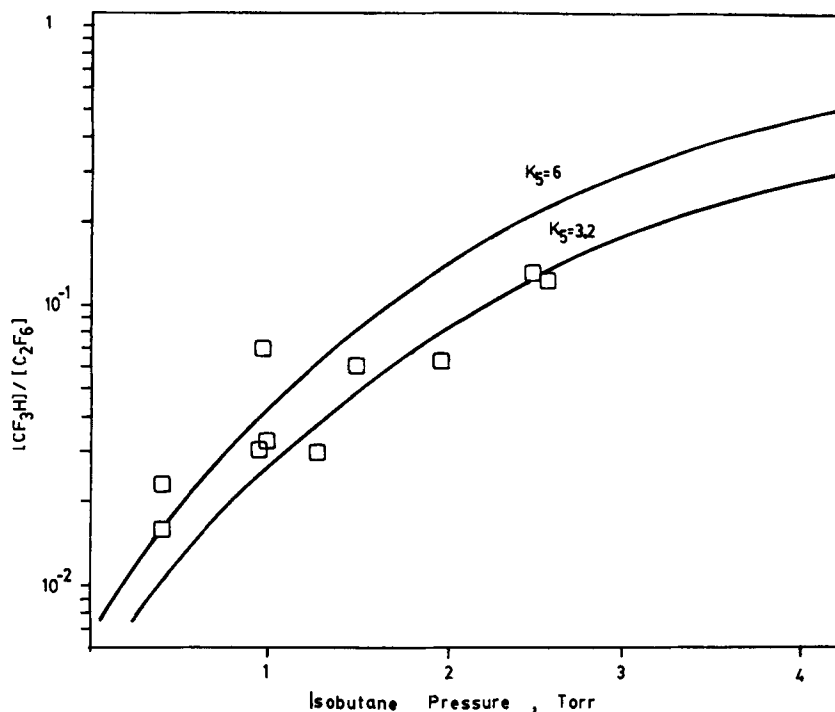


Figure 5. As figure 4 at a fluence of  $0.6 \text{ J/cm}^2$ . Solid lines are model calculations with the rate constants for H-abstraction as indicated (units of Torr/s).

followed by a monotonic decrease. This maximum is explained as a consequence of collisional filling of a rotational hole produced by the laser pumping and that not all of the  $CF_3I$  molecules are in resonance with the laser radiation. This positive effect on the reaction yield is then followed by a detrimental process at higher pressures due to vibrational deactivation of the absorbing molecules. An analysis of the results obtained in this region allows for the study of the energy transfer process of vibrationally excited species.

Model calculations of the results obtained with isobutane as a collider show that at different fluences the amount of energy transferred per collision  $\langle \Delta E \rangle_d$  is different, being higher at higher fluences. Thus, at  $\phi = 1.2 \text{ J/cm}^2$ ,  $\langle \Delta E \rangle_d = 3.0 \text{ kcal/mol}$  while at  $\phi = 0.6 \text{ J/cm}^2$ ,  $\langle \Delta E \rangle_d = 1.5 \text{ kcal/mol}$ . As the average excitation energy increases with fluence, this result is indicative of a dependence of  $\langle \Delta E \rangle_d$  with energy.

## References

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