plot of  $\ln \sigma_{\rm OM}$  vs.  $(\epsilon_{\rm MM}/k)^{1/2}$ .  $\sigma_{\rm QM}$  is the quenching cross section for the D<sub>2</sub>CC (<sup>3</sup>B<sub>2</sub>) with collision partner M, and  $\epsilon_{MM}$  is the well depth in the attractive potential between the pairs of M species. The values of  $(\epsilon_{MM}/k)^{1/2}$  are taken from ref 20. A linear relationship between these parameters is shown in Figure 3. Notably, in this case, the best fit to the data results in a line through the points for species in which no chemical reaction can occur, e.g., the inert gases, and a correlation coefficient of close to 1.0 is obtained. However, as noted previously, we were unable to discern any chemical reaction between triplet vinylidene and either H<sub>2</sub> or CH<sub>4</sub>. In the absence of evidence of direct chemical reaction, we attribute the observed removal of triplet vinylidene to physical quenching. The least-squares fit, shown in Figure 3, through all the data points has a correlation coefficient of 0.78. Several molecules for which a reactive channel may exist have data points that fall above the line. We have noted previously that a maximum of 10% of the vinylidene may react chemically with  $H_2$ . Even if we correct the rate constant for quenching of the  $D_2CC$  (<sup>3</sup>B<sub>2</sub>) by  $H_2$ , the maximum contribution due to chemical reaction, the single point for H<sub>2</sub> remains slightly above the least-squares line in Figure 3. Further, the predicted rate constants for abstraction from  $CH_4$ are quite comparable to that from  $H_2$ .<sup>8</sup> Yet, the cross section for quenching by CH<sub>4</sub> does correlate well with the well depth model. The correlation may indicate that interactions involving attractive forces are significant for quenching processes in vinylidene. It appears that this correlation method can be successful in describing quenching processes with rate constants slower than gas kinetic collision rates.

The model suggests that we sample the long-range attractive forces as the two species approach each other. Both the  ${}^{3}B_{2}$  and  ${}^{1}A_{1}$  states of D<sub>2</sub>CC have similar equilibrium geometries, and hence the respective potential energy minima would lie essentially directly above one another, separated by the energy gap. However, the singlet has only a 2 kcal/mol barrier to isomerization to acetylene. In these circumstances, the vinylidene potential surface will be bounded by the acetylene surface, permitting large excursions from the equilibrium geometry. The picture suggests the triplet levels may be perturbed by the large variations in the singlet structure and allow the occurrence of collision-induced quenching.

Lee and co-workers<sup>22</sup> have extended theoretical models to include electronic quenching of small molecules. The model has been applied successfully to  ${}^{1}SO_{2}$  fluorescence quenching. The model requires evaluation of several parameters which, in the case of triplet vinylidene, are not known. If a correlation was found, using estimates for the several parameters, it would be fortuitous and not likely to lead to greater insights into the quenching of triplet vinylidene in the absence of further experimental evidence.

## Summary

Rate constants for collisional quenching of  $D_2CC$  (<sup>3</sup>B<sub>2</sub>) by Ar, N<sub>2</sub>, H<sub>2</sub>, CO, and CH<sub>4</sub> have been measured for the first time, using vacuum-ultraviolet photolysis in conjunction with absorption spectroscopy techniques. Under our experimental conditions, no evidence of chemical quenching of vinylidene with these collision partners are observed.

A relatively good correlation between experimentally observed cross sections and the potential well depth model indicates that attractive forces may be significant in the quenching of excited vinylidene. These correlations are valuable in observing unusual behavior or in predicting nonreactive cross sections for additional gases.

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# Pulse-Duration Effects on Competitive Reactions in Infrared Multiple-Photon Decomposition of CH<sub>2</sub>CICHCIF and CHCIFCHCIF

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Vibrationally excited 1,2-dichlorofluoroethane and 1,2-dichloro-1,2-difluoroethane have been observed to dissociate competitively via two channels to form vibrationally excited HCl and HF. The fluence dependences of the branching ratio have been measured for both "short"-pulse (80-ns fwhm) and "long"-pulse (80-ns fwhm with  $1-\mu$ s-fwhm tail) irradiations. The branching ratio shows not only fluence dependence but also pulse-duration dependence, that is, intensity dependence. When the reactant pressure is 1.0 Torr, collisional deactivation is expected to occur to a considerable extent under long-pulse irradiation while it can be ignored under short-pulse irradiation. The experimental results are interpreted by using the exact stochastic method based on the energy-grained master equations, which take into account collisional deactivation.

## Introduction

The effects of laser intensity  $(I, W \text{ cm}^{-2})$  and laser fluence  $(\Phi, J \text{ cm}^{-2})$  on the dynamics of infrared multiple-photon excitation (IRMPE) and dissociation (IRMPD) have been extensively studied.<sup>1</sup> For many polyatomic molecules, the dissociation probability depends slightly on intensity but markedly on fluence

when collisions within the irradiation pulse duration can be ignored. For example, an increase of intensity by a factor of 200 has been observed to result in the increase of dissociation yield by only 30% in IRMPD of  $SF_{6}$ .<sup>2</sup> In such cases where the dissociation yield shows a fluence dependence, energy-grained master equations (EGME) have been shown to be valid to explain phenomenologically the mechanism of IRMPE and IRMPD<sup>3</sup>

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$$dN_n/dt = C_{n-1}{}^aN_{n-1} + C_n{}^eN_{n+1} - (C_{n-1}{}^e + C_n{}^a)N_n - k_nN_n \quad (I)$$

where  $C_n^{a}$  is the effective first-order rate constant for absorption from level n to n + 1 and  $C_n^{e}$  is the effective first-order rate constant for stimulated emission from level n + 1 to n. Thus

$$C_n^{\ a} = \sigma_n \frac{I}{\hbar\omega} \tag{II}$$

$$\frac{C_n^{e}}{C_n^{a}} = \frac{g_n}{g_{n+1}} \approx \frac{\rho(E_n)}{\rho(E_{n+1})}$$
(III)

where  $\sigma_n$  is the absorption cross section for the *n* to n + 1 transition, I is the laser intensity,  $\hbar\omega$  is the photon energy,  $g_n$  is the number of states with energies within the laser line width  $\delta E$  centered at energy  $n\hbar\omega$ , and  $\rho(E_n)$  is the density of states of level n.

On the other hand, there have been some reports that an increase of laser intensity results in the increase of decomposition yield. The interpretation of these phenomena is that the power broadening compensates the bottleneck effect in the discrete region so that the fraction of molecules with the ability to directly absorb laser photons increases. The intensity effect seems to be more important for the true continuum region above decomposition thresholds, where the excitation and microscopic unimolecular reaction channels compete dynamically with each other. The excitation rate constant  $C_n^a$  is proportional to the laser intensity as shown in eq II. Even when the bottleneck effect can be completely ignored in the discrete region, the laser intensity effects should be observed in the IRMPD, for example, in the energy population of fragments or in the product distribution. Some experimental results about the intensity effect have been reported. Brenner has reported that, in IRMPD of ethyl vinyl ether (EVE), the branching ratio between two channels, differing by about 25 kcal mol<sup>-1</sup> in activation energies, shows an intensity dependence:<sup>4</sup>

$$CH_2CHOCH_2CH_3 + mh\nu \rightarrow CH_3CHO + CH_2CH_2$$
 (1)

$$CH_2CHOCH_2CH_3 + nh\nu \rightarrow CH_2CHO + CH_2CH_3$$
 (2)

The fraction of reactions with higher activation energy increases with increasing laser intensity. Stephenson and King have reported that the ratio of  $CF_2(v = 5)/CF_2(v = 0)$  increases with laser intensity in IRMPD of  $CHClF_2$ .<sup>5</sup> Their results indicate that the energy levels, where the decomposition takes place, become higher with increasing laser intensity. These facts suggest that the competition between the excitation rate, the stimulated emission rate, and the microscopic unimolecular reaction rate in the continuum levels results in a product distribution.

Thus far, we have reported some results on the competition between two reaction channels in IRMPD of halogenated ethanes with an infrared emission spectroscopic technique.<sup>6,7</sup> In this paper, we investigated the fluence and intensity effects on the competitive reactions in IRMPD of CH<sub>2</sub>ClCHClF and CHClFCHClF. The experimental results obtained in "short"-pulse (80-ns fwhm) and in "long"-pulse (80-ns fwhm with  $1-\mu$ s-fwhm tail) irradiations have been interpreted on the basis of the EGME, taking into account the collisional deactivation because the collision cannot be ignored with the reactant pressure employed.

### **Experimental Section**

The experimental apparatus used in these studies has been previously described in the literature.<sup>8</sup> We restrict ourselves to a brief description, with particular emphasis toward the modification required for these studies. The apparatus consists of a

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CO<sub>2</sub> TEA laser (Lumonics 103-2), a flow reaction cell, a monochromator (Ritsu Oyo Kogaku, MC-20L), an infrared detector (InSb at 77K), and a signal-processing system.

When the laser is operated with He and  $CO_2$  as flowing gases, the laser pulse has about 80-ns-fwhm duration and consists of a train of mode-locked spikes of about a few nanoseconds. This pulse is referred to as a "short" pulse hereafter. The addition of  $N_2$  into the flowing gases resulted in a long tail, and the total width was increased to about 2  $\mu$ s. The profile showed an initial spike of 80-ns fwhm followed by a long tail containing about 75% of the total energy. The pulse is called a "long" pulse hereafter. The laser pulse energy was controlled by inserting appropriate BaF<sub>2</sub> windows or polyethylene films between the  $CO_2$  laser and the BaF<sub>2</sub> lens (focal length 20 cm). The laser energy was measured by the pyroelectric detector calibrated with a Scientech 364 disk calorimeter. Though the focused laser beam was used in this experiment, the maximum view field of the detection system is limited to a 2-cm range in the vicinity of the focus along the laser beam. Therefore, the fluence could be regarded as being nearly homogeneous. For the spectrum measurements, the signals were treated with a PAR Model 162 boxcar averager and a PAR Model 155 gated integrator. The aperture delay  $\tau_{\rm d}$  and the aperture duration  $\tau_g$  were 3 and 10  $\mu$ s, respectively.

The sample gases (1,2-dichlorofluoroethane and 1,2-dichloro-1,2-difluoroethane) were purchased from PCR Research Chemicals, Inc. The former was purified only by trap-to-trap distillation before use because its purity was found to be higher than 98% by gas chromatography (column, Porapak Q). The latter was purified up to 92% by column separation because it contains 1,2-dichlorofluoroethane as an impurity. The gas flow rate in the cell was about 30 Torr mL min<sup>-1</sup>

The products after CO<sub>2</sub> TEA laser irradiation were determined from infrared spectroscopic measurements (Japan Spectroscopic Co., Type A-102) and a GC-MS system (NEVA TE-150 mass spectrometer combined with a Shimadzu GC-7A gas chromatograph). A Porapak Q column (3 m) was employed at 70-180 °C (initial hold time, 16 min; raising rate, 8 °C min<sup>-1</sup>).

#### Results

Product Analysis. The final products in IRMPD of CH<sub>2</sub>Cl-CHClF and CHClFCHClF were examined on a gas chromatograph. The laser beam was focused by means of a 20 cm focal length BaF<sub>2</sub> lens. The fluence within the irradiation cell (cell length 36 cm) was considerably inhomogeneous owing to the use of focused geometry, about 0.2 J cm<sup>-2</sup> at the both ends of the cell and about 35 J  $cm^{-2}$  at the center, i.e., the focal point. The input pulse energy and the irradiation laser line were about 0.17 J and 9P(20) (1046.85 cm<sup>-1</sup>), respectively. For 2.0 Torr of CH<sub>2</sub>ClC-HClF, the following products were identified: CH=CF (5), CH $\equiv$ CH (4), CH $\equiv$ CCl (23), CH<sub>2</sub>=CClF (16), trans-CHCl=CHF (35), cis-CHCl=CHF (49), trans-CHCl=CHCl (3), and cis-CHCl=CHCl (4). These are written in the order of retention time. The values in parentheses represent the relative peak area when the total value of  $C_2H_2ClF$  is 100. For 2.0 Torr of CH-CIFCHCIF, the following products were obtained: CH==CF (9),  $CF_2 = CF_2$  (4), trans-CHF=CHF (8), cis-CHF=CHF (19), CClF=CF<sub>2</sub> (7), CHF=CClF (100), C<sub>2</sub>Cl<sub>2</sub>F<sub>2</sub> (7), trans-CHCl=CClF (4), and cis-CHCl=CClF (4). The products population supports the following molecular elimination mechanism for those primary processes

$$CH_2CICHCIF + mh\nu \rightarrow CHCI=CHF + HCI$$
 (3)

$$\rightarrow$$
 CH<sub>2</sub>=CClF + HCl (3')

$$CH_2CICHCIF + nh\nu \rightarrow CHCI = CHCI + HF$$
 (4)

and

$$CHClFCHClF + m'h\nu \rightarrow CHF = CClF + HCl \qquad (5)$$

$$CHClFCHClF + n'h\nu \rightarrow CHCl = CClF + HF \qquad (6)$$

The production of halogenated acetylene may suggest a secondary decomposition of the primary products, though it is not clear

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Figure 1. Infrared emission spectra for 1.0 Torr of CH<sub>2</sub>ClCHClF irradiated with a short pulse (irradiation laser wavenumber 1046.85 cm<sup>-1</sup> (9P20)).



Figure 2. Same as Figure 1, except that a long pulse was used for the irradiation.

whether the decomposition takes place within the same pulse or within the other sequential pulses. The focused geometry irradiation, where the volume under a mild fluence is fairly large compared to that under an intense fluence, seems to result in the dominant production of C<sub>2</sub>H<sub>2</sub>ClF for CH<sub>2</sub>ClCHClF and C<sub>2</sub>HClF<sub>2</sub> for CHClFCHClF which are formed via HCl elimination with the lowest decomposition threshold. For a vacuum-UV photolysis of halogenated ethanes, chlorine atom elimination has been reported.<sup>9</sup> For the IRMPD of these halogenated ethanes, however, such a chlorine atom elimination process can be considered to be minor because any C<sub>4</sub> compound was not detected as a final product. Moreover, no infrared emission due to DCl\* was observed upon the irradiation of a mixture of 0.85 Torr of CHClFCHClF and 1.74 Torr of  $D_2$ . This fact does not support the existence of a Cl atom. A molecular beam experiment also suggests that the four-center molecular elimination is a primary process in infrared multiple-photon decomposition of halogenated ethanes.<sup>10</sup>



Figure 3. Emission intensities of HCl<sup>\*</sup> (triangles) and HF<sup>\*</sup> (circles) vs. laser fluence observed for IRMPD of 1.0 Torr of CH<sub>2</sub>ClCHClF irradiated with a short pulse (a) and a long pulse (b) (irradiation laser wavenumber 1046.85 cm<sup>-1</sup> (9P20)).



Figure 4. Same as Figure 3, except that 1.0 Torr of CHClFCHClF was irradiated.

Infrared Emission. When 1,2-dichlorofluoroethane was irradiated with a 9P(20) line of a CO<sub>2</sub> TEA laser, the infrared emissions due to highly vibrationally excited HCl\* and HF\* were observed in the wavelength region of 3.2-4.2 and  $2.2-3.2 \mu m$ , respectively. Figures 1 and 2 present the fluence effects on the infrared emission spectra for 1.0 Torr of CH<sub>2</sub>ClCHClF irradiated with short and long pulses, respectively. The wavelength resolution was 0.068- $\mu m$  fwhm. For 1,2-dichloro-1,2-difluoroethane, the both emissions were also seen in the infrared emission spectra.<sup>6</sup>

Since all the spectra were observed under the same experimental conditions except for the fluence or the laser pulse width, the intensities of the HCl\* and HF\* emissions can be considered to be proportional to the yields of HCl\* and HF\*, respectively, among these spectra. It is easily found that the intensity of HF\* emission  $(I_{\rm HF})$  increases more promptly than that of HCl\* emission  $(I_{\rm HCl})$ . For a short-pulse irradiation (Figure 1),  $I_{\rm HF}$  is about the same as  $I_{\rm HCl}$  at 22 J cm<sup>-2</sup>, while for a long-pulse irradiation (Figure 2), this is the case at a higher fluence of 55 J cm<sup>-2</sup>.

The emission intensities of HCl<sup>\*</sup> and HF<sup>\*</sup> are plotted against laser fluence in Figure 3 for 1.0 Torr of CH<sub>2</sub>ClCHClF and in Figure 4 for 1.0 Torr of CHClFCHClF, where the wavelengths monitored are 3.7  $\mu$ m for HCl<sup>\*</sup> and 2.7  $\mu$ m for HF<sup>\*</sup>. The intensities obtained by a short-pulse irradiation can be compared to those by a long-pulse irradiation on the same scale. A similar fluence dependence is seen for both molecules. The intensities of HF<sup>\*</sup> emission continue to increase while those of HCl<sup>\*</sup> emission increase slowly and then reach a plateau. At higher fluence,  $I_{\rm HCl}$ seems to decrease slightly with increasing fluence.

#### Discussion

The experimental results suggest the following considerations: (1) HCl elimination reaction competes with HF elimination re-

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action in the unimolecular decomposition induced with infrared multiple-photon excitation. (2) The activation energy for HCl elimination is lower than that for HF elimination, and the preexponential factor for the lower energy channel is smaller than that for the higher energy channel. These tendencies in Arrhenius factors have been easily observed in the reported thermodynamic data for a number of halogenated hydrocarbons:  $\log A = 13-14$ and  $E_a = 55-70$  kcal mol<sup>-1</sup> for HF elimination; log A = 11-14and  $E_a = 50-60$  kcal mol<sup>-1</sup> for HCl elimination.<sup>11</sup>

The experimental results, showing both the strong laser power and fluence dependences for the products yields and ratios, seem to be interpreted by an energy-grained master equation, which takes into consideration collisional deactivation. The power dependence of the product ratio may be explained even if the collisional deactivation is not considered in the mechanism. However, the competition processes between excitation, stimulated emission, and unimolecular decomposition with two channels in the real continuum region cannot sufficiently explain the lower product yield at the lower power. Since the pressure of 1.0 Torr used in our experiment is fairly high, a collisional deactivation is expected to play a role in the energy acquisition mechanism. The simulation of fluence dependence of product yields, based on an the exact stochastic method proposed by Baker,<sup>12</sup> has been carried out by considering collisional deactivation. Since a detailed description has been reported elsewhere,<sup>12,13</sup> several of the modified points and parameters will be shown here. (1) Small absorption cross sections were  $1.58 \times 10^{-19}$  cm<sup>2</sup> for CH<sub>2</sub>ClCHClF and  $2.52 \times 10^{-19}$ cm<sup>2</sup> for CHClFCHClF at the irradiation wavenumber 1046.85 cm<sup>-1</sup>. (2) The absorption cross section  $\sigma_n$  was assumed to have the following form with respect to a vibrational level *n*:  $\sigma_n = \sigma_0/(n$ + 1)<sup> $\alpha$ </sup>, where  $\alpha$  was used as a fitting parameter to optimize the simulation. (3) A CO<sub>2</sub> laser pulse was assumed to have an 80-ns duration with a constant intensity for a short pulse and an initial spike of 80-ns duration followed by a 920-ns tail containing 75% of the total energy, both components having a constant intensity, for a long pulse. (4) At the end of the laser pulse, parent molecules pumped to energy levels higher than the reaction thresholds were assumed to competitively undergo three processes: HCl elimination, HF elimination, and collisional deactivation. The following collisional deactivation rate was assumed to be  $1.0 \times 10^7$  Torr<sup>-1</sup> s<sup>-1</sup>:

$$\mathbf{A}^*(v=n) + \mathbf{M} \to \mathbf{A}^*(v=n-1) + \mathbf{M}$$
(7)

(5) Arrhenius parameters (A and  $E_a$ ) for HCl and HF eliminations were used as fitting parameters to get the visual best-fit simulation for the simulation for the dependences of the HCl and HF product yields upon laser fluence for each pulse duration. (6) The fundamental frequencies (in cm<sup>-1</sup>) used for the calculation of specific unimolecular decomposition rates by QRRK theory<sup>11</sup> were 3000 (2) (CH str), 1355 and 1305 (CH out-of-plane bend), 1215 and 1138 (CH in-plane bend), 1105 and 1095 (CF str), 1060 (CC str), 830 and 785 (CCl str), 695 and 630 (CFCl def), 430 (2) (CCF def), 336 (d, CCl def), and 160 (torsion) for CHClFCHClF; 2980 (2) (CH<sub>2</sub> str), 2850 (CH str), 1112 (CF str), 1033 (CC str), 750 and 700 (CCl str), 1440 (CH<sub>2</sub> scis), 1364 and 1300 (CH bend), 1240 (CH<sub>2</sub> wag), 1185 (CH<sub>2</sub> twist), 800 (CH<sub>2</sub> rock), 867 (CFCl def), 463 (CCF def), 300 (2) (CCCl def), and 250 (torsion).

The simulation of the fluence dependence for each pulse was performed for various values in  $\alpha$  and Arrhenius parameters. The visual best-fit simulations for both pulse profiles were obtained when the following parameter sets were used: for CH2ClCHClF,  $\alpha = 0.5$ , log A = 12, and  $E_a = 47$  kcal mol<sup>-1</sup> for HCl elimination, log A = 14 and  $E_a = 68$  kcal mol<sup>-1</sup> for HF elimination; for CHClFCHClF,  $\alpha = 0.4$ , log A = 12, and  $E_a = 50$  kcal mol<sup>-1</sup> for HCl elimination, log A = 14 and  $E_a = 68$  kcal mol<sup>-1</sup> for HF elimination. The 2 orders of magnitude difference in HCl vs. HF



Figure 5. Comparison of calculated yields of HCl and HF to observed ones in IRMPD to 1.0 Torr of CH<sub>2</sub>ClCHClF as a function of laser fluence for a short pulse (a) and for a long pulse (b). Solid curves show the calculated fractions of HCl and HF by considering the collisional deactivation. Triangles and circles show the observed fractions of HCl\* and HF\*, respectively.



Figure 6. Same as Figure 5, except that 1.0 of Torr CHClFCHClF was irradiated

elimination seems to be fairly large, considering the reported A factors for four-center decomposition of halogenated compounds (typically log  $A = 13.5 \pm 1.0$ ).<sup>11,14</sup> The difference in activation energies between both elimination processes might be too large as compared to experimental ones for haloethanes. One possible explanation is that a small total entropy of activation  $\Delta S^*$  for HF elimination results in a large A factor for a cyclic activated complex with a higher thermal energy, because such a complex is expected to be "looser" than that with a threshold energy. However, the present determination of Arrhenius parameters has several assumptions and fitting parameters in the derivation. For example, the absorption coefficient probably decreases with increasing energy level in multiple-photon absorption. So far, there has been no direct measurement or reasonable theoretical estimate of the coefficient of a molecule at a higher level. Moreover, a collisional deactivation rate has not been measured for a highly vibrationally excited molecule. Thus, it is difficult to determine Arrhenius parameters without the uncertainty of 1 order of magnitude in the A factor or several kcal  $mol^{-1}$  in the activation energy by using the present model. Figures 5 and 6 show the comparison between the calculated fractions of HCl ( $F_{\rm HCl}$ ) and  $HF(F_{HF})$  elimination channels and the observed  $I_{HCI}$  and  $I_{HF}$  for IRMPD of CH<sub>2</sub>ClCHClF and CHClFCHClF, respectively. The ordinate scales for  $I_{\rm HCl}$  and  $I_{\rm HF}$  were chosen arbitrarily so that these data fitted the calculated fractions, while the ratio of  $I_{\rm HCI}/I_{\rm HF}$ was kept constant for both pulse profiles. It was assumed that  $I_{\rm HF}$  and  $I_{\rm HCl}$  are proportional to the total yields of HF and HCl,

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Figure 7. Typical vibrational energy distributions of CHCIFCHCIF irradiated with a short pulse at various fluences. Laser fluences are 4 (a), 8 (b), 14 (c), 20 (d), and 40 J cm<sup>-2</sup> (e). Cross-hatched and filled areas indicate the extents of HCl and HF elimination reactions, respectively.



Figure 8. Same as Figure 7, except that a long pulse was assumed for the calculations.

respectively, though the fluorescence experiment cannot provide any information concerning the production of HF and HCl in a ground vibrational state.

Figures 7 and 8 show the fluence dependences of the vibrational population distribution for CHClFCHClF irradiated with short and long pulses, respectively, which are calculated by using the above-mentioned method and parameters. For both cases, the mean value of vibrational level n increases with increasing laser fluence. The mean values for the long pulse, however, are smaller than those for the short pulse when the laser fluences are the same. For long-pulse irradiation, even at a higher fluence the reactants are restricted to lower vibrational levels, at which the unimolecular decomposition takes place. Therefore, the extent of the reaction channel with higher activation energy does not become so large compared to the case of short-pulse irradiation. It is thought that this phenomenon results from the fact that the excitation rate is

of the same order of magnitude as the unimolecular reaction rate within this continuum region. For CHClFCHClF, the HF elimination rate comes to the same value of about  $4 \times 10^8$  s<sup>-1</sup> as the HCl elimination rate when the vibrational level n is about 36. At this vibrational level, the absorption rates are  $1.4 \times 10^9$  s<sup>-1</sup> for a short pulse and  $3.5 \times 10^8$  s<sup>-1</sup> for the initial spike and  $9.1 \times 10^7$  $s^{-1}$  for the tail of a long pulse, where the laser fluence is assumed to be 40 J cm<sup>-2</sup>. These calculated values for long-pulse irradiation show that the decomposition takes place prior to the excitation at vibrational levels lower than 36 even at a fluence as high as 40 J cm<sup>-2</sup>. Consequently, it seems difficult for HF elimination to occur. Moreover, the reactants collide with each other about 10 times within the long-pulse duration so that the reactant is suppressed at lower vibrational levels. These effects result in the low decomposition yields compared with those of short-pulse irradiation. The simulation data show that the dissociation yields are influenced mainly by the collisional deactivation and that the product distributions are influenced mainly by the laser intensity, i.e., the excitation rate in the true continuum region.

Some quantities of chloroacetylene were found in the product analysis of irradiated CH<sub>2</sub>ClCHClF. This fact may suggest that the energy-rich chlorofluoroethylene, which probably is produced through HCl  $\alpha, \alpha$ -elimination,<sup>15,16</sup> emits an HF molecule. Infrared emission measurements cannot distinguish between the primary and the secondary channels for this molecule. However, the fluence dependences observed in this molecule do not seem to be interpreted only by the secondary decomposition effects. Jalenak and Nogar have reported that there are two channels, i.e., HCl and HF molecular elimination, in IRMPD of CH<sub>2</sub>CClF.<sup>17</sup> The following Arrhenius parameters were used for the interpretation of the observed fluence dependence: for HF elimination,  $E_a =$ 54.7 kcal mol<sup>-1</sup> and  $A = 2.15 \times 10^{14} \text{ s}^{-1}$ ; for HCl elimination,  $E_a = 56.5 \text{ kcal mol}^{-1}$  and  $A = 2.85 \times 10^{14} \text{ s}^{-1}$ . These parameter values suggest that the HCl production occurs in preference to the HF one at higher fluence. Such secondary decomposition does not seem to be consistent with our results which show the prior production of HF at higher fluence. An  $\alpha$ , $\alpha$ -elimination may be expected to occur to some extent, and hydrogen halides produced via such channels may be thought to be produced in a vibrational ground state.<sup>16,18</sup> Our calculation did not take into consideration such  $\alpha, \alpha$ -elimination channels, because the extents of  $\alpha, \alpha$ -elimination channels would not be estimated in the emission measurement. However,  $\alpha, \alpha$ -elimination has been reported to be a minor process in some halogenated ethanes and ethylenes.<sup>6,18-20</sup>

The increase of fluence raises the vibrational levels of the parent molecule, which results in the increase of the reaction with higher activation energy, i.e., HF elimination. The observed saturation of HCl yield shows that the higher fluence depresses the lowest reaction channel and promotes the higher one. The low production yield in a long-pulse irradiation has been interpreted by EGME introducing the collisional quenching terms, where one photon energy (about 3 kcal mol<sup>-1</sup>) was assumed to be lost per collision.

Registry No. CH<sub>2</sub>ClCHClF, 430-57-9; CHClFCHClF, 431-06-1; CH=CF, 2713-09-9; CH=CH, 74-86-2; CH=CCl, 593-63-5; CH<sub>2</sub>= CClF, 2317-91-1; trans-CHCl=CHF, 2268-32-8; cis-CHCl=CHF, 2268-31-7; trans-CHCl=CHCl, 156-60-5; cis-CHCl=CHCl, 156-59-2; CF2=CF2, 431-06-1; trans-CHF=CHF, 1630-78-0; cis-CHF=CHF, 1630-77-9; CClF=CF<sub>2</sub>, 79-38-9; CHF=CClF, 359-04-6; C<sub>2</sub>Cl<sub>2</sub>F<sub>2</sub>, 27156-03-2; trans-CHCl=CClF, 13245-54-0; cis-CHCl=CClF, 13245-53-9; HCl, 7647-01-0; HF, 7664-39-3.

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