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Theoretical modeling study of the reaction H + CF$_4$ → HF + CF$_3$

Carlos J. Cobos[1] | **Gary Knight**[2] | **Paul Marshall**[3] | **Jürgen Troe**[4] (iD)

[1] INIFTA, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CONICET, La Plata, Argentina

[2] Edwards Innovation Centre, Clevedon, UK

[3] Department of Chemistry and Center for Advanced Scientific Computing and Modeling, University of North Texas, Denton, Texas, USA

[4] Max-Planck-Institut für biophysikalische Chemie and Institut für Physikalische Chemie, Universität Göttingen, Göttingen, Germany

Correspondence
J. Troe, Max-Planck-Institut für bio-physikalische Chemie, Am Fassberg 11, Göttingen D-37077, Germany.
Email: juergen.troe@mpibpc.mpg.de

Abstract

The high-temperature hydrogenation of CF$_4$ in mixtures of CF$_4$ and H$_2$ is assumed to involve the reaction H + CF$_4$ → HF + CF$_3$. The hydrogen atoms here are either formed by the reaction of F and CF$_3$ (i.e., the products of the thermal dissociation of CF$_4$) with H$_2$, or by the thermal dissociation of H$_2$. In the former case, a complicated chain process is started, while the reaction proceeds in a more direct way in the latter. This article determines the rate constant of the reaction H + CF$_4$ → HF + CF$_3$, characterizing its transition state by quantum-chemical methods. Over the temperature range 1000–3000 K, the most accurate results for the rate constant can be represented in the form 1.64×10^{14} $(T/1000 \text{ K})^{1.95}$ exp(-178.8 kJ mol^{-1}/RT) cm^3 mol^{-1} s^{-1}, based on coupled cluster theory extrapolated to the complete basis set limit, and incorporating vibrational anharmonicity, electron correlation through CCSDT(Q), and relativistic and non-Born–Oppenheimer effects.

1 | INTRODUCTION

Tetrafluoromethane is effectively chemically inert in the atmosphere and so has an exceptionally long atmospheric lifetime which, combined with its strong infrared absorption, leads to a high global warming potential of over 6000 (see, e.g., Ref. 1). Industrial emissions of CF$_4$ might be mitigated by incineration, but the low reactivity outlined below indicates that careful evaluation of its high-temperature chemistry is required. Initial steps in this area were pursued in the context of the potential of CF$_4$ as a non-ozone-depleting fire extinguishing agent (see, e.g., Ref. 2). However, because of the strength of the C–F bond, CF$_4$ requires high temperatures to be decomposed. For example, temperatures between 2000 and 3000 K were applied in the 2016 shock wave experiments of

Knight et al.,[3] who studied the dissociation,

$$CF_4 (+M) \rightarrow CF_3 + F (+M)$$

$$\Delta_r H^o (0K) = 539.8 \text{ kJmol}^{-1} \quad (1)$$
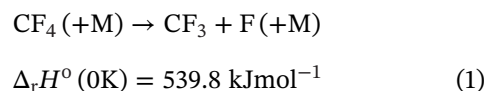
(values for the reaction enthalpies at 0 K, $\Delta_r H^o$(0 K), are from Goos et al.[4]). Nevertheless, as the H–F bond is even stronger than the C–F bond, CF$_4$ may react with H atoms in the exothermic reaction

$$H + CF_4 \rightarrow HF + CF_3 \qquad \Delta_r H^o (0 \text{ K}) = -26.3 \text{ kJ mol}^{-1}. \quad (2)$$
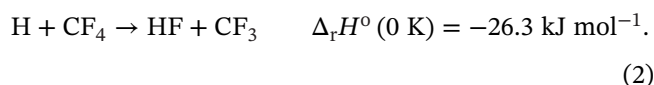
Hydrogen atoms, therefore, may play an important role in a high-temperature reaction of CF$_4$ with H$_2$, being an

alternative to incineration as a method for abatement of CF_4 emissions. In this case, H atoms can either be formed by reaction of F and CF_3 from reaction (1) with H_2, or by thermal dissociation of molecular hydrogen. In the former case, the reaction will proceed as a chain process, while the reaction is more direct in the latter case.
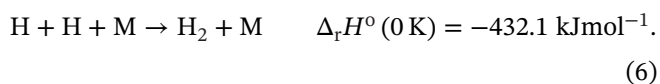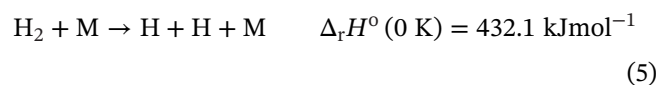
In order to assess the importance of a radical mechanism against a molecular hydrogenation

$$CF_4 + H_2 \rightarrow CF_3H + HF \quad \Delta_r H^o \, (0 \, K) = -32.0 \, \text{kJmol}^{-1}, \tag{3}$$
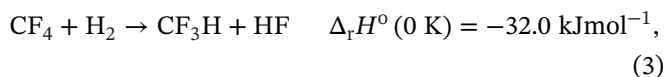
the rate constant of reaction (2) needs to be known. It has been determined in 1969 by Kochubei and Moin in a flow system study of mixtures of CF_4 with H_2 over the range 1323–1523 K by measuring the rate of conversion of the reactants to HF and CH_4.[5] By end product analysis, an overall rate law

$$d \, [CF_4] \, /dt = -k \, [CF_4] \cdot [H_2]^{1/2} \tag{4}$$

was observed. The $[H_2]^{1/2 \, -}$ dependence suggested that the thermal dissociation of H_2 was the dominant source of hydrogen atoms whose concentration was governed by the equilibrium

$$H_2 + M \rightarrow H + H + M \quad \Delta_r H^o \, (0 \, K) = 432.1 \, \text{kJmol}^{-1} \tag{5}$$

$$H + H + M \rightarrow H_2 + M \quad \Delta_r H^o \, (0 \, K) = -432.1 \, \text{kJmol}^{-1}. \tag{6}$$

Combining the equilibrium constant k_5/k_6 with the measured k, the analysis of the results led to

$$k_2 = 7.1 \times 10^{14} \exp \, (-22,000 \, K/T) \, \text{cm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}. \tag{7}$$

In 1970, Kochubei and Moin studied hydrogen–oxygen flames containing CF_4.[6] Here, the competition of reaction (2) with the reaction

$$H + CO_2 \rightarrow OH + CO \quad \Delta_r H^o \, (0 \, K) = -100.4 \, \text{kJmol}^{-1} \tag{8}$$
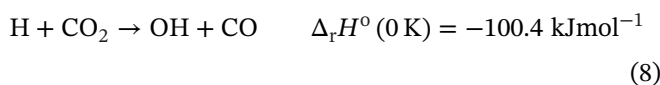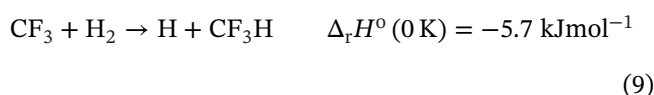
was exploited and the ratio k_2/k_8 was determined. With the then accepted value for k_8, good agreement between the two values for k_2 was obtained.

Since the publication of Refs. 5 and 6, several of the assumptions made can today be examined. For example, the recommended value of k_8 was reduced (see Ref. 7). On the theoretical side, quantum-chemical calculations of k_2 at the G2(MP2) level by Berry et al.[8] in 1997 led to smaller values than suggested by Equation (7). This called for a recalculation o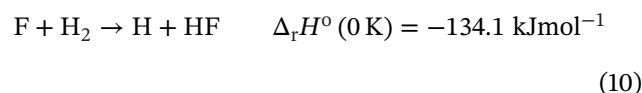f k_2 with more advanced theoretical methods. Furthermore, the dominance of the mechanism of reactions (5), (6), and (2) appears questionable. Results for k_2 in comparison to k_5 help to distinguish between the mentioned direct and chain pathways of the high-temperature hydrogenation of CF_4.

2 | HYDROGEN ATOMS IN THE HYDROGENATION OF CF_4

In order to assess the role of reaction (2) in the hydrogenation of CF_4, it is important to identify the source of hydrogen atoms. We do this first by considering experiments under the conditions of the flow system study of Ref. 5. Here mixtures of 24% of CF_4, 36% of N_2, and 40% of H_2, at 1473 K and atmospheric pressure, were heated for up to 5 s and the degree of CF_4 conversion was determined (it was found that HF was the only fluorine-containing reaction product, providing an argument against the molecular mechanism of reaction (3)). Under the conditions described, the thermal dissociation of H_2 (reaction (5)), in Ref. 5, was assumed to dominate the generation of hydrogen atoms. However, there may be other sources for hydrogen atoms. Reactions of the products CF_3 and F of the dissociation (1) of CF_4 with H_2, for example, through

$$CF_3 + H_2 \rightarrow H + CF_3H \quad \Delta_r H^o \, (0 \, K) = -5.7 \, \text{kJmol}^{-1} \tag{9}$$

and

$$F + H_2 \rightarrow H + HF \quad \Delta_r H^o \, (0 \, K) = -134.1 \, \text{kJmol}^{-1} \tag{10}$$

at sufficiently high concentrations of H_2 can also rapidly generate hydrogen atoms. Thermal dissociation of CF_3H by

$$CF_3H \, (+M) \rightarrow HF + CF_2 \, (+M)$$
$$\Delta_r H^o \, (0 \, K) = 219.7 \, \text{kJmol}^{-1} \tag{11}$$
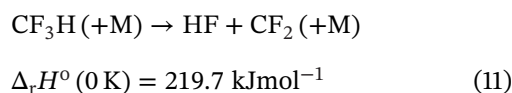
and further reactions of CF_2 then carry on the reaction. As the rate constants for reactions (1), (5) (with M = H_2), (9), and (10) by now are known, one may compare the rate of hydrogen atom formation by reaction (5) with that of the sequence of reactions (1), (9), and (10). With $k_9 = 1.5 \times 10^{13} \exp \, (- \, 8550 \, K/T) \, \text{cm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}$ from Ref. 9 and $k_{10} = 6.6 \times 10^{13} \exp \, (- \, 450 \, K/T) \, \text{cm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}$ from Ref. 10, one realizes that H atoms are formed almost instantaneously after F and CF_3 have been produced (effective first-order rate constants larger than $10^5 \, \text{s}^{-1}$).

One, therefore, must ask whether CF_4 dissociation can compete with H_2 dissociation. This question can be answered with the results of Ref. 5. Accounting for the fact that reaction (1) under the conditions of Ref. 5 is in the fall-off range, at 1 bar of bath gas pressure (for M = Ar) and $T = 1473$ K from Ref. 5 one obtains $k_1 \approx 9 \times 10^{-4}$ s^{-1}. On the other hand, with $k_5 = [H_2] \times 9.0 \times 10^{14}$ exp $(-48,350$ K/$T)$ cm^3 mol^{-1} s^{-1} from Ref. 11, for the conditions of Ref. 5 one obtains $k_5 = 1.6 \times 10^{-5}$ s^{-1}. The dominant primary source for hydrogen atoms in the experiments of Ref. 5 thus may not have been the dissociation of H_2, but that of CF_4 followed by reactions (9) and (10).

The situation hardly changes for higher temperatures. For example, under typical shock wave conditions with equimolar mixtures of 1000 ppm CF_4 and H_2 in Ar, [Ar] = 5×10^{-5} mol cm^{-3}, and at temperatures near 2400 K, $k_1 \approx 3 \times 10^3$ s^{-1} again would be considerably larger than $k_5 \approx 1.0 \times 10^1$ s^{-1} such that the dominant source for H atoms here would be the sequence of reactions (1), (9), and (10) instead of reaction (5) (following reaction (1), hydrogen atoms again are formed by reactions (9) and (10) on a μs timescale). Without going into further details of the radical reactions governing later stages of the reaction, one concludes that the experimental information on k_2 so far is inconclusive. This justifies new theoretical calculations of this rate constant as described in the following section.

3 | METHODOLOGY OF MODELING k_2

Our approach for obtaining high-accuracy energies for the reactants, products, and transition state of reaction (2) is inspired by the HEAT model chemistry of Stanton and coworkers.[12,13] However, with five nonhydrogen atoms involved rather than the one to three addressed previously, various compromises had to be made, notably that smaller basis sets had to be employed in the coupled cluster calculations. Unless otherwise noted, the computations were made with versions 1.0 and 2.1 of the CFOUR program.[14] In the spirit of the HEAT345-(Q) method, but with some significant deviations, we define a total electronic energy E_{total} as follows:

$$E_{total} = E_{HF}^{\infty} + \Delta E_{CCSD(T)}^{\infty} + E_{zpe} + \Delta E_{CCSDT(Q)}$$
$$+ \Delta E_{rel} + \Delta E_{DBOC} \tag{12}$$

where E_{HF}^{∞} represents the Hartree–Fock energy at the infinite basis set limit, $\Delta E_{CCSD(T)}^{\infty}$ represents the correlation energy at this limit evaluated via coupled-cluster theory with double electron substitutions and a perturbative triples contribution, E_{zpe} is the vibrational zero-point energy, $\Delta E_{CCSDT(Q)}$ is a further correction for electron cor-

relation with up to quadruple excitations treated perturbatively, ΔE_{rel} accounts for scalar relativistic effects, and the ΔE_{DBOC} term addresses the Born–Oppenheimer approximation, details follow.

First, the geometry was optimized at the CCSD(T) = full/cc-pVTZ level of theory, where "full" indicates that all orbitals were included in the electron correlation treatment, so that core–valence correlation effects were included implicitly. Harmonic frequencies ω_i were obtained with this level of theory. Density functional theory (DFT) at the B2PLYP/aug-cc-pVTZ level was applied to evaluate anharmonic coupling coefficients x_{ij} via vibrational second-order perturbation theory using third and fourth energy derivatives, as implemented in the Gaussian 16 code.[15] Following the hybrid procedure of Barone and coworkers,[16] we added the anharmonic corrections for zero-point energy and fundamental frequency from DFT to the harmonic quantities from CCSD(T). In effect, DFT values of x_{ij} were used to correct the higher level ω_i, rather than computing x_{ij} with CCSD(T) theory as in the HEAT method. No generalized scale factors were therefore employed to obtain the zero-point energy or fundamental frequencies.

Hartree–Fock calculations were made with aug-cc-pCVXZ basis sets, with X = T, that is, 3, Q, that is, 4, and 5. These HF energies were extrapolated to the infinite or complete basis set limit E_{HF}^{∞} via the relation

$$E_{HF}^X = E_{HF}^{\infty} + a \exp(-bX), \tag{13}$$

where E_{HF}^{∞}, a, and b are obtained by a fit through the three values of E_{HF}^X. The energy change due to CCSD(T) correlation energy at the infinite basis set limit, $\Delta E_{CCSD(T)}^{\infty}$, was evaluated through

$$\Delta E_{CCSD(T)}^X = \Delta E_{CCSD(T)}^{\infty} + c/X^3, \tag{14}$$

where two data points are sufficient. We used CCSD(T) = full/aug-cc-pCVTZ and CCSD(T) = full/aug-cc-pCVQZ energies, that is, X = 3 and 4, and ΔE^X here refers to the difference between total energy with electron correlation and the HF energy. Note that the original HEAT method is based on X = 4 and 5, but correlated calculations with the aug-cc-pCV5Z basis set were prohibitively demanding for our five heavy atom system.

We allow for correlation effects beyond CCSD(T), where the effect of triple excitations is approximated by perturbation theory, up to CCSDT(Q), where triples are treated exactly and quadruple excitations are evaluated via perturbation theory, through the term

$$\Delta E_{CCSDT(Q)} = E_{CCSDT(Q)} - E_{CCSD(T)} \tag{15}$$

TABLE 1 Enthalpies at 0 K for reaction (2) and its transition state TS (in kJ mol^{-1}, entries rounded to closest 0.1 kJ mol^{-1})

Process	JANAF[20]	ATcT[4]	CBS-QB3[21]	CCSDT(Q) = Full/CBS this work
H + CF$_4$ → HF + CF$_3$	−28.8 ± 4.5	−26.4 ± 0.6	-24.2	−26.9
H + CF$_4$ → TS	–	–	187.4	190.0

Both energies were obtained with the cc-pVDZ basis set and the frozen core approximation, with only valence orbitals included in the correlation treatment, using the MRCC extension of CFOUR.

ΔE_{rel} reflects the scalar component of the impact of relativistic effects, and here we use the sum of the expectation values of the mass-velocity and Darwin terms computed with configuration interaction with single and double substitutions, CISD, and the cc-pwCVTZ basis set, using the Molpro 2010.1 program.[17] Modest breakdown of the Born–Oppenheimer approximation is accounted for through the ΔE_{DBOC} term, for which we use the diagonal Born–Oppenheimer correction (DBOC) evaluated at the CCSD = full/aug-cc-pCVTZ level of theory.[18]

As we often employ simpler modeling methods (see, e.g., Refs. 8 and 19), and these may be employed in alternative kinetic analyses, we use the opportunity to compare their results with the results from the method described above. In particular, the features of the potential energy surface of reaction (2) were also derived from BMK, M06-2X, and ωB97X-D models combined with a 6−311++G(3df,3pd) basis set. More accurate CCSD(T), CBS-QB3, and G4 calculations were also performed (thermochemistry results for the TS of the reaction from these calculations are illustrated in section SI-1 of the Supplementary Information, SI).

4 | CALCULATED THERMOCHEMICAL AND KINETIC RESULTS

We first compare the results of our calculations of thermochemical quantities with experimental data for H, CF$_4$, CF$_3$, HF, and the transition state TS of reaction (2). Table SI-2 of the Supplementary Information provides calculated values of the various terms in Equations (12)–(15) (vibrational frequencies and rotational constants of the species involved as well of TS are listed in Table SI-3). The final E_{total} results for H, CF$_4$, CF$_3$, HF, and TS are given in Table SI-2. The comparison of the corresponding enthalpy of reaction $\Delta_r H^o(0 \text{ K})$ with literature values gives some idea of the likely accuracy of the computed barrier height of reaction (2). Table 1 shows the results for $\Delta_r H^o(0 \text{ K})$ along with evaluated experimental data from the JANAF[20] and the Active Thermochemical Tables (ATcT, used in Ref. 2).

The computed reaction enthalpy $\Delta_r H^o(0 \text{ K})$ is in close accord with the literature values within their stated uncertainties, even within the small ATcT uncertainty of 0.6 kJ mol^{-1}. There is also accord with the less precise JANAF value. The main difference between the two literature values is due to the fact that in the 50 years since the JANAF data sheet for CF$_3$ was prepared, more accurate and precise information has become available for CF$_3$ (a value of −467.5 kJ mol^{-1} for the enthalpy of formation of CF$_3$ was given in Ref. 20, in contrast to a value of −465.1 kJ mol^{-1} from Ref. 4).

Inspection of the individual components in Equation (12) (see Table SI-2) shows that the smallest contributions to the reaction enthalpy and barrier height are from the last three terms, where the impacts of electron correlation beyond perturbative triples, diagonal Born–Oppenheimer effects, and scalar relativistic terms are between −2.1 and −0.4 kJ mol^{-1} for each correction. Zero-point vibrational energy largely cancels for the vibrationally adiabatic barrier height $\Delta H^{\#}(0 \text{ K})$ (where it contributes 4 kJ mol^{-1}), while it contributes 11 kJ mol^{-1} to $\Delta_r H^o(0 \text{ K})$. That these influences are modest, thanks to cancellation between reactants and products, may be the reason why a much simpler analysis such as the CBS-QB3[21] approach performs fairly well. Depending on the context, deviations of up to 3 kJ mol^{-1} for a savings of several orders of magnitude in computer time may be an appropriate compromise.

The rate constant k_2 was calculated via simple transition state theory (TST), incorporating an Eckart tunneling correction, and based on the estimated fundamental vibrational frequencies. The results over the temperature range 1000–3000 K can be well fitted by the expression

$$k_2 = 2.18 \times 10^{14} (T/1000K)^{1.96}$$
$$\times \exp\left(-179.9 \text{ kJmol}^{-1}/RT\right) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}. \quad (16)$$

A comparison with the rate constant results from the simpler methods mentioned above is given in Table 2. A comparison of the barrier heights computed with these methods is given in Table S-1 of the Supporting Information. Notably the BMK and M06-2X functionals, and CCSD(T) theory, performed well with values within 4 kJ mol^{-1} of our best estimate. The comparison of simpleTST rate constants in Table 2 reveals the best performance is

TABLE 2 Comparison of calculated and measured rate constants k_2 (in $cm^3\ mol^{-1}\ s^{-1}$)

Model	1000 K	1200 K	1600 K	2000 K	2500 K
BAC-MP4[a]	1.61×10^5	6.85×10^6	8.18×10^8	1.56×10^{10}	1.77×10^{11}
G2(MP2)[a]	1.85×10^4	9.70×10^5	1.52×10^8	3.43×10^9	4.51×10^{10}
BMK	2.79×10^4	1.49×10^6	2.35×10^8	5.27×10^9	6.83×10^{10}
M06-2X	2.30×10^4	1.27×10^6	2.10×10^8	4.85×10^9	6.41×10^{10}
ωB97X-D	1.00×10^5	4.36×10^6	5.35×10^8	1.04×10^{10}	1.19×10^{11}
G4//BMK	6.24×10^4	2.91×10^6	3.89×10^8	7.88×10^9	9.43×10^{10}
G4//M06-2X	6.42×10^4	2.99×10^6	3.99×10^8	8.10×10^9	9.66×10^{10}
G4//ωB97X-D	7.14×10^4	3.29×10^6	4.33×10^8	8.79×10^9	1.04×10^{11}
CCSDT(Q) = full/CBS[b]	8.74×10^4	4.60×10^6	7.34×10^8	1.70×10^{10}	2.29×10^{11}
CCSDT(Q) = full/CBS[c]	7.51×10^4	3.86×10^6	5.97×10^8	1.36×10^{10}	1.80×10^{11}
Experimental[d]		7.81×10^6	7.62×10^8		
Experimental[e]		4.44×10^6	7.73×10^8		

[a]Simple TST calculations from Ref. 8.

[b]Simple TST results from Equation (16).

[c]Refined results from Equation (17) including variational corrections.

[d]Experimental values from Ref. 5, that is, Equation (7), reevaluation with k_5/k_6 from Ref. 20 would increase k_2 by a factor of 1.06.

[e]Reevaluated experimental values from Ref. 6, using the measured k_2/k_7 and k_7 from Ref. 7).

with ωB97X-D density functional theory, which yields rate constants to within a factor of 2 of our best estimate.

Quantum mechanical tunneling is not very important for reaction (2), decreasing from a factor of 1.6 at 1000 K, through a factor of 1.3 at 1400 K when its rate constant is about $6 \times 10^7\ cm^3\ mol^{-1}\ s^{-1}$, to a factor of 1.08 at 2500 K. Because of the high enthalpy barrier, the transition state is tightly located and variational effects are not expected to be large. To explore this idea quantitatively, classical canonical variational transition state theory (essentially maximization of the Gibbs energy of activation, with no tunneling) was implemented at the M06-2X/6-311++G(3df,3p) level of theory, chosen because it reasonably reproduces the high-level barrier calculations at a feasible cost for analysis along the reaction coordinate. We find the influence of vibrational and rotational entropy to be small, and the effect is to reduce the computed k_2 by 16% at 1000 K and 24% at 3000 K. Incorporating these corrections finally yields an improved rate constant expression

$$k_2 = 1.64 \times 10^{14}(T/1000\ \text{K})^{1.95}$$
$$\times \exp\left(-178.8\ \text{kJmol}^{-1}/RT\right)\ cm^3 mol^{-1} s^{-1}. \quad (17)$$

Vibrational anharmonicity has an important influence, increasing the rate constant by close to a factor of 4, through large reductions (25–30%) of the frequencies of the two lowest pairs of bending modes in the transition state. These are H–F*–C and F*–C–F bending, where F* is the departing F atom. For comparison, an error of 5 kJ mol^{-1} leads to a much smaller change in the rate constant, by a factor of 1.5 at 1500 K. Thus, a more detailed

analysis of the anharmonic frequencies in the TS would be desirable.

With respect to the calculations in 1997 by Berry et al.,[8] their G2(MP2) barrier height is fairly accurate, but the rate constants were lower than those reported in Ref. 6 by Kochubei and Moin by almost an order of magnitude. This likely reflects a too tight transition state (perhaps arising from vibrational frequencies that are too large). It is argued above that the experiments may need a reinterpretation. When the experiments of Ref. 6 are reevaluated with the more recent k_7 from Ref. 8, this leads to smaller experimental values of k_2 (see Table 2). The BAC-MP4 calculations yield the smallest barrier in Table SI-1, yet appeared in 1997 to match experimental rate constants well. This reveals a fortuitous cancellation of a too low computed barrier and a somewhat too high of an experimental value of k_2.

5 | CONCLUSIONS

The comparison in Table 2 of the calculated k_2 with the experimental values from Refs. 5 and 6 (the latter after recalibration with the more recent value for k_7 from Ref. 8) support the suggestion from the introduction of this article, that is, that Equation (7) overestimates k_2. Nevertheless, the difference between the reevaluated experimental values and the refined theoretical results from the present work is only small. Figure 1 illustrates this conclusion. However, it was also shown in the present article that in further modelings of the hydrogenation of CF_4 one needs to account for the fact that the dominant
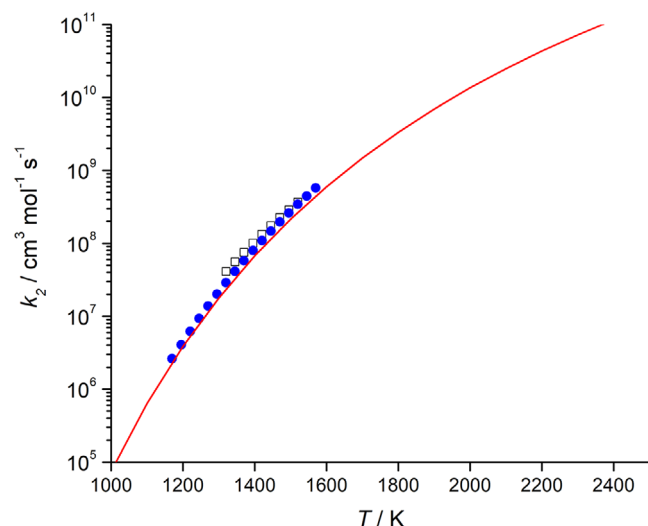
FIGURE 1 Rate constants k_2 (full line: calculation from the present work, Equation (17); open squares: fit by Equation (7) of the experimental data from Ref. 5; filled circles: fit of the experimental data from Ref. 6 after recalibration with more recent values for k_g, for example, from Ref. 7; see the text) [Color figure can be viewed at wileyonlinelibrary.com]

source of hydrogen atoms may not be the thermal dissociation of H_2, but the reaction of fluorine atoms F or CF_3 radicals with H_2, after F and CF_3 have been formed by thermal dissociation of CF_4. It, therefore, may appear surprising that the reevaluated experimental results from Ref. 6 agree so well with the refined calculations. This may change when higher temperatures than those used in Refs. 5 and 6 are of interest. In further work, the square root dependence on $[H_2]^{1/2}$ of Equation (4) also needs to be explained for the case when hydrogen atoms are dominantly formed by reaction of F and CF_3 with H_2. This was beyond the scope of the present work.

Finally, Table 2 illustrated that various simple theoretical treatments agreed relatively well with the refined results from Equation (17) which has to be attributed to fortuitous cancellations of contributions. Such cancellation is less effective for the overall reaction enthalpy.

ORCID
Jürgen Troe https://orcid.org/0000-0002-4347-0307

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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