The effect of fluence in collisional dissociation of Si_2F_6

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Abstract

The model of McRae et al. is used to investigate the effect of laser fluence and collisions in the dissociation of vibrationally excited Si_2F_6. The parameters of the model are obtained and their dependence on laser fluence is discussed. Vibrational energy pooling mechanism dominates over quenching of vibrational excitation in homogeneous (Si_2F_6–Si_2F_6) collisions. Heterogeneous collisions between Si_2F_6 parent molecule and SiF_4 as dissociation product are found to hinder dissociation for low laser fluence and to enhance it, as fluence increases. ©2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The dependence of IRMPD on laser fluence and pressure is complex and difficult to predict. Extracting this dependence from experimental data can be complicated because, for practical reasons, it is desirable to have a substantial fractional decomposition. This usually requires a large number of pulses, during which the pressure and composition of the irradiated mixture significantly changes with the target gas disappearing and the products accumulating. The increase of pressure with the number of pulses must be taken into account in the study of collisional IRMPD process, as dissociation products may significantly affect the subsequent excitation process through their collisions with parent molecules. Although dissociation products generally increase vibrational quenching, sometimes they can help to overcome vibrational and rotational bottlenecks. We refer, especially, to the cases when the reaction products absorb the infrared radiation, and, becoming vibrationally hot, enhance the dissociation process by vibrational energy pooling.

The multiphoton absorption and dissociation processes induced by the pulsed infrared radiation in the ν_7 normal mode of Si_2F_6 was investigated by us [1,2] both as a potential method for Si isotope separation [4] and as the most efficient way of generating the SiF_2 long-lived radical [5,6]. The purpose of the present work is to examine in more detail (than our previous study) the effect of laser fluence on Si_2F_6 dissociation [1]. The change of pressure during multipulse irradiation experiments as well as the above mentioned effects which the reaction products may have upon dissociation process were not taken into account in our previous work. In particular, by using the method proposed by McRae et al. [3], we will concentrate on dissociation processes occurring after the laser pulse, as a result of heterogenous and homogenous collisions. One benefit is that new information can be extracted concerning the postpulse dissociation and additional conclusions may be drawn if the experiment is stopped for analysis after different number of pulses.

2. Methods

For MPD measurement we used a stainless steel cell of 10 cm length with KBr windows on both ends. A mixture of He and CO_2 of 6:1 ratio was used for the CO_2 laser. The temporal profile, measured with a photon-drag detector (Hamamatsu), shows a pulse duration of 100 ns FWHM with no tail. For 0.1 Torr of neat Si_2F_6 gas, the average time between collisions at room temperature is 1.5 µs, therefore the collisionless conditions hold. The fluence was varied from 0.1 to 2 J/cm^2 by putting various thickness of CaF_2 attenuators before the cell and by using two confocal BaF_2 lenses of focal length 40 and 20 cm. We also monitored the transmitted beam with a pyroelectric detector so that we could skip incomplete laser pulses. After irradiating with a number of pulses which was varied depending on the fluence, we measured the FTIR absorption spectrum (Perkin–Elmer 1600 series FTIR, resolution 4 cm^{-1}). The amount of Si_2F_6 remaining in the cell is proportional to the integrated absorption of the ν_7 band. The gas contains SiF_4 as an impurity

but most of it can be separated by fractional distillation, so that the concentration of SiF_4 in Si_2F_6 gas was around 2%.

The method proposed by McRae et al. [3] is devoted to the analysis and quantification of the contributions from different collisional processes in multipulse dissociation experiments. The number of parent molecules N_n left in the cell after n irradiation pulses is given by

$$N_n = N_0 \prod_{k=1}^{n} \left[1 - \frac{V_I}{V_C} f_k(\Phi_k, \alpha_{k-1}, \beta_{k-1}) \right] \tag{1}$$

where N_0 is the initial number of molecules in the cell, V_I and V_C are, respectively, the irradiation and the total cell volumes (for our irradiation geometry $V_I/V_C=0.191$), and $f(\Phi, \alpha, \beta)$ is the single-pulse decomposition probability. This is a function of fluence, Φ, and the partial pressures of parent molecules, α, and of the dissociation products, β. The target gas partial pressure after n pulses, α_n can be expressed as

$$\alpha_n = \frac{N_n}{N_0} \alpha_0 \tag{2}$$

and the accumulated partial pressure of the products after n pulses is

$$\beta_n = \sum_p S_p (\alpha_0 - \alpha_n) \tag{3}$$

where the sum runs over all dissociation products. The proportionality constants S_p, depends on the stoichiometry of the dissociation reaction and takes specific values for each dissociation product. The method takes into account the variation in the pulse-to-pulse yield induced by the change of the pressures α_n and β_n, during the time of the experiment.

It was assumed that a power dependence of f on partial pressures is given by

$$f(\Phi, \alpha, \beta) = \sum_{i=1} \sum_{j=0} h_{ij}(\Phi) \alpha^{i-1} \beta^j \tag{4}$$

where the coefficients h_{ij} are associated with Lindenmann-like collision reactions. The sum $i+j-1$ is inferred to be the number of effective collisions between i molecules of the target gas and j molecules of some buffer gas (in our case dissociation products). After $i+j-1$ collisions, the target gas decomposes. If values of the h_{ij} coefficients are positive this indicates that the composition is enhanced by collision with target or buffer gas, while negative coefficients would correspond to collisional deactivation. As pressure is low, we restricted our fit to first-order coefficients, i.e. $i+j-1=1$, so that Eq. (4) takes on the form

$$f(\alpha, \beta) = h_{10} + h_{20}\alpha + h_{11} \sum_p S_p(\alpha_0 - \alpha_n) \tag{5}$$

where the sum runs over all dissociation products. For a given fluence we fitted the experimental data (N_n versus n) to Eq. (1), by using a computer program written by us and standard minimization subroutines [7]. We started from the
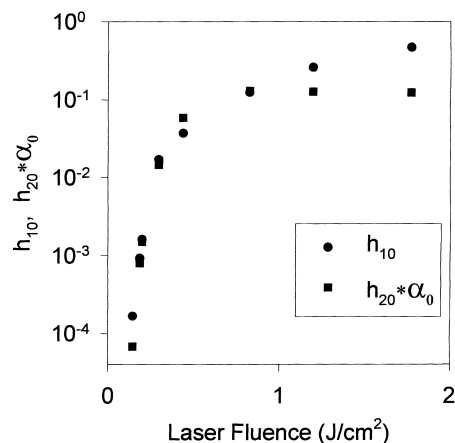

Fig. 1. The dependence of h_{10} and $h_{20}\alpha_0$ coefficients on laser fluence.

data corresponding to the lowest laser fluence with an initial guess of all $h_{ij}=0$ and use the obtained h_{ij} parameters for one fluence as initial guess for the next higher fluence.

3. Results and discussions

The h_{10} coefficient and the $h_{20}\alpha_0$ quantity are plotted in Fig. 1 as a function of laser fluence. Both quantities increase steadily with fluence. In particular, h_{10} follows closely the dependence of the dissociation probability on fluence (Fig. 4 of [1]). It sharply increases for low values of fluence then asymptotically approaches unity for fluence values greater than $1.5 \, \text{J/cm}^2$.
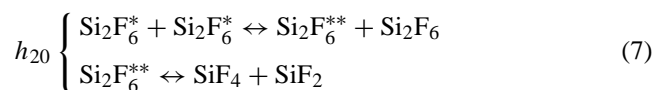
The h_{10} coefficient is responsible for that part of the dissociation which is only induced by the infrared radiation

$$h_{10} \begin{cases} Si_2F_6 \overset{h\nu}{\rightarrow} Si_2F_6^* \\ Si_2F_6^* \overset{h\nu}{\rightarrow} SiF_4 + SiF_2 \end{cases}$$
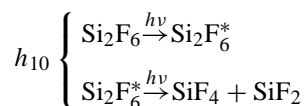
where the * superscripts indicate a generalized excitation energy distribution due to photon absorption or collision.

We represented in Fig. 1 the dimensionless quantity $h_{20}\alpha_0$ (see Eq. (5)) in order to compare it with h_{10} coefficient. As one can see from Fig. 1, the contribution of homogenous collisions to dissociation probability is comparable, for low fluences, to the contribution of the laser field itself. This is consistent with recent results on CF_2HCl [8] IRMPD. By monitoring the CF_2 radical density in the interaction zone, it was found that large quantities of CF_2 are formed after the laser pulse, by collisions [8]. As fluence increases the contribution of homogenous collisions to the dissociation saturates (even slowly decreases) for values of laser fluence greater than $1 \, \text{J/cm}^2$, while the collisionless dissociation probability continues to grow. This means that, as fluence increases, more and more molecules will be dissociated by the laser field, while the fraction of molecules which are excited and then dissociated through homogenous collisions will saturate.

There are at least three processes which can potentially contribute to the h_{20} coefficient [9]: (a) weakening of the anharmonic barrier effect (through rotational hole filling and overcoming of the vibrational bottleneck via rotational–translational and vibrational–vibrational, V–V′, intermolecular energy transfer, respectively), (b) quenching of the vibrational excitation via vibrational–translational energy transfer, and, (c) vibrational energy pooling which is a V–V′ transfer between molecules excited to quasicontinuum

$$h_{20} \begin{cases} \mathrm{Si_2F_6^*} + \mathrm{Si_2F_6^*} \leftrightarrow \mathrm{Si_2F_6^{**}} + \mathrm{Si_2F_6} \\ \mathrm{Si_2F_6^{**}} \leftrightarrow \mathrm{SiF_4} + \mathrm{SiF_2} \end{cases} \tag{7}$$

Here the $\mathrm{Si_2F_6^{**}}$ is excited to where it can absorb further nonresonantly or can decompose with a unimolecular rate that is fast when compared with deactivation. For our case, i.e. when there are no collisions during the laser pulse, the process (a) does not contribute to the value of h_{20}. The positive sign of this coefficient indicates that mechanism (c) is dominant over (b), which means that the energy transfer described by Eq. (7) is very efficient.

The h_{11} parameters are associated with collisional-energy transfer between excited target molecules ($\mathrm{Si_2F_6^*}$) and buffer gases. In our case, the dissociation products are $\mathrm{SiF_4}$ and the radical $\mathrm{SiF_2}$. This latter one easily combines to form $(\mathrm{SiF_2})_n$ polymer which usually adheres to the cell walls and windows, forming a whitish film [4,6], so that $\mathrm{SiF_4}$ remains the only collision partner to be considered for $\mathrm{Si_2F_6}$.

The negative h_{11} values for low fluences indicate that $\mathrm{SiF_4}$ collisions with $\mathrm{Si_2F_6^*}$ will diminish the dissociation probability through a process like

$$h_{11} < 0, \quad \mathrm{Si_2F_6^{**}} + \mathrm{SiF_4} \rightarrow \mathrm{Si_2F_6^*} + \mathrm{SiF_4^*} \tag{8}$$
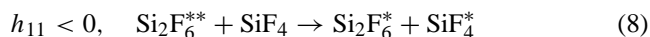
For this low laser fluences $\mathrm{SiF_4}$ does not absorb energy from laser field (see below), thus, heterogenous collisions could only produce $\mathrm{Si_2F_6}$ vibrational deexcitation.

However, as fluence increases the h_{11} coefficient continuously increases and becomes positive. A positive h_{11} has been also observed in the $\mathrm{CH_2Br}$–$\mathrm{CH_2F}$ IRMPD experiments [10] and has been explained by the collisions of the excited parent molecules with $\mathrm{CH_2}{=}\mathrm{CHF}$ dissociation product which becomes vibrationally hot as a result of photons absorption. Previous investigations on the $\mathrm{SiF_4}$ molecule shows that it absorbs both cw [11] and pulsed [12,13] laser photons at $979.7\,\mathrm{cm}^{-1}$. A decomposition reaction was observed to occur when irradiating $\mathrm{SiF_4}$ with $\mathrm{CO_2}$ cw laser in the spectral region from 974.6 to $982.1\,\mathrm{cm}^{-1}$. The maximum of the multiphoton absorption in supersonic molecular beam [12] is reported to be around $1020\,\mathrm{cm}^{-1}$, and to occur at $979.7\,\mathrm{cm}^{-1}$ only under two frequency irradiation. This suggests that multiphoton absorption and dissociation could be induced at this wavelength through combination bands of $\mathrm{SiF_4}$. Indeed, room temperature $\mathrm{SiF_4}$ irradiation [13] with pulses of $100\,\mathrm{ns}$ and $979.7\,\mathrm{cm}^{-1}$ produces visible luminescence, and the authors conclude that this is a direct proof of the multiphoton absorption and dissociation
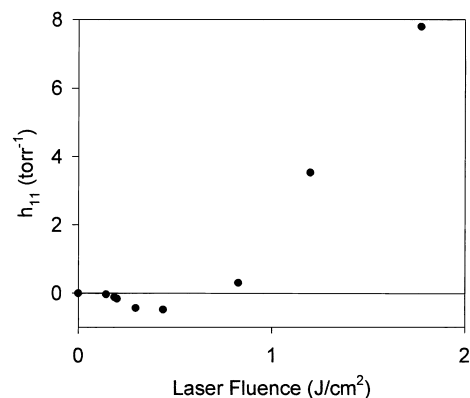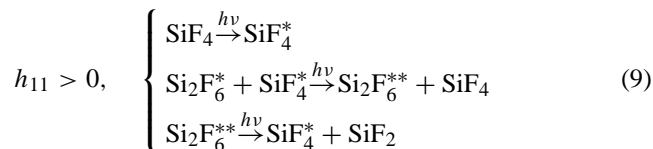
Fig. 2. The dependence of h_{11} coefficient on laser fluence. The zero line is for reference only.

as a unimolecular process. Emission was observed within the duration of the laser pulse, even at pressure as low as $10\,\mathrm{mTorr}$, but only starting from laser pulses higher than $60\,\mathrm{mJ}$. The irradiation geometry was not fully specified to estimate the fluence but the threshold in energy to observe the luminescence suggests that sizeable absorption will be produced at higher fluence values. We can therefore assume that, for higher laser fluences, $\mathrm{SiF_4}$ will enhance the $\mathrm{Si_2F_6}$ dissociation in a collisional process

$$h_{11} > 0, \quad \begin{cases} \mathrm{SiF_4} \xrightarrow{h\nu} \mathrm{SiF_4^*} \\ \mathrm{Si_2F_6^*} + \mathrm{SiF_4^*} \xrightarrow{h\nu} \mathrm{Si_2F_6^{**}} + \mathrm{SiF_4} \\ \mathrm{Si_2F_6^{**}} \xrightarrow{h\nu} \mathrm{SiF_4^*} + \mathrm{SiF_2} \end{cases} \tag{9}$$

We conclude that this is the main process responsible for the increase of h_{11} with laser fluence (Fig. 2). It shoud be stressed, however, that there is another process which could not be taken into account by the McRae model. The laser diode spectroscopic studies [6] reported that in IIRMPD of the $\mathrm{Si_2F_6}$, the $\mathrm{SiF_2}$ radical is produced in the ground vibrational state while $\mathrm{SiF_4}$ results vibrationally hot. Postpulse collisions between hot $\mathrm{SiF_4}$ and $\mathrm{Si_2F_6}$ excited by the laser field close to dissociation, could give a contribution to the dissociation. As this is a unipulse contribution, it is proportional to the quantity of $\mathrm{SiF_4}$ produced per pulse, thus, it will be much smaller than the contribution given by Eq. (9), which is proportional to the accumulated $\mathrm{SiF_4}$ from pulse to pulse.

In conclusion, by using the model of McRae et al. [3], we studied the importance of various dissociation processes of $\mathrm{Si_2F_6}$ on the laser fluence. The emerging picture is that even when apparent dissociation takes place in collisionless conditions, the collisions play a significant role in enhancing or inhibiting dissociation. At low fluences homogenous collisions play a positive role and enhance dissociation through vibrational energy pooling while heterogenous collisions contribute to vibrational deactivation of the $\mathrm{Si_2F_6}$ molecules. As fluence increases the contribution of laser field to dissociation becomes dominant, while homogenous collisions'

contribution slowly decreases. An interesting feature is that at higher fluence values the dissociation product, SiF_4 also absorbs IR photons, and, by collisions with Si_2F_6, contribute to the enhancement of the overall dissociation field.

Acknowledgements

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