A computational study of the reaction kinetics of methyl radicals with trifluorohalomethanes

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Abstract

Ab initio calculations have been used to characterize the transition states for halogen abstraction by CH₃ in reactions with CF₄, CF₃Cl, CF₃Br and CF₃I (1-4). Geometries and frequencies were obtained at the HF/6-31G(d) and MP2=full/6-31G(d) levels of theory. Energy barriers were computed via the Gaussian-2 methodology, and the results were employed in transition state theory analyses to obtain the rate constants over 298-2500 K. There is good accord with literature measurements in the approximate temperature range 360-500 K for reactions (2-4), and the computed activation energies are accurate to within ± 6 kJ mol⁻¹. Recommended rate constant expressions for use in combustion modeling are $k_1 = 1.6 \times 10^{-19} (T/K)^{2.41} \exp(-13150 \text{ K}/T)$, $k_2 = 8.4 \times 10^{-20} (T/K)^{2.34} \exp(-5000 \text{ K}/T)$, $k_3 = 4.6 \times 10^{-19} (T/K)^{2.05} \exp(-3990 \text{ K}/T)$ and $k_4 = 8.3 \times 10^{-19} (T/K)^{2.18} \exp(-1870 \text{ K}/T)$ cm³ molecule⁻¹ s⁻¹. The results are discussed in the context of flame suppression chemistry.

INTRODUCTION

Information about the kinetics of the reactions

is important for understanding the combustion chemistry of halogenated methanes. This chemistry is central in several contexts. CF_3Br is a typical halon fire extinguishing agent, and there have been several studies of its behavior in flames [1][2][3][4][5]. Halons are thought to damage the ozone layer and two candidates for possible replacements are perfluorocarbons, exemplified by CF_4 , and the iodofluorocarbon CF_3I [6]. Chlorofluorocarbons, such as CF_3Cl , also have large ozone depletion potentials and there is interest in destruction of CFCs via incineration [7]. There are few studies of reactions (1-4). CF_4 reacts slowly in flames by other pathways [6] so that reaction (1), even if slow, may be a significant contributor to CF_4 destruction. This possibility has not been previously considered, a reflection of the absence of data for evaluation. For reactions (2-4), kinetic information is available from the analysis of pyrolysis studies at up to about 500 K, where decomposition of methyl radical sources in the presence of halogenated methanes was modeled with multi-step mechanisms [8][9]. In the case of CF_3Br , there is also a rate constant expression derived for the temperature range 900 to 1600 K from modeling flames [1]. As discussed below, this expression is in poor accord with the lower temperature information.

In this work we describe *ab initio* investigations of the transition states for the halogen transfer reactions (1-4), carried out in order to characterize the rate constants, to resolve the

discrepancy for reaction (3), and to fill gaps in the kinetic database. Rate expressions are derived for use in combustion modeling at temperatures up to 2500 K.

AB INITIO CALCULATIONS

The quantum computations were carried out with the Gaussian 94 program [10]. Geometries of the reactants, transition states (TSs) and products were initially optimized at the HF/6-31G(d) level of theory, and the vibrational frequencies were computed and scaled by a standard factor of 0.8929 [11]. The geometries and frequencies were then refined at the MP2=full/6-31G(d) level of theory, which includes a partial correction for the effects of electron correlation. Correlation is expected to be important for the description of partial bonds in the TSs, and thus these MP2 frequencies, scaled by a factor of 0.95, were employed for the calculation of zero-point vibrational energy and thermodynamic properties. Next, the MP2-optimized geometries were employed in a series of single point energy calculations as prescribed by the Gaussian-2 method [12] to approximate the QCISD(T)/6-311+G(3df,2p) energy. For systems containing Br and I the all-electron basis sets and G2 extensions described by Glukhovstev et al. [13] were employed.

RESULTS AND DISCUSSION

Geometries and Frequencies

The TSs were found to have linear C-X-C bonds, where X is the exchanged halogen, which leads to C_{3v} symmetry, and at the MP2=full/6-31G(d) level of theory the C-H and C-F bonds were eclipsed. These geometries are summarized in Fig. 1 and Table I, along with *ab initio*

results for the reactants and products. The computed vibrational frequencies are listed in Table II together with the G2 energies (which include zero point energies derived from the scaled HF/6-31G(d) frequencies). The TSs exhibited spin-contamination, with $\langle S^2 \rangle$ of about 0.89, rather than the ideal value of 0.75, but this will only weakly influence the QCISD(T)-based energies.

Gurvich et al. [14] have summarized the structures and vibrational frequencies of CH_3X and CF_3X obtained from experiments. For the species in Table I, MP2=full/6-31G(d) theory slightly overestimates the bond distances. The root-mean-square deviation between experimental and computed C-H bond lengths is 0.4 pm. The C-F distances are similarly well-reproduced, with an rms deviation of 0.6 pm. There are two bound molecules that contain each of the other possible C-X bonds (X = Cl, Br and I), and the rms deviations are 0.6, 1.2 and 2.9 pm, respectively.

With one exception, the computed vibrational frequencies (Table II) agree well with the observed values [14]. The exception is the “umbrella” out-of-plane bending mode of CH_3 , for which scaled HF/6-31G(d) and MP2=full/6-31G(d) theory yield 273 and 384 cm^{-1} , respectively, in poor agreement with the observed [14] frequency of 607 cm^{-1} . All the other modes are in excellent accord. Ignoring degeneracies, the mean deviations of the other tabulated HF/6-31G(d) and MP2=full/6-31G(d) frequencies from experiment [14] are -10 and +4 cm^{-1} , respectively, and the rms deviations are 29 and 31 cm^{-1} , respectively.

Thermochemistry

Table III shows that the experimental reaction enthalpy changes at 0 K, $\Delta_r H_0$, are moderately well reproduced at the G2 level of theory for reactions (2-4). There is a consistent

error of around +10 kJ mol⁻¹. The major source of uncertainty in these experimental $\Delta_f H_0$ values is $\Delta_f H_0(\text{CF}_3)$ for which Gurvich et al. [14] quote -469.2 ± 5.0 kJ mol⁻¹. We note that had we employed the more positive $\Delta_f H_0(\text{CF}_3)$ values of Tsang [15] or Kumaran et al. [16] the discrepancy with the G2 results would be eliminated. One interpretation is that the uncertainty limits for $\Delta_f H_0(\text{CF}_3)$ should be increased. Agreement between theory and experiment is much poorer for reaction (1), but this involves $\Delta_f H_0(\text{CH}_3\text{F})$ which is an unusually uncertain experimental quantity [14].

Kinetics

Rate constants were derived as a function of temperature T via canonical transition state theory [17]:

$$k_{\text{TST}} = \Gamma \frac{k_B T}{h} \frac{Q_{\text{TS}}}{Q_{\text{CH}_3} Q_{\text{CF}_3\text{X}}} \exp\left(-\frac{E_0^\ddagger}{RT}\right) \quad (5)$$

The Q s represent partition functions (including rotational symmetry factors), and were computed via the harmonic oscillator - rigid rotor assumption with the exception of the lowest frequency mode. The lowest MP2 frequency for each TS lies at 8-15 cm⁻¹. This mode corresponds to essentially free rotation of the CH₃ group relative to the CF₃ group, with a reduced moment of inertia of 5.4×10^{-47} kg m² and a symmetry factor of 3. The symmetry factors of reagents and TSs combine to give the correct reaction path degeneracies, 8 for reaction (1) and 2 for reactions (2-4). For each reaction the barrier to formation of the TS at 0 K, $E_0^\ddagger$, was derived from the G2 energies of reactants and TS, followed by a small adjustment (typically 1-4 kJ mol⁻¹) for the

replacement of scaled HF/6-31G(d) contributions to the vibrational zero-point energy by scaled MP2=full/6-31G(d) values. Γ represents a correction for tunneling, derived for an Eckart function [18][19] fitted to the forward and reverse barriers and the scaled imaginary MP2=full/6-31G(d) frequency of the TS. The reduced masses for the imaginary modes were about 15 amu. The reverse barriers were derived from the computed forward barriers and the experimental $\Delta_r H_0$ values [14]. Because of the high sensitivity of Γ to the input parameters when this correction becomes large, the simple tunneling correction employed here is then not expected to be quantitatively accurate. We found that tunneling was the major pathway (i.e. $\Gamma > 2$) for reactions (1-3). Indeed, for the high-barrier process $\text{CH}_3 + \text{CF}_4$ the tunneling correction relative to the very small classical reaction rate became extremely large, for example a factor of 4×10^5 at 1000 K. Nevertheless, the absolute rate of tunneling is small and reaction (1) is slow. Tunneling had a negligible impact on the fastest reaction, $\text{CH}_3 + \text{CF}_3\text{I}$. The value of k_{TST} was computed over the temperature range 298-2500 K for reactions (1-4), and the results are plotted on Fig. 2. The dimensionless parameters that define fits to these *ab initio* results in the modified Arrhenius form

$$k_{\text{TST}} = A (T/\text{K})^n \exp(-B \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

are given in Table IV.

We have tested the likely significance of reaction (1) in the flame chemistry of CF_4 using our computed rate expression. k_1 is similar to k_7 for

at 2000 K and about 16 times larger at 1000 K [20]. Modeling of a stoichiometric adiabatic premixed methane-air flame at 1 atm [21][22] indicates that the peak concentration of CH_3 radicals is about $1 \times 10^{16} \text{ molecule cm}^{-3}$, at a temperature of about 1500 K, and the peak atomic H

concentration is about 2.5×10^{16} molecule cm^{-3} at about 1900 K. Figure 3 shows the reciprocal lifetimes for CF_4 with respect to reaction with H and CH_3 in the flame, on the assumption that only a trace of CF_4 is added so that the C/H/O chemistry is unaffected. Early in the flame reaction (1) is the dominant removal pathway, which suggests that it should be included in consideration of any chemical inhibition by CF_4 of lower-temperature processes such as ignition delay. At higher flame temperatures consumption of CF_4 through reaction (7) dominates, because the peak [H] occurs at a higher temperature than the peak [CH_3], and $k_7(1900 \text{ K}) > k_1(1500 \text{ K})$. Reaction (1) therefore makes only a small contribution to overall CF_4 destruction and can probably be safely neglected in most flame models.

There is one previous measurement of k_2 for $\text{CH}_3 + \text{CF}_3\text{Cl}$ [9]. The computed k_2 is lower than the experimental value by a factor of about 5 at 400 K. It is hard to measure such slow processes ($k_2 \approx 10^{-18} \text{ cm}^3 \text{ s}^{-1}$) because of the possibility of interference by secondary chemistry, but if the discrepancy is ascribed entirely to computational errors, then this difference is equivalent to an overestimate of the activation energy by about 6 kJ mol^{-1} . A value of B (see equation (6)) adjusted to match the experimental data at 400 K is given in Table IV.

There is a similar level of accord with the two measurements of the faster $\text{CH}_3 + \text{CF}_3\text{Br}$ reaction at around 360-500 K [8,9]. Agreement with these data at $T \approx 400 \text{ K}$ becomes exact if the computed activation energy is increased by 5 kJ mol^{-1} . High-temperature k_3 results are also available in the literature [1] and are plotted on Fig. 2. The high and low temperature measurements are contradictory [23]. It is hard to reconcile the computed k_3 and the flame modeling results, which would require reduction of the *ab initio* barrier by around 30 kJ mol^{-1} . This would be an uncharacteristically large error in a G2 energy for a stable species [12] or a TS

[24][25][26][27]. It is more likely that the two lower temperature measurements, which required simpler kinetic modeling to extract k_3 than was needed for the multi-reaction combustion system employed in the high temperature measurement, are more accurate. In order to obtain a rate constant expression for use in combustion modeling we have adjusted the B term in the modified Arrhenius expression (equation (6)) slightly, to fit the lower temperature measurements, and this TST fit is given in Table IV.

Figure 2 shows that the computed rate constant for $\text{CH}_3 + \text{CF}_3\text{I}$ lies between the two experimental determinations [8,9]. We therefore did not make any adjustments to the *ab initio* k_4 expression (Table IV), and recommend it for combustion modeling.

CONCLUSIONS

Ab initio calculations and transition state theory have yielded rate constants for CH_3 reactions with CF_3X ($\text{X} = \text{F} - \text{I}$). By comparison with $\text{H} + \text{CF}_4$, the reaction $\text{CH}_3 + \text{CF}_4$ is predicted to be too slow under flame conditions to be significant in the combustion chemistry of CF_4 . The calculations reproduce the experimental trend of increasing reactivity along the series CF_3Cl , CF_3Br and CF_3I , and there is good agreement with literature measurements in the approximate temperature range 360-500 K. There appear to be no systematic errors in the computed activation energies and moderate adjustments of up to $\pm 6 \text{ kJ mol}^{-1}$ yield very close accord between theory and experiment. Fitting TST to the measurements provides an extrapolation of these data to higher temperatures. For the reaction $\text{CH}_3 + \text{CF}_3\text{Br}$ there are contradictory results from experiments carried out in low and high temperature regimes; our *ab initio* analysis supports the lower temperature measurements and suggests that attack by CH_3 on

the halon flame suppressant under combustion conditions is slower than previously thought.

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REFERENCES

1. J. C. Biordi, C. P. Lazzara and J. F. Papp, *J. Phys. Chem.*, **82**, 125 (1978).
2. C. K. Westbrook, *Combust. Sci. Tech.*, **34**, 201 (1983).
3. F. Battin-Leclerc, G. M. Côme and F. Baronnet, *Combust. Flame*, **99**, 644 (1994).
4. V. Babushok, T. Noto, D. R. F. Burgess, A. Hamins and W. Tsang, *Combust. Flame*, **107**, 351 (1996).
5. A. R. Masri, B. B. Dally, R. S. Barlow and C. D. Carter, *Combust. Sci. Tech.*, **113/114**, 17 (1996).
6. W. Tsang and A. W. Miziolek, eds, *Halon Replacements: Technology and Science* (ACS Symposium Series 611, 1995).
7. P. H. Taylor, B. Dellinger and D. A. Tirey, *Int. J. Chem. Kinet.*, **23**, 1051 (1991).
8. D. M. Tomkinson and H. O. Pritchard, *J. Phys. Chem.*, **70**, 1579 (1966).
9. H. Sidebottom and J. Treacy, *Int. J. Chem. Kinet.*, **16**, 579 (1984).
10. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN 94* (Gaussian, Pittsburgh, PA, 1995).
11. J. A. Pople, A. P. Scott, M. W. Wong and L. Radom, *Israel J. Chem.*, **33**, 345 (1993).
12. L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, *J. Chem. Phys.*, **94**, 7221 (1991).
13. M. N. Glukhovtsev, A. Pross, M. P. McGrath and L. Radom, *J. Chem. Phys.*, **103**, 1878 (1995).
14. L. V. Gurvich, I. V. Veyts and C. B. Alcock, *Thermodynamic Properties of Individual Substances Vol. II*, 4th Ed., Hemisphere, New York, 1992.
15. W. Tsang, *J. Phys. Chem.*, **90**, 414 (1986).
16. S. S. Kumaran, M.-C. Su, K. P. Lim, J. V. Michael, *Chem. Phys. Lett.*, **243**, 59 (1995).

17. J. I. Steinfeld, J. S. Francisco and W. L. Hase, *Chemical Kinetics and Dynamics*, Prentice hall, Englewood Cliffs, 1989, Chap. 10.
18. H. S. Johnston, *Gas Phase Reaction Rate Theory*, Ronald, New York, 1966, Chap. 2.
19. P. Marshall, T. Ko and A. Fontijn, *J. Phys. Chem.*, **93**, 1922 (1989).
20. V. F. Kochubei and F. B. Moin, *Kinet. Catal.*, **11**, 712 (1971). Russ. orig. p. 86.
21. M. Frenklach, H. Wang, C.-L. Yu, M. Goldenberg, C. T. Bowman, R. K. Hanson, D. F. Davidson, E. J. Chang, G. P. Smith, D. M. Golden, W. C. Gardiner and V. Lissianski, *GRI-Mech 1.2*, <http://www.gri.org>.
22. R. J. Kee, F. M. Rupley and J. A. Miller, *Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics* (Sandia National Laboratories Report No. SAND89-8009B, 1991).
23. An Arrhenius fit through the three data sets is of course possible, but yields a physically implausible preexponential factor for a CH_3 reaction, of $7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. By contrast, Arrhenius fits to the computed k_2 , k_3 and k_4 over $298 \text{ K} \leq T \leq 1000 \text{ K}$ yield preexponential factors in the range $10^{-12} - 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
24. L. Ding and P. Marshall, *J. Chem. Phys.*, **98**, 8545 (1993).
25. A. Goumri, W.-J. Yuan, L. Ding, Y. Shi and P. Marshall, *Chem. Phys.*, **177**, 233 (1993).
26. A. Goumri, D. Laakso, J.-D. R. Rocha, C. E. Smith and P. Marshall, *J. Chem. Phys.*, **102**, 161 (1995).
27. R. J. Berry, C. J. Ehlers, D. R. Burgess, Jr., M. R. Zachariah and P. Marshall, *Chem. Phys. Lett.*, **269**, 107 (1997).

Table I. Geometries of stationary points on the $\text{CH}_3 + \text{CF}_3\text{X} \rightarrow \text{CH}_3\text{X} + \text{CF}_3$ potential energy surfaces at the MP2=full/6-31G(d) level of theory (see Fig. 1).

Species	$r_{\text{CH}}, 10^{-10} \text{ m}$	$r_{\text{CF}}, 10^{-10} \text{ m}$	$r_1, 10^{-10} \text{ m}$	$r_2, 10^{-10} \text{ m}$	$a_{\text{H CX}}, \text{ deg}$	$a_{\text{F CX}}, \text{ deg}$
CH_3	1.078				90.0	
CF_4		1.329		1.329		109.5
CF_3Cl		1.335		1.749		110.4
CF_3Br		1.334		1.929		110.1
CF_3I		1.335		2.169		110.3
CF_3		1.327				107.7
CH_3F	1.092		1.390		109.1	
CH_3Cl	1.088		1.777		108.9	
CH_3Br	1.087		1.949		107.9	
CH_3I	1.086		2.162		107.7	
TS for F exchange	1.082	1.327	1.705	1.694	102.7	108.6
TS for Cl exchange	1.085	1.331	2.031	2.014	104.1	109.2
TS for Br exchange	1.084	1.331	2.182	2.149	103.7	109.3
TS for I exchange	1.084	1.335	2.385	2.327	103.6	109.7

Table II. Gaussian-2 energies and vibrational frequencies of stationary points on the $\text{CH}_3 + \text{CF}_3\text{X} \rightarrow \text{CH}_3\text{X} + \text{CF}_3$ potential energy surfaces.

Species	G2, au ^a	HF/6-31G(d), cm ^{-1b}	MP2=full/6-31G(d), cm ^{-1c}
CH_3	-39.74508	273, 1375 (2), 2934, 3091 (2)	384, 1407 (2), 3061, 3240 (2)
CF_4	-437.06631	422 (2), 610 (3), 896, 1315 (3)	410 (2), 597 (3), 872, 1282 (3)
CF_3Cl	-797.04098	340 (2), 465, 544 (2), 768, 1121, 1267 (2)	337 (2), 462, 531 (2), 752, 1095, 1220 (2)
CF_3Br	-2909.87237	298 (2), 341, 531 (2), 742, 1089, 1259 (2)	295 (2), 339, 517 (2), 724, 1060, 1215 (2)
CF_3I	-7254.30726	263 (2), 278, 521 (2), 726, 1070, 1242 (2)	261 (2), 275, 505 (2), 708, 1041, 1200 (2)
CF_3	-337.22371	491 (2), 677, 1086, 1285 (2)	479 (2), 669, 1070, 1252 (2)
CH_3F	-139.55421	1059, 1171 (2), 1474, 1476 (2), 2888, 2960 (2)	1053, 1165 (2), 1480, 1489 (2), 2959, 3054 (2)
CH_3Cl	-499.55383	699, 1016 (2), 1373, 1455 (2), 2918, 3011 (2)	747, 1032 (2), 1396, 1470 (2), 2993, 3100 (2)
CH_3Br	-2612.39046	571, 946 (2), 1325, 1448 (2), 2930, 3032 (2)	604, 961 (2), 1339, 1461 (2), 3005, 3122 (2)
CH_3I	-6956.82999	498, 886 (2), 1282, 1441 (2), 2930, 3036 (2)	526, 901 (2), 1298, 1453 (2), 3008, 3126 (2)
TS for F exchange	-476.71907	984i, 15, 90 (2), 228, 254 (2), 507 (2), 665 (2), 678, 1030, 1062, 1304 (2), 1411 (2), 2941, 3069 (2)	1573i, 24, 97 (2), 285 (2), 384, 499 (2), 707, 803 (2), 1010, 1152, 1259 (2), 1438 (2), 3032, 3190 (2)
TS for Cl exchange	-836.75513	565i, 10, 90 (2), 196, 232 (2), 510 (2), 666, 680 (2), 1019, 1077, 1287 (2), 1405 (2), 2937, 3078 (2)	701i, 14, 79 (2), 242 (2), 274, 483 (2), 647, 755 (2), 951, 1131, 1190 (2), 1379 (2), 2908, 3052 (2)

TS for Br exchange	-2949.59824	364i, 9, 74 (2), 187, 203 (2), 508 (2), 637 (2), 662, 1006, 1057, 1280 (2), 1403 (2), 2937, 3078 (2)	508i, 12, 67 (2), 220 (2), 265, 497 (2), 662, 739 (2), 969, 1143, 1224 (2), 1427 (2), 3017, 3168 (2)
TS for I exchange	-7294.04463	248i, 8, 61 (2), 163, 190 (2), 506 (2), 580 (2), 655, 977, 1026, 1270 (2), 1397 (2), 2935, 3079 (2)	391i, 10, 39 (2), 207 (2), 239, 494 (2), 656, 694 (2), 952, 1120, 1204 (2), 1421 (2), 3017, 3168 (2)

^a1 au $\approx$ 2625 kJ mol⁻¹. Standard G2 energy including scaled HF/6-31G(d) zero-point energy.

^bScaled by 0.8929. Degeneracy indicated in parentheses.

^cScaled by 0.95.

Table III. Enthalpies of products and transition states relative to reactants at 0 K, kJ mol⁻¹.

Reaction	$\Delta_r H_0$		$E_0^\ddagger$
	G2	Expt ^a	G2
1	86.5	61.3 ± 15.8	245.2
2	21.4	9.9 ± 5.7	77.5
3	7.4	-3.2 ± 5.5	50.9
4	-4.8	-11.7 ± 5.6	20.7

^aGurvich et al., ref. 14.

Table IV. Parameters of modified Arrhenius expressions in the form $k = A (T/K)^n \exp(-B K/T)$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reactions of CH_3 with CF_3X ($\text{X} = \text{F} - \text{I}$).

Reactant	A^a	n^a	B^a	B^b
CF_4	1.6×10^{-19}	2.41	13150	13150
CF_3Cl	8.4×10^{-20}	2.34	5670	5000
CF_3Br	4.6×10^{-19}	2.05	3370	3990
CF_3I	8.3×10^{-19}	2.18	1870	1870

^aFitted to *ab initio* results ($k > 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

^bRecommended value (adjusted to match experimental measurements at $T \approx 400 \text{ K}$ for CF_3Cl and CF_3Br).

Figure captions.

Fig. 1 C_{3v} structure of the transition state for the reaction $CH_3 + CF_3X \rightarrow CH_3X + CF_3$.

Parameters are listed in Table I.

Fig. 2 Comparison of computed (solid lines) and measured rate constants (reported fits over the temperature ranges investigated) for $CH_3 + CF_3X \rightarrow CH_3X + CF_3$. Dot-dash line, ref. 1; dashed lines, ref. 8; dotted lines, ref. 9.

Fig. 3 Reciprocal lifetimes for traces of CF_4 in an adiabatic premixed stoichiometric CH_4 /air flame at atmospheric pressure with respect to attack by H and CH_3 (dotted and solid lines, respectively, left axis), and the temperature profile (dashed line, right axis).

Fig. 1

Fig. 2

Fig. 3