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J. Phys. Chem. A, Just Accepted Manuscript • DOI: 10.1021/acs.jpca.9b10393 • Publication Date (Web): 24 Jan 2020

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Falloff Curves of the Reaction

\[ \text{CF}_3 (+\text{M}) \rightarrow \text{CF}_2 + \text{F} (+\text{M}) \]

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November 2019
revised January 2020
to be published in J. Phys. Chem. A

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Abstract

The thermal dissociation reaction \( \text{CF}_3 (+\text{Ar}) \rightarrow \text{CF}_2 + \text{F} (+\text{Ar}) \) was studied in incident and reflected shock waves by monitoring UV absorption signals of the primary dissociation product \( \text{CF}_2 \). \( \text{CF}_3 \) radicals were produced by thermal decomposition of \( \text{CF}_3\text{I} \). Accounting for secondary reactions of \( \text{F} \) atoms, rate constants for the unimolecular dissociation were derived. Experimental parts of the falloff curves were obtained over the ranges \( 1544 \) – \( 2106 \) K and \( 1.0 \times 10^{-5} \leq [\text{Ar}] \leq 9.3 \times 10^{-5} \text{ mol cm}^{-3} \). Theoretical modelling allowed for a construction of the full falloff curves connecting the limiting low pressure rate constants \( k_0 = [\text{Ar}] \times 2.5 \times 10^{18} \left( \frac{T}{2000} \text{ K} \right)^{-5.1} \exp \left( -42450 \frac{\text{K}}{T} \right) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \) with the limiting high pressure rate constants \( k_\infty = 1.6 \times 10^{16} \left( \frac{T}{2000 \text{ K}} \right)^{-1.3} \exp \left( -43250 \frac{\text{K}}{T} \right) \text{ s}^{-1} \) (center broadening factors of \( F_{\text{cent}} = 0.25, 0.22, \) and 0.20 at 1500, 2000, and 2500 K, respectively, were used). The influence of simplifications of falloff expressions and of limiting rate constants on the representation of experimental data is discussed.
I. Introduction

The thermal dissociation reaction

\[ \text{CF}_3 (+ \text{Ar}) \rightarrow \text{CF}_2 + \text{F} (+ \text{Ar}) \quad (1) \]

under typical shock wave conditions offers the opportunity to investigate unimolecular reaction behaviour close to the low pressure limit. The reaction has found some interest\(^1-3\) because it plays a role in flame retardation by halons as well as in the high-temperature oxidation of fluorinated materials. In a first investigation\(^1\) it was assumed to be in the low pressure limit. However, deviations from this behaviour have been taken into consideration in later studies.\(^2,3\) These were based on theoretical modelling of the limiting high pressure rate constants \(k_\infty\) and estimates of the limiting low pressure rate constants \(k_0\), the latter employing adjusted average energies transferred per collision \(\langle \Delta E \rangle\). This practice is quite common, when direct measurements of \(\langle \Delta E \rangle\) are not available. One of the rare exceptions to this practice is the precursor of reaction (1), i.e. the dissociation of \(\text{CF}_3\),\(^4\)

\[ \text{CF}_3 (+ \text{Ar}) \rightarrow \text{CF}_3 + \text{I} (+ \text{Ar}) \quad (2) \]

for which \(\langle \Delta E \rangle\) has been determined in separate IR multiphoton excitation experiments (see work cited in \(^4\)). This reaction is also used in the present work. As measurements of \(k_0\) continue to provide an important method to access \(\langle \Delta E \rangle\), it appears of interest to inspect the accuracy of the approach. This not only concerns the analysis of \(k_0\), but also the difference between modelled and measured rate constants \(k\) in the falloff range of the reaction. This is the focus of the present article.

A systematic modelling of falloff curves of unimolecular bond breaking and the reverse radical recombination reactions showed\(^5,6\) that limiting low and high pressure rate constants are approached in different ways. Expressed in terms of broadening factors \(F(x)\), defined by \(k/k_\infty = [x/(1 + x)]F(x)\) with \(x = k_0/k_\infty\), this means that \(F(x) \neq F(1/x)\). In a first systematic analysis of \(F(x)\),\(^3\) “symmetric broadening factors” (i.e. \(F(x) = F(1/x)\)) were assumed and approximated in the form

\[ F(x) \approx F_{\text{cent}}^{1/[1 + (\log N)^2]} \quad (3) \]

with "center broadening factors" \(F_{\text{cent}}\) and "widths" \(N\) given by \(N \approx 0.75 - 1.27 \log F_{\text{cent}}\). The more detailed, master-equation based, study of \(^5,6\) led to asymmetric broadening factors (i.e. \(F(x) \neq F(1/x)\)) of the form

\[ F(x) \approx \left(1 + x/x_0\right) \left[1 + \left(x/x_0\right)^n\right]^{1/h} \quad (4) \]
with

\[
    n = \left[ \ln^2 \left( \frac{2}{F_{\text{cent}}} \right) \right] \left[ 1 - b + b \left( \frac{x}{x_0} \right)^q \right]
\]  

(5)

where \( q = \frac{(F_{\text{cent}} - 1)}{\ln(F_{\text{cent}}/10)} \), \( x_0 \) in the range of 0.9 – 1.1 (mostly \( x_0 \approx 1 \)), and \( b \) in the range 0.1 – 0.25 (mostly \( b \approx 0.2 \)). Obviously, the \( F_{\text{cent}} \) in eqs. (3) – (5) dominate the broadening of the falloff curves in comparison to the Lindemann-Hinshelwood model (\( F_{\text{cent}} = 1 \)), but the detailed form of \( F(x) \) is of importance as well. The following study compares the approach of the falloff curves of reaction (1) to the low pressure limit, considering eqs. (3) – (5) as well as a master equation solution described in \(^2\). The present analysis is also accompanied by new experimental work.

In connection with the interest in extrapolations of falloff curves to limiting rate constants, the earlier decomposition studies of CF\(_3\) decomposition were extended. The use of the decomposition of C\(_2\)F\(_6\) or CF\(_3\)I as CF\(_3\) precursors under the applied conditions led to contributions from secondary reactions. Since the work of \(^2\) and \(^3\) more information on secondary reactions has been collected\(^4\) such that their influence can be established with more certainty. Furthermore, theoretical modelling of the limiting rate constants has been advanced and applied to reaction (1). The earlier modelling from \(^2\) and \(^3\) thus can be extended.
II. Experimental technique and results

The present measurements were carried out in a shock tube using both reflected and incident shock waves and the technique is described in detail in earlier work (see, e.g., 3, 4, 8, 9). Like the previous studies, 1-3 the precursor for CF$_3$ was CF$_3$I, dissociating by reaction (2). As the UV absorption of CF$_3$ near 200 nm is too weak to allow for sufficiently sensitive detection of CF$_3$, the broad UV continuum absorption of CF$_3$I was used to follow the dissociation. Absorption signals were recorded in the standard way, using a high-pressure Xe arc lamp (Osram XBO 150W/4) as the light source, a quartz prism monochromator (Zeiss MQ3), photomultiplier, and an electronic data acquisition system.

Compared to the earlier work of 8, more accurate absorption coefficients of CF$_2$ are now available which allows for a more quantitative analysis of CF$_2$ yields recorded in the reaction. Reaction mixtures between 100 and 1000 ppm of CF$_3$I in Ar were employed and used as described in 4. CF$_2$ absorption-time profiles were followed at wavelengths in the range 230 – 270 nm, mostly at 248 nm, i.e. at the maximum of the broad absorption continuum. Typical signals are shown in Figs. 1 and 2. The shown absorption signals OD$_5$ correspond to the product OD$_5$ = $\varepsilon$ x [CF$_2$] where $\varepsilon$ = 9.4 cm and $\varepsilon$ is the absorption coefficient of the Lambert-Beer law in the form $I = I_0 \exp(-\text{OD}_5)$. The absorption behind the incident wave in Fig. 1 is due to the precursor CF$_3$I. At the temperature of the incident wave (977 K), the decomposition of CF$_3$I just becomes noticeable. At the temperature of the reflected wave (1874 K), CF$_3$I almost instantaneously dissociates and only the formation of CF$_2$ is recorded. In Fig. 2, the formation of CF$_2$ behind the reflected wave at 2048 K is rapid and just becomes separable from the Schlieren peak of the shock front. After CF$_3$ dissociation, CF$_2$ is essentially stable for the observation time of about 1.3 ms in Fig. 1. In Fig. 2, CF$_2$ dissociation starts to become noticeable, like those investigated in more detail in 3.

The approach to the final level of CF$_2$ could always be represented in the form

$$[\text{CF}_2] = [\text{CF}_2]_{t=\infty}(1 - \exp(-kt)) \quad (6)$$

The final CF$_2$ concentration, $[\text{CF}_2]_{t=\infty}$, over the full range of precursor concentrations $[\text{CF}_3I]_{t=0}$ (100 – 1000 ppm of CF$_3$I in Ar) near 1900 K was found to be mostly of the order of $\frac{1}{2}$ $[\text{CF}_3I]_{t=0}$ but increased to values near $[\text{CF}_3I]_{t=0}$ when the temperature was increased to values above 2000 K. This observation indicates that not only the unimolecular dissociation (1) was taking place but that secondary reactions like

$$\text{F} + \text{CF}_3 (+\text{Ar}) \rightarrow \text{CF}_4 (+\text{Ar}) \quad (7)$$

partly removed CF$_3$, e.g. by conversion into the thermally more stable CF$_4$, which does not absorb noticeably over the employed wavelength range. In addition to reaction (7), speculation about other
secondary reactions were made in but a quantitative analysis was difficult in that work. The work of 2, employing the dissociation of CF$_3$I in the presence of H$_2$O, focussed on contributions of OH, O, and H to the CF$_3$/CF$_2$/F system but, for the higher temperatures applied, could neglect reaction (7) and other reactions of the pure CF$_3$ system. Besides reaction (7), the present analysis of the CF$_3$

\[
\text{F} + \text{CF}_2 (+ \text{Ar}) \rightarrow \text{CF}_3 (+ \text{Ar}) \tag{8}
\]

has to be taken into account. A possible influence of iodine atoms in the chain

\[
\text{I} + \text{CF}_3 \rightarrow \text{IF} + \text{CF}_2 \tag{9}
\]

\[
\text{IF} (+ \text{Ar}) \rightarrow \text{I} + \text{F} (+ \text{Ar}) \tag{10}
\]

considered in [4], is also inspected. Reaction (8) would reduce the final CF$_2$ yield, $Y(\text{CF}_2) = \frac{[\text{CF}_2]_t}{[\text{CF}_3]_0}$, to values below $\frac{1}{2}$ as long as steady-state of F atoms is established in the sequence of reactions (1) and (7). On the other hand, the CF$_2$ yield would increase when reactions (9) and (10) are important. Besides the effective rate constant $k_1$ in eq. (6), therefore, the CF$_2$ yield $Y(\text{CF}_2)$ were of interest. Rate constants $k_1$ were derived from $k$ and $Y(\text{CF}_2)$ by fitting modelled [CF2] - profiles to the experimental observations, see the following details.

While temperatures between 1803 and 2204 K were applied in 2, the present work extended the temperature range to 1544 – 2106 K. Furthermore, the range of bath gas concentrations $2.06 \times 10^{-6} < [\text{Kr}] < 5.71 \times 10^{-6}$ mol cm$^{-3}$ from 2 in the present work was extended to $1.04 \cdot 10^{-5} < [\text{Ar}]$ $< 9.28 \times 10^{-5}$ mol cm$^{-3}$. Consequently deviation from the limiting low pressure behaviour became visible more clearly in the present work. The difference between the rate constant $k_1$ for reaction (1) and the measured $k$ in eq. (6) required a simulation of the mechanism of reactions (1), (7) and (8). A potential influence of the chain process (9) and (10) was also examined. The simulation of the mechanism used tabulated equilibrium constants $k_1/k_8$ from 11 and results for $k_7$ from 9 (values for $k_9$ and $k_{10}$ were only tentative, see 4). Modelled values of CF$_2$ yields $Y$ ranged between about 0.35 near 1750 K and 0.92 near 2100 K. One should note that even with reactant concentrations as low as 100 ppm (at temperatures near 1800 K) the effects of secondary bimolecular reactions could not be suppressed. Only at temperatures above 2000 K the influence of secondary reactions decreased. Furthermore, at temperatures above 1600 K any influence by reactions (9) and (10), which would have increased the CF$_2$ yield $Y$, was not detected. The modelled kinetic profiles were characterized by a rapid initial increase of [CF2] with time represented by eq. (6), followed by only minor changes of the absorption levels attained on a much slower time scale. As the main part of the profile was given by eq. (6), modelled kinetic profiles are not shown here. The experimental $k$ and $Y$ through $k_1 \approx Y k$
were converted to $k_1$; minor deviations from this simple analysis, whenever observed in the kinetic modelling, were accounted for, but always were smaller than the experimental scattering.

Table 1 summarizes representative rate constants $k_1$ as determined in the described way. Near 1800 K, $k_1/\text{[Ar]}$ is found to decrease by about a factor of two, when [Ar] increases from about $10^{-5}$ to $10^{-4}$ mol cm$^{-3}$. The reaction was thus studied close to (but not quite at) the low pressure limit. The present results for $[\text{Ar}] \approx 10^{-5}\text{mol cm}^{-3}$ connect well with the results from $^2$ (for [Kr] ranging up to $5.6 \times 10^{-6}\text{mol cm}^{-3}$). The dependence of $k_1$ on the bath gas concentrations $[M]$ is illustrated in Fig. 3 where experimental data from the present work (with $M = \text{Ar}$) and from $^2$ (with $M = \text{Kr}$) are compared with modelled falloff curves, see below. Falloff curves are shown for 1800 and 2000 K; small “temperature mismatches” in the figure were accounted for by the modelled temperature dependences of $k_1$ at the given $[M]$; the temperature dependences of $k_1$ for two values of $[\text{Ar}]$ here were represented as

$$k_1 \propto \exp(-30200 K/T) \text{ s}^{-1}$$  \hspace{1cm} (11)

at $[\text{Ar}] \approx 10^{-5}\text{mol cm}^{-3}$ (for 1600 – 1800 K) and

$$k_1 \propto \exp(-29860 K/T) \text{ s}^{-1}$$  \hspace{1cm} (12)

at $[\text{Ar}] \approx 10^{-4}\text{mol cm}^{-3}$ (for 1800 – 2000 K). On the basis of these experimental results, complete falloff curves $k_1 ([M], T)$ were obtained with the help of the theoretical modelling described in the following section.
III. Modelling of limiting rate constants

The present calculations of molecular parameters, as used for the modelling of rate constants were performed at the G4//B3LYP/6-311+G(3df) ab initio level and, therefore, go beyond the less accurate G3//B3LYP/6-311G(d) calculations employed earlier. Our procedure follows that described in detail in and is not repeated here (details of the calculations are given in the Electronic Supporting Information, ESI). Morse parameters of the CF₂-F potential \( V(r) \) were found to be \( \beta_e = 2.42 \text{ Å}^{-1} \) (over the range \( 1.25 \leq r \leq 2.75 \text{ Å} \)) or \( \beta_e = 2.90 \text{ Å}^{-1} \) (over the range \( 2.0 \leq r \leq 2.75 \text{ Å} \)).

The frequencies of the two torsional transitional modes were found to decay exponentially with increasing bond length \( r \) (decay parameters of \( \alpha = 1.71 \) and \( 1.77 \text{ Å}^{-1} \) were derived), such that the ratio \( \alpha/\beta_e \) was found to be near to 0.6. This ratio is only slightly above the “standard value” of 0.5 \(^{12}\) used in \(^{3}\). Using molecular parameters for CF₃ and CF₂ as given in the ESI, and the derived value of \( \alpha/\beta_e \), the limiting high pressure rate constant was determined with the help of the classical trajectory version of the statistical adiabatic channel model (SACM/QT).\(^{13}\) Values of

\[
k_{1,\infty} = 1.6 \times 10^{16}(T/2000 \text{ K})^{-1.3} \exp(-43250 \text{ K}/T) \text{ s}^{-1}
\]

were obtained, approximately corresponding to

\[
k_{1,\infty} \approx 4.6 \times 10^{15} \exp(-40760 \text{ K}/T) \text{ s}^{-1}
\]

The apparent activation energy of \( k_{1,\infty} \) (339 kJ mol\(^{-1}\)) thus is not far from the threshold energy of reaction (1), i.e. 347.7 kJ mol\(^{-1}\), see the ESI. The rate constant of the reverse recombination of F with CF₂ followed as

\[
k_{-1,\infty} = 1.0 \times 10^{14}(T/2000 \text{ K})^{0.09} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}
\]

Using an alternative quantum-chemical approach to the potential and variational transition state theory (VRC-TST), \( k_{-1,\infty}(2000 \text{ K}) \) in \(^{2}\) was calculated to be \( 2.22 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). The difference of about a factor of 4.5 between the two approaches to \( k_{1,\infty} \) has only a small influence on the experimentally observed part of the falloff curves. Nevertheless, it deserves an explanation which is given in the ESI.

Limiting low pressure rate constants \( k_{1,0} \) in the present work were obtained with the method of \(^{7}\), fitting the average energy \( \langle \Delta E \rangle \) transferred per collision with the help of the experimental results shown in Fig. 3, and accounting for centrifugal barriers with the \( r \)-dependent rotational constants of CF₃ given in the ESI. Values of \( \langle \Delta E \rangle/hc \approx 300 \text{ cm}^{-1} (\pm 100 \text{ cm}^{-1}) \) were fitted and - at least for the
studied temperature range were assumed to be independent of the temperature. Over the range 1500–2500 K, this led to rate constants

\[ k_{1,0} = [\text{Ar}] \times 10^{18} (T/2000 \text{ K})^{-5.1} \exp(-42450 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \]  

which can be approximated by

\[ k_{1,0} = [\text{Ar}] \times 10^{16} \exp(-32835 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \]  

The master equation approach of [2] over the range 1300–2500 K has given

\[ k_{1,0} = [\text{Kr}] \times 10^{24} (T/298 \text{ K})^{-6.362} \exp(-45649 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \]  

such that \( k_{1,0}(2000 \text{ K}) = [\text{Kr}] \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \), in comparison to \( k_{1,0}(2000 \text{ K}) = [\text{Ar}] \times 1.6 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) from the present modelling. A value of \( -\langle \Delta E \rangle / \hbar c \approx 420 \text{ cm}^{-1} \) was estimated in ², which corresponds to a collision efficiency \( \beta_c(2000 \text{ K}) \approx 0.16 \), close to the value \( \beta_c(2000 \text{ K}) \approx 0.11 \) in the present calculation. The agreement between the two quite different approaches to \( k_{1,0} \) thus appears quite satisfactory (one should note that the differences of the collision frequencies for M = Ar and Kr as well as the differences of \( \langle \Delta E \rangle \) are only of minor importance).
IV. Modelled falloff curves

Besides $k_{1,0}$ and $k_{1,\infty}$, center broadening factors $F_{\text{cent}}$ enter the falloff expressions (3) – (5). As before [4], we estimate their strong collision contribution $F_{\text{cent}}^{\text{sc}}$ by the method of $^{14}$, while a weak-collision contribution $F_{\text{cent}}^{\text{wc}} \approx 0.64$ in $F_{\text{cent}} \approx F_{\text{cent}}^{\text{sc}} F_{\text{cent}}^{\text{wc}}$ follows from $^5$. The resulting values here are $F_{\text{cent}} \approx 0.25, 0.22, \text{and } 0.20$ for $T = 1500, 2000, \text{and } 2500 \text{ K}$, respectively. A value of 0.27 was derived in $^2$ (the difference, however, is of only small practical relevance, because the present experiments were conducted close to the low pressure limit of the reaction. The difference is related to the different $k_{1,\infty}$ derived in the present work and in $^2$, see below).

In the following, two factors influencing the shape of the “broad” falloff curves of the present reaction [6] are inspected: (i) differences between the falloff expressions of eq. (3) (from strong-collision, rigid-activated complex, Rice-Ramsperger-Kassel-Marcus (RRKM) theory$^7$) and the falloff expressions of eqs. (4) and (5) (from weak-collision master equations, loose-activated complex calculations$^5$); (ii) differences due to different $k_{1,0}$ and $k_{1,\infty}$.

Fig. 4 compares falloff curves constructed with the simple falloff curves from eq. (3) and the more elaborate expressions of eqs. (4) and (5) (using the same values of $k_{1,0}$, $k_{1,\infty}$ and $F_{\text{cent}}$ as derived from the present modelling). The differences are clearly within the scatter of the experimental points shown in Fig. 3 such that the simple eq. (3) could be used as an alternative to eqs. (4) and (5). Fig. 5 provides a comparison of the present falloff curves with those from $^2$, employing markedly different values of $k_{1,\infty}$. Although the experimental scatter precludes any safe conclusions on $k_{1,\infty}$, the proximity of $k_1$ to $k_{1,0}$ is sufficient to permit a unique determination of $-\langle \Delta E \rangle / \hbar c$ (within an estimated accuracy of about $\pm 100 \text{ cm}^{-1}$).
V. Conclusions

It was shown that shock wave studies of the thermal dissociation (1) of CF$_3$ from $^2$ and from the present work are consistent with each other, provided that the influence of the secondary reactions (7) and (8) are taken into account. An influence of reactions (9) and (10), involving IF as an intermediate, could not be detected. The deduced rate constant $k_1$ was shown to correspond to conditions near to the limiting low pressure rate constant $k_{1,0}$ of the reaction. The influences of different falloff expressions (eq. (3) vs. eqs. (4) and (5)) and of different high pressure rate constants $k_{1,\infty}$ on the evaluation of $k_{1,0}$ were investigated. Although the experimental scatter was apparently larger than the modelling differences of the falloff analysis, the present determination of a value of the total average energy $\langle \Delta E \rangle$ transferred per collision with the bath gas Ar, i.e. $-\langle \Delta E \rangle/\hbar c \approx 300 \text{ cm}^{-1} (\pm 100 \text{ cm}^{-1})$, seems well founded. Although this value is somewhat higher than usually observed (see $^4$ and $^{15}$), it does not appear unreasonable (the experiments from $^2$ for M = Kr would be evaluated with a very similar value of $\langle \Delta E \rangle$).

VI. Acknowledgment

Financial support of this work from the Deutsche Forschungsgemeinschaft (Project TR 09/20-1) is gratefully acknowledged.

Associated Content

Electronic Supporting Information (ESI)

Modelling of the Potential Energy Surface and of Rate Constants in the Falloff Range
References


Table 1: Representative experimental rate constants for the dissociation of CF<sub>3</sub> (\([\text{CF}_3]_t = 0/\text{[Ar]}\) in ppm; \(T\) in K; [Ar] in mol cm\(^{-3}\); rate constants \(k_1\) in s\(^{-1}\) corrected for secondary reactions contributing to \(k\) in eq. (6), see text; \(Y = [\text{CF}_2]_t = \infty/[\text{CF}_3]_t = 0\))

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</table>
Figure Captions

Fig. 1  Absorption-time profile of CF₂ at 248 nm in the thermal decomposition of CF₃ behind a reflected shock wave (precursor 1054 ppm of CF₃I in Ar, incident shock wave: T = 977 K, [Ar] = 3.3 \cdot 10^{-5} \text{ mol cm}^{-3}; \text{reflected shock wave: } T = 1874 \text{ K, } [Ar] = 7.1 \cdot 10^{-5} \text{ mol cm}^{-3}; \text{OD5 } = \varepsilon \times [CF₂] \text{ with } x = 9.4 \text{ cm and } \varepsilon = 2.7 \cdot 10^{6} \text{ cm}^{2} \text{ mol}^{-1}; \varepsilon \text{ defined by Lambert-Beer's law in the form } I = I₀ \exp(-\text{OD5}).$

Fig. 2  As Fig.1, but at T = 2049 K and [Ar] = 6.6 \cdot 10^{-5} \text{ mol cm}^{-3} \text{ behind the reflected shock (527 ppm of CF₃I in Ar, } \varepsilon = 2.3 \cdot 10^{6} \text{ cm}^{2} \text{ mol}^{-1})$

Fig. 3  Experimental pseudo-first order rate constants $k_1$ of the dissociation of CF₃ in Ar (representative points from this work, ●) and in Kr (representative points from [2], ○) converted to 1800 K (lower set of points) and 2000 K (upper set of points), in comparison with modelled falloff curves from this work (lines, see text).

Fig. 4  Comparison of modelled falloff representations by eq. (3) (black line) and eqs. (4) and (5) (grey line). The uppermost curves correspond to the low-pressure limiting $k_{1,0}$.

Fig. 5  Comparison of modelled falloff curves from the present work (black line, eqs. (4) and (5)) and from the modelling of ² (grey line) using different $k_{1,0}$ and $k_{1,∞}$ (values given in the text). The uppermost curves correspond to the low-pressure limiting $k_{1,0}$. 
Figures

![Graph of OD5 vs. time in ms for Fig. 1.](image1)

**Fig. 1**

![Graph of OD5 vs. time in µs for Fig. 2.](image2)

**Fig. 2**
Fig. 3

Fig. 4
Fig. 5