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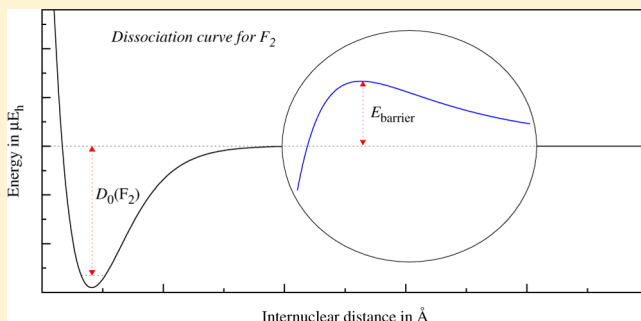
Dissociation of the Fluorine Molecule

Botond Csontos, Balázs Nagy, József Csontos,* and Mihály Kállay

Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, P.O. Box 91, Budapest H-1521, Hungary

Supporting Information

ABSTRACT: The primary purpose of the present study is to resolve the discrepancy that exists between the two most recently published dissociation energies for the fluorine molecule [$D_0(\text{F}_2)$] and, consequently, for the associated heats of formation of the fluorine atom [$\Delta_f H_0^\circ(\text{F})$]. We hope to provide a reliable, well-established theoretical estimate for these thermochemical quantities. To this end, a high-accuracy coupled-cluster-based composite ab initio model chemistry has been utilized. The protocol involves contributions of up to pentuple excitations in coupled-cluster theory augmented with basis set extrapolation techniques and additional corrections beyond the nonrelativistic and Born–Oppenheimer approximations. The augmented core–valence correlation consistent basis set families, aug-cc-pCVXZ, have been successively used, in some cases, up to octuple- ζ quality. Our best theoretical results for $D_0(\text{F}_2)$ and $\Delta_f H_0^\circ(\text{F})$ obtained in this study are 154.95 ± 0.48 and 77.48 ± 0.24 kJ/mol, respectively. Because conflicting theoretical results are also reported about the existence of a barrier along the dissociation curve of F_2 , extensive multireference configuration interaction and coupled-cluster calculations have been performed using reference orbitals taken from all-electron complete active space self-consistent field computations. Extrapolations from the results obtained with the aug-cc-pCVXZ ($X = \text{T, Q, 5}$) basis sets clearly indicate that the barrier indeed exists. It is located at 3.80 ± 0.20 Å along the dissociation curve with a height of $42 \pm 10 \mu\text{E}_h$ ($\sim 0.11 \pm 0.03$ kJ/mol). Because of the neglect of this effect during the evaluation of the raw experimental data used to obtain $D_0(\text{F}_2) = 154.52 \pm 0.12$ kJ/mol and $\Delta_f H_0^\circ(\text{F}) = 77.26 \pm 0.06$ kJ/mol [Stevens; et al. *J. Phys. Chem. A* **2010**, *114*, 13134], an additional error should be attached to these latter values. Obviously, the barrier does not affect either the experimental results, $D_0(\text{F}_2) = 154.92 \pm 0.10$ kJ/mol and $\Delta_f H_0^\circ(\text{F}) = 77.46 \pm 0.05$ kJ/mol [Yang; et al. *J. Chem. Phys.* **2005**, *122*, 134308; **2007**, *127*, 209901], which are based on the ion-pair dissociation of the molecule, or the data calculated theoretically. It is also noteworthy that our best estimates are in excellent agreement with those obtained from the ion-pair dissociation experiment.



1. INTRODUCTION

The first reliable report on the dissociation energy of the fluorine molecule at 0 K, $D_0(\text{F}_2)$, is the 1976 paper of Colbourn and co-workers.¹ In that study, $D_0(\text{F}_2)$ was determined as 154.56 ± 0.60 kJ/mol from the high-resolution absorption spectra of fluorine. This result is in good agreement with several previous experimental findings.^{2–7} Taking the half of Colburn's dissociation energy data 77.28 ± 0.30 kJ/mol can be obtained for the heat of formation of the fluorine atom at 0 K [$\Delta_f H_0^\circ(\text{F})$]. This value is recommended by most thermochemical databases, e.g., CODATA,⁸ NIST-JANAF,⁹ Gurvich's book,¹⁰ the JPL compendium,¹¹ and Burcat's thermochemical tables.¹²

Within its associated uncertainty, this data is consistent with the two most recent $\Delta_f H_0^\circ(\text{F})$ values, viz., the experimental result of 77.46 ± 0.05 kJ/mol by Yang and associates^{13,14} as well as that of 77.26 ± 0.06 kJ/mol^{15,16} listed in the Active Thermochemical Tables (ATcT).¹⁷ The former result can be derived from $D_0(\text{F}_2)$, 1.6056 ± 0.0010 eV (154.92 ± 0.10 kJ/mol), obtained by Yang and co-workers^{13,14} by measuring the threshold for ion-pair dissociation of the fluorine molecule and

combining it with well-established literature data for the ionization potential and electron affinity of the fluorine atom. The ATcT value, 77.26 ± 0.06 kJ/mol, is obtained from the latest version of the ATcT database.¹⁸ Although both of the two recent values surpass Colbourn's earlier result in accuracy, they are not consistent. The discrepancy between them, 0.20 kJ/mol, is larger than the sum, 0.11 kJ/mol, of the corresponding error bars, 0.05 and 0.06 kJ/mol, associated with the data provided by Yang and associates and the ATcT approach, respectively.

The accurate calculation of $D_0(\text{F}_2)$ and, consequently, that of $\Delta_f H_0^\circ(\text{F})$ has been the subject of numerous theoretical studies utilizing various composite model chemistries. These results are summarized in Table 1 and discussed briefly in the following.

The earlier families of thermochemical protocols, viz., the Gaussian- n ^{19–22} theories of Pople and co-workers and the complete basis set (CBS) approach of Petersson and

Received: April 5, 2013

Revised: June 1, 2013

Published: June 3, 2013

Table 1. Previous Results on the Dissociation Energy of the Fluorine Molecule [$D_0(\text{F}_2)$] and Standard Heat of Formation of the Fluorine Atom at 0 K $\Delta_f H_0^\circ(\text{F})$] (All Values in kJ/mol)

investigation	$D_0(\text{F}_2)$	$\Delta_f H_0^\circ(\text{F})$
Colbourn (1976) ^a	154.56 \pm 0.60	77.28 \pm 0.30
Yang (2005, 2007) ^b	154.92 \pm 0.10	77.46 \pm 0.05
ATcT (2010) ^c	154.52 \pm 0.12	77.26 \pm 0.06
G1 (1989) ^d	156.90	78.45
G2 (1991) ^e	153.13	76.57
G3 (1999) ^f	158.32	79.16
CBS-4 (1996) ^g	135.98	67.99
CBS-Q (1996) ^g	157.32	78.66
CBS-QB3 (1999) ^h	154.81	77.40
Feller (1999) ⁱ	160.25	80.12
Feller (2003) ^j	152.30	76.15
Feller (2008) ^k	154.39 \pm 0.84	77.19 \pm 0.42
W1 (1999) ^l	152.38	76.19
W2 (1999) ^l	152.05	76.02
W3 (2004) ^l	154.93	77.47
W3A (2004) ^l	154.52	77.26
W3K (2004) ^l	154.39	77.19
W4a (2004) ^l	154.64	77.32
W4b (2004) ^l	154.01	77.01
W2.2 (2006) ^m	151.21	75.60
W3.2 (2006) ^m	153.64	76.82
W4lite (2006) ^m	154.18	77.09
W4 (2006) ^m	154.14	77.07
W4.2 (2006) ^m	154.26	77.13
W4.3 (2006) ^m	154.68	77.34
W4.4a (2007) ⁿ	154.60	77.30
W4.4b (2007) ⁿ	154.56	77.28
HEAT (2004) ^o	154.44	77.22
HEAT-345(Q) (2008) ^p	154.91	77.46
HEAT-456QP (2008) ^p	154.48	77.24
HEAT-456Q (2008) ^p	154.32	77.16
HEAT-456(Q) (2008) ^p	154.76	77.38

^aReference 1. ^bReferences 13 and 14. ^cReference 17. ^dReference 19.^eReference 20. ^fReference 32. ^gReference 27. ^hReference 28.ⁱReference 29. ^jReference 30. ^kReference 31. ^lReference 33.^mReference 34. ⁿReference 35. ^oReference 36. ^pReference 38.

associates^{23–28} yield $\Delta_f H_0^\circ(\text{F})$ values from 67.99 to 79.16 kJ/mol. If one takes into account that the target accuracy of these models was planned to be a few kJ/mol, then the aforementioned results seem to be acceptable. Nevertheless, several more sophisticated model chemistries that pursue more ambitious and challenging accuracy ranges have been used to calculate $\Delta_f H_0^\circ(\text{F})$.

In a study based on the coupled-cluster (CC) singles, doubles, and perturbative triples [CCSD(T)] method Feller and Peterson²⁹ obtained $\Delta_f H_0^\circ(\text{F}) = 80.12$ kJ/mol. In their work the frozen-core (FC) CCSD(T) calculations were further augmented by (i) scalar relativistic calculations, (ii) experimental spin–orbit contributions, and (iii) taking into account the effects of electron correlation in the core region. The FC-CCSD(T) total energy was extrapolated to the complete basis set (CBS) limit using the aug-cc-pV(Q,5,6)Z basis sets and an exponential formula. The contribution due to the core–core and core–valence electron correlation was obtained from CCSD(T)/cc-pwCVQZ calculations, whereas the scalar

relativistic contribution was obtained at the FC-CISD/cc-pVTZ level of theory.

In a subsequent extensive study, Feller and associates³⁰ investigated the performance of their composite approach on small halogenated species, and obtained 76.15 kJ/mol for $\Delta_f H_0^\circ(\text{F})$. The computational method was similar to that used in ref 29 and described above, but the contribution of the scalar relativistic effects was obtained from Douglas–Kroll–Hess (DKH) calculations at the FC-CCSD(T)/cc-pVQZ level and the FC-CCSD(T) total energies were extrapolated from results obtained with the aug-cc-pV(5,6)Z basis sets using a two-point formula.

Recently, Feller and co-workers³¹ surveyed several factors that contribute to the accurate theoretical predictions of atomization energies and molecular structures. Beyond the extrapolated FC-CCSD(T) contribution, their composite method included extrapolated core–core and core–valence contributions, higher-order CC singles, doubles, and triples (CCSDT) and CCSDT with perturbative quadruples [CCSDT(Q)], estimated full configuration interaction (FCI) energies along with second-order DKH computations as well as harmonic and anharmonic contributions to the zero-point vibrational energy (ZPE). This approach yielded $\Delta_f H_0^\circ(\text{F}) = 77.19 \pm 0.42$ kJ/mol.

The Weizmann-*n* (W_{*n*}) family of model chemistries,^{32–35} developed by Martin and associates to provide atomization energies and other thermochemical quantities in the kJ/mol as well as in the sub-kJ/mol accuracy range, has also been utilized to calculate $\Delta_f H_0^\circ(\text{F})$. Early members of these protocols, the W1 and W2 methods,³² yielded, respectively, 76.19 and 76.02 kJ/mol for $\Delta_f H_0^\circ(\text{F})$. The different variants of the W3 and W4 models,³³ W3, W3A, W3K, W4a, and W4b provided 77.47, 77.26, 77.19, 77.32, and 77.01 kJ/mol, respectively, for $\Delta_f H_0^\circ(\text{F})$. Subsequently, W4 theory has undergone further development and several other versions of the model have been proposed.³⁴ In addition, more accurate variants of the previously established W2 and W3 methods also appeared. The application of W2.2, W3.2, W4lite, W4, W4.2, and W4.3 yielded 75.60, 76.82, 77.09, 77.07, 77.13, and 77.34 kJ/mol, respectively, for $\Delta_f H_0^\circ(\text{F})$. The two most recent variants of the W4 protocol, W4.4a and W4.4b,³⁵ which differ in the treatment of the extrapolated valence CCSD(T) contribution, provided, respectively, 77.30 and 77.28 kJ/mol.

The above-mentioned model chemistries have a notable common feature: the electron correlation problem in the valence and core regions is treated at different levels. In the high-accuracy extrapolated ab initio thermochemistry (HEAT) approach^{36–38} both regions are handled equally. For $\Delta_f H_0^\circ(\text{F})$ the original HEAT protocol (or HEAT-345Q if we use the notation introduced in ref 37) provided 77.22 kJ/mol.³⁶ Several variants of the original protocol have been proposed to achieve even higher accuracy or reduce computational cost. An important simplification deals with the treatment of the higher-order CC contributions, in particular, the iterative CCSDTQ calculation is replaced by the CCSDT(Q) method. This led to the HEAT-345(Q) method³⁷ whose slightly modified versions were recently applied to several atmospherically important chemical species.^{39–42} For the fluorine atom the HEAT-345(Q) approach yielded $\Delta_f H_0^\circ(\text{F}) = 77.46$ kJ/mol.³⁸ Besides other important factors, such as the treatment of higher-order correlation, diagonal Born–Oppenheimer correction (DBOC) at the correlated level or the separation of the core and valence correlation contribution, the effects of the

basis set sizes on the extrapolated results have also been discussed in detail in the most recent HEAT paper.³⁸ In particular, the HEAT-345 protocol has been extended to HEAT-456 where the numbers refer to cardinal numbers of the basis sets applied in the extrapolation formulas; i.e., the former model uses aug-cc-pCV(T,Q,5)Z basis sets to estimate the Hartree–Fock self-consistent field (HF-SCF) and CCSD(T) limit energies whereas the latter employs the aug-cc-pCV-(Q,5,6)Z sets. Consequently, extension of the original HEAT-345Q and the HEAT-345(Q) model chemistries led to the HEAT-456Q and HEAT-456(Q) methods which yielded, respectively, 77.16 and 77.38 kJ/mol for $\Delta_f H_0^\circ(\text{F})$.³⁸ When these results are compared with those obtained by the original methods, it is clear that no convergence has been reached with the HEAT-345-based protocols.

Recently, in a series of papers Bytautas and co-workers^{43–46} studied the ab initio potential energy curve for the dissociation of the F_2 molecule. In their most recent study,⁴⁶ the long-range interactions along the dissociation curve were studied using calculations at the complete active space self-consistent field (CASSCF) and multireference configuration interaction singles and doubles (MR-CISD) levels of theory, including the Davidson correction for the latter (MR-CISD+Q). The nonaugmented cc-pVQZ and cc-pCVQZ basis sets were used for the valence-only and core-correlation calculations, respectively. Additional contributions due to spin–orbit coupling and scalar relativistic effects were also taken into account. Near the internuclear separation of 4 Å a barrier was found along the dissociation curve calculated at the MR-CISD/cc-pVTZ level of theory. Considering the long-range interactions it was concluded in ref 46 that the repulsive interaction between the atomic quadrupoles is inversely proportional to the fifth power of the internuclear distance R , whereas the attractive London dispersion interaction is proportional to R^{-6} . The different decay rates of the two interactions with respect to R resulted in a barrier with a height of approximately +40 μE_h (~ 0.10 kJ/mol).⁴⁶

In contrast to the above results, Evangelista and co-workers⁴⁷ have found no trace of the barrier. In their extensive investigation on the implementation of the state-specific multireference coupled-cluster (SS-MRCC) theory of Mukherjee and co-workers,^{48,49} calculations with single and double excitations (SS-MRCCSD) have been performed. The reference orbitals for the correlated calculations were CASSCF-(2,2) natural orbitals (i.e., two electrons in two orbitals were included in the active space), and the dissociation curve was calculated with the cc-pVTZ basis set.

The discrepancies between the best estimates for D_0 and $\Delta_f H_0^\circ$ as well as the uncertainty surrounding the existence of the barrier are crucial points that need to be clarified. We note here that the existence of a barrier only affects those D_0 values derived from experiments based on the symmetric bond breaking of the molecule. This means that the barrier leaves the result of Yang et al.^{13,14} unchanged because their $D_0(\text{F}_2)$ value is established by measuring the threshold energy for the ion-pair production of F_2 . On the other hand, the ATcT^{15–17} approach uses $D_0(\text{F}_2)$ reported by Colbourn and co-workers,¹ which is derived from extrapolation of the vibrational levels for the ground state F_2 molecule to the dissociation limit. In this latter case the barrier may slightly increase the dissociation limit and, consequently, this effect has an influence on the final dissociation energy. Therefore, an additional error may be introduced into experimental values of $D_0(\text{F}_2)$ and $\Delta_f H_0^\circ(\text{F})$

derived from homolytic dissociation studies. Because this error could be at least as large as the barrier height itself, reliable and accurate theoretical estimate for this effect is undoubtedly desirable.

Because the value of $D_0(\text{F}_2)$ can be calculated in a manner that it is by definition not affected by the shape of the dissociation curve, it is also advantageous to establish a benchmark theoretical value for it by means of a highly accurate ab initio model chemistry that is reasonably built from a set of properly converged contributions calculated at the highest levels of theory affordable. On the other hand, the need for an exhausting high-level multireference study on the dissociation curve is clearly necessary.

2. METHODS

2.1. Total Energies. Total energies were calculated, assuming the additivity of the various contributions, according to the following scheme,

$$E = E_{\text{HF}} + \Delta E_{\text{MP2}} + \Delta E_{\text{CCSD}} + \Delta E_{(\text{T})} + \Delta E_{\text{T}} + \Delta E_{(\text{Q})} \\ + \Delta E_{\text{Q}} + \Delta E_{(\text{P})_{\Lambda}} + \Delta E_{\text{P}} + \Delta E_{\text{DBOC}} + \Delta E_{\text{SR}} \\ + \Delta E_{\text{DC}} + \Delta E_{\text{Gaunt}} \quad (1)$$

In eq 1 E_{HF} is the HF-SCF energy. To reach the CBS limit, the extrapolation of the HF energies is a widely applied procedure, and several extrapolation formulas have been devised in the literature.^{50–53} In this study the two-point extrapolation formula of Karton and Martin,⁵³ $E(X) = E_{\text{CBS}}^{\text{HF}} + a(X + 1)\exp(-9\sqrt{X})$, was used.

ΔE_{MP2} is the correlation energy evaluated by the second-order Møller–Plesset (MP2) method⁵⁴ and extrapolated to the basis set limit. To extrapolate the correlation energy to the CBS limit, the two-point formula

$$E(X) = E_{\text{CBS}} + B \cdot X^{-3} \quad (2)$$

was utilized as recommended by several authors.^{55–57} ΔE_{CCSD} and $\Delta E_{(\text{T})}$ are the correlation contributions defined as $\Delta E_{\text{CCSD}} = \Delta E_{\text{CCSD}} - \Delta E_{\text{MP2}}$ and $\Delta E_{(\text{T})} = E_{\text{CCSD}(\text{T})} - E_{\text{CCSD}}$, where E_{MP2} , E_{CCSD} , and $E_{\text{CCSD}(\text{T})}$ are the total energies obtained with the MP2,⁵⁴ CCSD,⁵⁸ and CCSD(T)⁵⁹ methods, respectively. The ΔE_{CCSD} and $\Delta E_{(\text{T})}$ contributions were also extrapolated to the basis set limit using the aforementioned formula.

The correlation energy was also investigated beyond the CCSD(T) level using higher excitations in CC theory.⁶⁰ The CCSDT,^{61,62} CCSDT(Q),^{63–65} the CCSDT with iterative quadruples (CCSDTQ),^{66,67} and the CCSDTQ including perturbative pentuples [CCSDTQ(P)_Λ]^{64,65} contributions were also extrapolated to the basis set limit. The effect of the iterative pentuple excitations (CCSDTQP)⁶⁴ was calculated with the cc-pVDZ basis set. These higher-order CC contributions were defined as follows: $\Delta E_{\text{T}} = E_{\text{CCSDT}} - E_{\text{CCSD}(\text{T})}$, $\Delta E_{(\text{Q})} = E_{\text{CCSD}(\text{Q})} - E_{\text{CCSDT}}$, $\Delta E_{\text{Q}} = E_{\text{CCSDTQ}} - E_{\text{CCSDT}(\text{Q})}$, $\Delta E_{(\text{P})_{\Lambda}} = E_{\text{CCSDTQ}(\text{P})_{\Lambda}} - E_{\text{CCSDTQ}}$, and $\Delta E_{\text{P}} = E_{\text{CCSDTQP}} - E_{\text{CCSDTQ}(\text{P})_{\Lambda}}$, where E_X is the total energy obtained with the corresponding method X. In the CCSDTQ(P)_Λ and CCSDTQP calculations the effects of the core–electrons were not studied; e.g., the FC approximation was used in these cases.

The deficiencies of the Born–Oppenheimer approximation were corrected by calculating ΔE_{DBOC} at the CCSD/cc-pCVXZ ($X = \text{D}, \text{T}, \text{Q}$) level as described in ref 68.

The scalar relativistic contributions (ΔE_{SR}) were taken into account using the fourth-order DKH Hamiltonian⁶⁹ in CCSD(T), CCSDT, and CCSDT(Q) calculations. ΔE_{DC} is defined as the difference of energies between the four-component Dirac–Coulomb^{70,71} and the DKH treatment; in these calculations the relativistic CCSD(T), CCSDT, and CCSDT(Q)⁷² methods with uncontracted aug-cc-pCVXZ basis sets were used. The Gaunt correction, ΔE_{Gaunt} which is the lowest order quasi-Lorentz-invariant correction to the Coulomb term of the Dirac–Coulomb Hamiltonian,⁷³ was obtained with the HF method using uncontracted aug-cc-pCVXZ basis sets. In addition, approximate values of the leading quantum electrodynamic (QED) corrections, the one- and two-electron Lamb-shift effects, ΔE_{Lamb}^1 and ΔE_{Lamb}^2 , respectively, were evaluated by simply rescaling the corresponding one- and two-electron Darwin terms obtained at the all-electron CCSD(T) level using uncontracted aug-cc-pCVXZ basis sets.⁷⁴

The nonrelativistic CCSDT(Q), CCSDTQ, and CCSDTQP calculations were carried out with the MRCC suite of quantum chemical programs⁷⁶ interfaced to the C_{FOUR} package.⁷⁷ In the DKH calculations at the CCSD(T) level, the MOLPRO package⁷⁸ was utilized, whereas the CCSDT and CCSDT(Q) terms were calculated with the MRCC code interfaced to MOLPRO. The four-component Dirac–Coulomb and Dirac–Coulomb–Gaunt calculations at the CCSD(T) and HF levels, respectively, were performed with the DIRAC code.⁷⁹ The higher-order coupled-cluster calculations of the Dirac–Coulomb term were evaluated with MRCC interfaced to DIRAC. Calculations that involved basis sets with angular momentum k and l were performed with the Psi3 package.⁸⁰ All other results were obtained with C_{FOUR}.⁷⁷

For the fluorine molecule the ZPE correction of 3.63 kJ/mol,⁸¹ and the equilibrium bond length of 1.4124 Å,⁸² were taken from experiment.

The remaining errors in the various extrapolated contributions discussed below were estimated as the signed difference between the results obtained with $(X - 2, X - 1)$ - and $(X - 1, X)$ -based extrapolations where X is the cardinal number of the largest aug-cc-pCVXZ basis set used to calculate the contribution in question. That is, the $(X - 2, X - 1)$ -based value was subtracted from the $(X - 1, X)$ -based one. Similarly, in the case of the nonextrapolated terms, errors were obtained by subtracting the result obtained with the $(X - 1)$ basis set from that calculated using the basis set with the highest cardinal number X .

2.2. Basis Sets. The aug-cc-pCV7Z and aug-cc-pCV8Z basis sets for fluorine have been developed during this study. They were assembled according to the principles laid down by Dunning and co-workers for the preceding members of the correlation consistent basis set family.^{83–88} To obtain the core–valence (CV) 7- ζ basis set, the aug-pV7Z basis set of Feller and Peterson²⁹ obtained from the Environmental Molecular Sciences Laboratory Basis Set Library^{89,90} was extended with core functions. The k -function exponents were extracted from the basis set library of the Psi3 package.⁸⁰ The exponents of the core functions, 6s6p5d4f3g2h1i, added to the basis set were optimized with the second-order Møller–Plesset (MP2)⁵⁴ method and restricted to be even-tempered. Previous experience with core functions⁹¹ and test calculations (Table S15 in the Supporting Information) show that this level of theory is sufficient to obtain accurate exponents in the core region.

The aug-cc-pCV8Z basis set was generated from scratch. The initial (sp) set was selected to be (22s14p). The exponents in the initial (sp) set were fully optimized in restricted open-shell HF calculations. The exponents of the polarization, 7s7p7d6f5g4h3i2k1l, and core, 7s7p6d5f4g3h2i1k, functions were restricted to be even-tempered. During the determination of the augmenting functions no constraint was forced. The exponents of the polarization and core functions were optimized in CCSD(T) and MP2 calculations, respectively. To optimize the exponents of the basis functions, the downhill simplex method of Nelder and Mead⁹² was implemented. For the optimization of the (sp) sets the TURBOMOLE package⁹³ was used. Other calculations related to basis set development were carried out by the Psi3 package.⁸⁰

2.3. Dissociation Curve. To locate the exact position and determine the height of the above-mentioned barrier on the dissociation curve, fully uncontracted MR-CISD⁹⁴ calculations have been performed. With the intention of overcoming the size-consistency problem of the MR-CISD method and ensuring that the barrier is not the consequence of this issue several additional approaches have been applied. On one hand, the multireference analog of the Davidson correction^{95–97} was added to the MR-CISD results (MR-CISD+Q). On the other hand, the dissociation curve has been calculated with the multireference averaged coupled-pair functional (MR-ACPF),⁹⁸ the multireference averaged quadratic coupled-cluster (MR-AQCC),^{99,100} and the single-reference-based multireference coupled-cluster (SRMRCC)^{67,101,102} methods using CASSCF reference orbitals. For SRMRCC, single and double (SRMRCCSD) as well as single, double, and triple (SRMRCCSDT) excitations were considered.

As been discussed previously,^{44,103–106} in the full-valence CASSCF calculations of molecules N₂, O₂, and F₂ the 2s (2 σ_g and 2 σ_u , D_{2h} symmetry) orbitals become doubly occupied and mix with the 1s (1 σ_g and 1 σ_u , D_{2h} symmetry) core orbitals. This mixing does not affect the CASSCF results but artificially raises the CI energy if the core orbitals are not correlated. To avoid this artifact, the reference orbitals for the correlated multireference methods were taken from all-electron CASSCF calculations; i.e., all 18 electrons in a total of 10 orbitals were included in the active space [CASSCF(18,10)] and the core orbitals were also correlated. However, they were set to be doubly occupied in all reference configurations. During the selection of the configuration space for the MR- N calculations, where N stands for CISD(+Q), ACPF, or AQCC, reference configurations with symmetries other than the proper state symmetry were also included. In this manner the MR- N results become comparable with those obtained with the SRMRCC method which includes reference configurations with all spatial symmetries.

Relative energies along the dissociation curve, $V(R)$ where R is the internuclear distance, were calculated as follows:

$$V(R) = E(R) - E(\infty) \quad (3)$$

$$E(R) = E_{\text{CASSCF}}(R) + \Delta E_{\text{MR-}N}(R) \quad (4)$$

In eq 4, $E_{\text{CASSCF}}(R)$ is the CASSCF(18,10) total energy obtained with the aug-cc-pCV5Z basis set.⁸⁸ $\Delta E_{\text{MR-}N}(R)$ is the correlation energy defined as $\Delta E_{\text{MR-}N}(R) = E_{\text{MR-}N}(R) - E_{\text{CASSCF}}(R)$, where the corresponding total energies were calculated with the aug-cc-pCVXZ ($X = Q, 5$) basis sets. Using the two-point formula of eq 2, the energy differences, $\Delta E_{\text{MR-}N}$, were extrapolated to the complete basis set limit. By

Table 2. Nonrelativistic Contributions (kJ/mol) to the Dissociation Energy of Fluorine, $D_0(\text{F}_2)$, at Various Levels of Theory

X^a	E_{HF}^b	ΔE_{MP2}^b	ΔE_{CCSD}^b	$\Delta E_{(\text{T})}^b$	higher-order terms					
					ΔE_{T}^b	$\Delta E_{(\text{Q})}^b$	ΔE_{Q}^c	$\Delta E_{(\text{P})\text{L}}^d$	ΔE_{P}^e	ΔE_{DBOC}^e
2	−166.23	314.17	−45.57	22.42	−0.32	4.67	−0.54	0.16	0.00	0.00
3	−154.73	329.26	−53.40	30.81	−1.09	4.14	−0.52	0.29		0.01
4	−155.50	335.60	−55.35	32.24	−1.09	4.24				0.01
5	−155.53	338.00	−56.32	32.73	−1.14					
6	−155.54	339.14	−56.82	32.93	−1.18					
7	−155.54	339.71	−57.08	33.03						
8	−155.54	340.07	−57.26	33.07						
(D,T) ^f	−153.78	335.62	−56.70	34.34	−1.41	3.91	−0.51	0.34		
(T,Q) ^f	−155.60	340.22	−56.77	33.28	−1.10	4.31				
(Q,5) ^f	−155.53	340.53	−57.33	33.25	−1.20					
(5,6) ^f	−155.54	340.70	−57.51	33.21	−1.24					
(6,7) ^f	−155.54	340.68	−57.53	33.19						
(7,8) ^f	−155.55	340.80	−57.62	33.17						
error ^g	−0.01	0.12	−0.09	−0.02	−0.04	0.07 ^h	0.01	0.05	0.00	0.00

^aCardinal number of the basis set used. ^bResults obtained with aug-cc-pCVXZ basis sets. ^cResults obtained with the aug-cc-pVXZ basis. ^dResults obtained with cc-pVXZ basis sets. ^eResults obtained at the CCSD/aug-cc-pCVXZ level of theory. ^fBasis sets with cardinal numbers ($X - 1, X$) were used to extrapolate the HF energies using the exponential formula $E(X) = E_{\text{CBS}}^{\text{HF}} + a(X + 1)\exp(-9\sqrt{X})$ and correlation contributions with the cubic formula $E(X) = E_{\text{CC}}^{\infty} + B \cdot X^{-3}$ to the basis set limit. ^gSee the Methods for the definition of the remaining error. ^hObtained by subtracting the pure aug-cc-pCVQZ result from the (T,Q) extrapolated value.

full analogy with the MR- N methods, relative energies of the SRMRCCSD curve were calculated according to eq 3, where, in this case, $E(R)$ was obtained as

$$E(R) = E_{\text{CASSCF}}(R) + \Delta E_{\text{SRMRCCSD}}(R) \quad (5)$$

In eq 5, E_{CASSCF} is the all-electron CASSCF energy calculated with the aug-cc-pCV5Z basis set and $\Delta E_{\text{SRMRCCSD}}(R)$ is the correlation contribution obtained by extrapolations from the aug-cc-pCV(T,Q)Z results. Calculations involving contributions from triple excitations (SRMRCCSDT) were performed using the aug-cc-pCVTZ basis set. In these calculations the maximum level of excitations in the cluster operator was set to four; i.e., only the quadruple excitations were taken into consideration. Further restrictions were also imposed on the cluster operators by dropping those triple clusters which have more than two inactive particle/hole labels.¹⁰⁷ The final values of this contribution were obtained by substituting $\Delta E_{\text{SRMRCCSDT}}(R)$ for $\Delta E_{\text{SRMRCCSD}}(R)$ in eq 5, where the iterative triples contribution was calculated with the aug-cc-pCVTZ basis set.

In eq 3 the energy of the supermolecule $[E(\infty)]$ was calculated by setting R to be 1000 Å rather than taking the double of the energy associated with the individual fluorine atom.

The effect of the basis set superposition error (BSSE) at the barrier was also studied. To this end, conventional counterpoise (CP) correction calculations were performed at the MR- N levels of theory with the aug-cc-pCVXZ basis sets ($X = \text{T, Q, 5}$).

Based on the results of refs 44 and 46, additional corrections due to spin–orbit coupling as well as scalar relativistic effects are considered to be negligible at those relatively large internuclear distances where the barrier occurs. (See Table 2 of ref 44 and Table 5 of ref 46.)

SRMRCC calculations have been performed with the MRCC code⁷⁶ using CASSCF orbitals obtained with MOLPRO.⁷⁸ In all other multireference calculations the COLUMBUS program system¹⁰⁸ was utilized.

3. RESULTS AND DISCUSSION

3.1. Energy Contributions up to CCSD(T). Table 2 lists the various nonrelativistic contributions to the dissociation energy. If one considers the HF-SCF term, it can be seen that it converges smoothly and monotonically from the quadruple- ζ basis set and it is practically converged with the aug-cc-pCV6Z set. Although the convergence of the extrapolated HF-SCF results is smooth and stable from the (T,Q)-based to the (7,8)-based extrapolations, the (D,T)- and (T,Q)-based results are less accurate than those obtained with pure triple- and quadruple- ζ basis sets, respectively. This indicates that the extrapolation works well with large basis sets only. To calculate the final dissociation energy, the (7,8) extrapolated result of −155.55 kJ/mol was taken into account.

The convergence of the nonextrapolated ΔE_{MP2} , ΔE_{CCSD} , and $\Delta E_{(\text{T})}$ terms is smooth and monotonic, and the $\Delta E_{(\text{T})}$ contribution shows the fastest convergence behavior. In this latter case, the pure 6- ζ and 7- ζ results differ by only 0.10 kJ/mol. For MP2 and CCSD this difference is still small, it is 0.57 and 0.26 kJ/mol, respectively. Considering the 8- ζ and 7- ζ results for MP2, CCSD, and CCSD(T) the differences decrease further to 0.36, 0.22, and 0.04 kJ/mol, respectively. The monotonic convergence behavior is retained for the extrapolated correlation energies as well; however, the (6,7) extrapolated MP2 contribution shows a slight divergence: it underestimates the CBS limit by approximately 0.1 kJ/mol. Nevertheless, the two-point extrapolation formula performs well and it is fair to say that for all the three correlation contributions the extrapolated results surpass in accuracy the pure basis set values.

3.2. Beyond the CCSD(T) Approximation. When the convergence properties of higher-order terms are examined, a similar conclusion can be drawn as in the case of the dissociation of chlorine reported by Csontos and Kállay⁹¹ or in the work of Martin and associates³⁵ who studied the basis set convergence in post-CCSD calculations. That is, a double- ζ quality basis set is not appropriate to describe accurately the effects of the iterative triples and/or the perturbative quadruples even if all electrons are correlated in the

Table 3. Relativistic Contributions (kJ/mol) to the Dissociation Energy of Fluorine, $D_0(\text{F}_2)$, at Various Levels of Theory^a

X^b	ΔE_{SR}				ΔE_{DC}				$\Delta E_{\text{Gaunt}}^g$	$\Delta E_{\text{Lamb}}^1^h$	$\Delta E_{\text{Lamb}}^2^h$
	HF ^c	CCSD(T) ^d	CCSDT ^e	CCSDT(Q) ^f	HF ^c	CCSD(T) ^d	CCSDT ^e	CCSDT(Q) ^f			
2	−0.44	0.36	−0.01	0.01	−3.30	0.12	−0.04	−0.05	0.27	0.00	0.00
3	−0.50	0.38	−0.01	0.01	−3.46	0.26	−0.20		0.29	0.00	0.00
4	−0.50	0.38			−3.51	0.25			0.29	0.00	0.00
5	−0.50	0.38			−3.52				0.29	0.00	0.00
error ⁱ	0.00	0.00	0.00	0.00	−0.01	−0.01	−0.16	−0.05	0.00	0.00	0.00

^aAll results were obtained with the uncontracted aug-cc-pCVXZ basis sets. ^bCardinal number of the basis set used. ^cRelativistic correction obtained at the HF level. ^dRelativistic correction due to the correlation treatment with the CCSD(T) method. ^eRelativistic correction due to the correlation treatment with the CCSDT method. ^fRelativistic correction due to the correlation treatment with the CCSDT(Q) method. ^gCalculated at the HF level of theory. ^h ΔE_{Lamb}^1 and ΔE_{Lamb}^2 obtained by rescaling the one- and two-electron Darwin terms, respectively, calculated at the CCSD(T) level. ⁱSee the Methods for the definition of the remaining error.

calculations. At least a triple- ζ basis set or extrapolations from triple- ζ and quadruple- ζ results should be used to achieve sub-kJ/mol accuracy. Considering the results in Table 2, the poor performance of the (D,T)-based extrapolation in CCSDT and CCSDT(Q) calculations is obvious, but somewhat surprising because for chlorine the (D,T) extrapolations performed well.⁹¹ For CCSDT the (D,T) extrapolated value is less than the (T,Q)-based result by 0.31 kJ/mol; nevertheless, the difference between the (D,T) and (S,6) results decreases to 0.17 kJ/mol. In CCSDT(Q) calculations the (D,T)- and (T,Q)-based extrapolations differ by 0.40 kJ/mol. These differences and the data in Table 2 clearly indicate that the pure double- ζ level considerably overestimates, and consequently, the (D,T)-based extrapolation underestimates, the CBS limits for the CCSDT and CCSDT(Q) methods. The results of the double- ζ and triple- ζ all-electron CCSDTQ calculations show much more consistency as compared to CCSDT and CCSDT(Q). The triple- ζ value differs by 0.02 kJ/mol from the double- ζ result and by only 0.01 kJ/mol from the (D,T) extrapolated final contribution.

To sum up the higher-order contributions, one can see that the considerably large contribution due to CCSDT(Q) increases the final result by 4.31 kJ/mol, which is converged within 0.07 kJ/mol. The (S,6) extrapolated CCSDT term lowers the dissociation energy by 1.24 kJ/mol with an expected uncertainty of 0.04 kJ/mol. The CCSDTQ term decreases further the final result by 0.51 kJ/mol, and this contribution is converged within an error of at most 0.01 kJ/mol. The valence-only CCSDTQ(P)_A and full CCSDTQP contributions imply an additional 0.34 kJ/mol increment to the final dissociation energy. This value rises solely from the (P)_A term, the P contribution at the double- ζ level is essentially zero. The estimated remaining error in these results is approximately 0.05 kJ/mol.

3.3. Beyond the Born–Oppenheimer and Nonrelativistic Approximations. The DBOC contribution converges rapidly with the basis set size, and its effect on the final dissociation energy, +0.01 kJ/mol, is practically negligible. Scalar relativistic effects, as shown in Table 3, also converge rapidly at the HF-SCF and CCSD(T) as well as at the higher-order levels of theory. In all cases the triple- ζ basis set proved to be sufficient to reach convergence. However, the surprisingly good performance of the double- ζ basis set, especially in CCSDT and CCSDT(Q) calculations, is also notable; the differences between the aug-cc-pCVDZ results and the converged values are only 0.06 and 0.02 kJ/mol for HF and CCSD(T) levels, respectively, and they are essentially zero for both CCSDT and CCSDT(Q). The overall correlated scalar

relativistic contribution, however, is not more than −0.12 kJ/mol and its error is negligible.

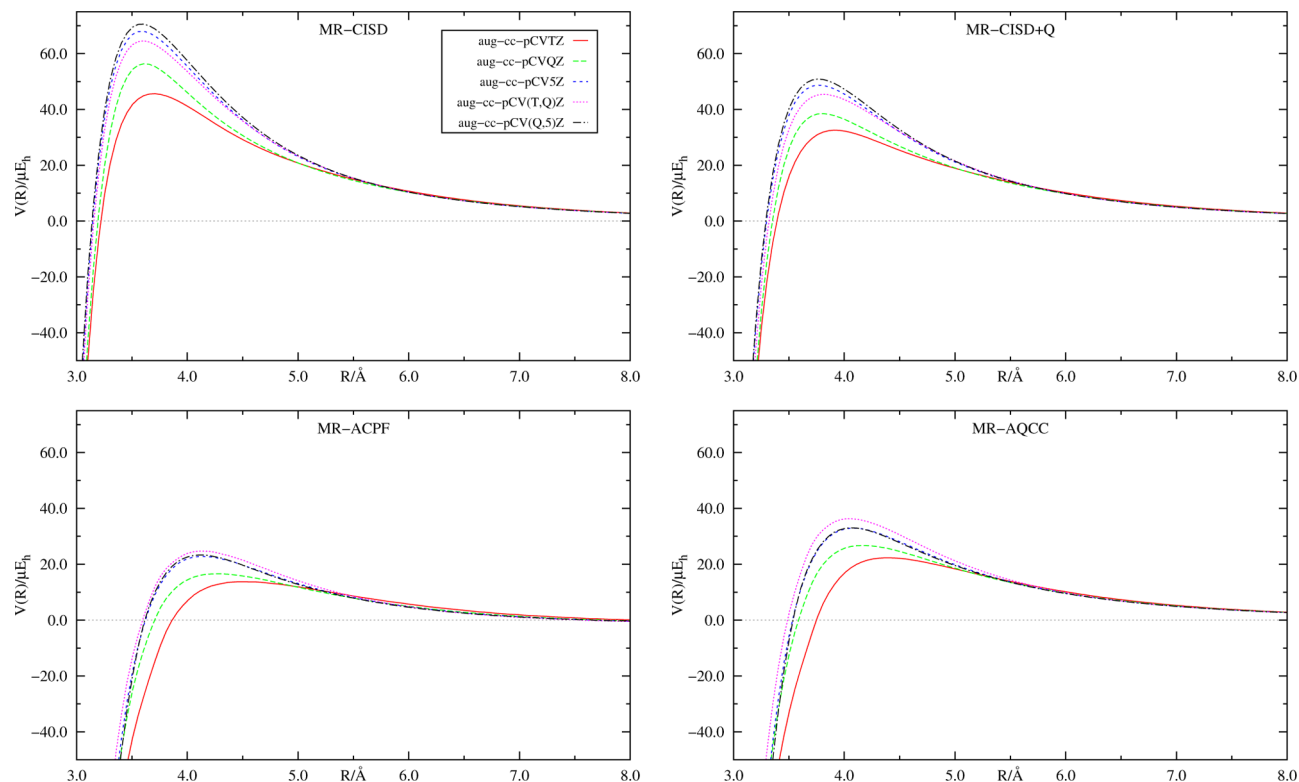
Although the results obtained at both the HF and CCSD(T) level converged within 0.01 kJ/mol with the pentuple- and quadruple- ζ basis sets, fast convergence is not the case for the four-component Dirac–Coulomb (DC) terms. In addition, the DC contribution also shows weak convergence with respect to the level of theory used in the correlation treatment; in particular, it is not converged at the CCSD(T) and even at the CCSDT levels. The overall contribution of the DC term to $D_0(\text{F}_2)$, −3.51 kJ/mol, is almost exactly equal with the HF value of this contribution due to a fortuitous cancellation of the correlation part. The largest error is due to the CCSDT term, 0.16 kJ/mol, which gives one of the largest contributions to the uncertainty associated with our best theoretical estimate for $D_0(\text{F}_2)$.

The Gaunt correction reaches its converged value, 0.29 kJ/mol, with the triple- ζ basis set at the HF-SCF level. This result is in line with the previously established value of 0.21 kJ/mol obtained by Visscher and Dyall¹⁰⁹ at the HF-SCF level of theory using the cc-pVTZ basis set augmented with an additional tight p function. The effects of electron correlation on this contribution are expected to be significant but probably do not exceed the value of the HF-SCF counterpart. Therefore, it is fair to say that the lack of correlation treatment introduces an error that is not larger than 0.29 kJ/mol. Further sources of errors due to relativistic effects are the truncation of the Dirac–Coulomb–Breit Hamiltonian, i.e., neglecting the contributions beyond the Gaunt term, as well as lack of the QED effects. Because the effect of the truncation can be as large as the Gaunt correction itself,¹¹⁰ the approximated total relativistic uncertainty should be increased by 0.29 kJ/mol. To estimate the magnitude of the QED effects, the Lamb shift, which is the leading term in QED, was approximated via the straightforward rescaling of the one- and two-electron Darwin terms.⁷⁴ Our results clearly indicated that both the one- and two-electron QED contributions are less than 0.005 kJ/mol and neglecting them has no significant influence on the uncertainty of the relativistic effects.

3.4. Best Theoretical Estimates for $D_0(\text{F}_2)$ and $\Delta_f H_0^\circ(\text{F})$. Estimating error bars associated with the results of a composite model chemistry is hardly a straightforward task. It is well-known that computational chemistry benefits from error cancellations and it is a pivotal question in the field of ab initio thermochemistry to what extent one can rely on them. Nevertheless, when contributions taken into account are close to convergence, one can expect the effect of error cancellation is about to disappear. In the case of $D_0(\text{F}_2)$ if we rely on error

Table 4. Location (R_{barrier} , Å) and Height (E_{barrier} , μE_h) of the Barrier along the Dissociation Curve of F_2 Calculated with Various Multireference Techniques

basis set	MR-CISD		MR-CISD+Q		MR-ACPF ^a		MR-AQCC		SRMRCCSD		SRMRCCSDT	
	R_{barrier}	E_{barrier}	R_{barrier}	E_{barrier}	R_{barrier}	E_{barrier}	R_{barrier}	E_{barrier}	R_{barrier}	E_{barrier}	R_{barrier}	E_{barrier}
aug-cc-pCVTZ	3.70	46	3.90	33	4.50	14	4.40	22	3.80	36	3.90	20
aug-cc-pCVQZ	3.60	56	3.80	39	4.25	17	4.15	27	3.75	44		
aug-cc-pCVSZ	3.60	68	3.75	49	4.15	23	4.10	33				
CBS (T,Q)	3.60	65	3.80	45	4.05	25	4.05	36	3.70	51	3.70	34 ^b
CBS (Q,5)	3.60	71	3.70	51	4.05	23	4.05	33				

^aDue to convergence problems the MR-ACPF curve was calculated by allowing reference configurations only with the proper state symmetry.^bCalculated as $E_{\text{MCSCF}}^{\text{aug-cc-pCVSZ}} + \Delta E_{\text{MRCCSDT}}^{\text{aug-cc-pCVTZ}}$, where $\Delta E_{\text{MRCCSDT}}^{\text{aug-cc-pCVTZ}} = E_{\text{MRCCSDT}}^{\text{aug-cc-pCVTZ}} - E_{\text{CASSCF}}$.**Figure 1.** Barrier along the dissociation curve calculated with the MR- N methods using the aug-cc-pCVXZ basis sets and $(X-1, X)$ -based extrapolations. The complete dissociation curves are shown in the Supporting Information.

cancellation and therefore sum the errors in the nonrelativistic terms, as listed in Table 2, 0.09 kJ/mol can be obtained. Because the remaining error in the DBOC contribution is essentially zero, further uncertainties come solely from the relativistic terms. The DC and the Gaunt term related errors are 0.23 and 2×0.29 kJ/mol, respectively. These yield, using the standard formulas of error propagation in a linear case (i.e., calculation of the square root of the sum of squares (RSS)), an overall uncertainty of $[(0.09)^2 + (0.23)^2 + 2 \times (0.29)^2]^{1/2} = 0.48$ kJ/mol. When the errors of all the terms are considered piece by piece (i.e., no error cancellation), the RSS agrees with the previous value to two decimal places. However, this only justifies that the nonrelativistic and scalar relativistic terms are converged because largest uncertainties are due to DC and Gaunt related errors, which give the same amount to both RSSs. Nevertheless, our estimates about the magnitude of these uncertainties are definitely on the conservative side. Thus, our best theoretical value for $D_0(F_2)$ is 154.95 ± 0.48 kJ/mol, and consequently, 77.48 ± 0.24 kJ/mol can be derived for $\Delta_f H_0^\circ(F)$.

3.5. Barrier along the Dissociation Curve. Table 4 lists the numerical results for the barrier height, E_{barrier} , and its location in terms of the internuclear distance, R_{barrier} , along the dissociation curve of F_2 , and Figures 1 and 2 show the section of the curve where the barrier occurs. For relative energies calculated with the various multireference methods according to eq 3 as well as for figures with the complete dissociation curves see, respectively, Tables S10–S14 and Figure S1 in the Supporting Information.

Considering the basis set dependence of the barrier height and its location along the dissociation curve, it can be seen that E_{barrier} increases while R_{barrier} decreases as the basis set expands. It is also notable that the height slightly decreases as one takes the size-consistency issue of the CI method into account. For instance, by adding the Davidson correction to the pure MR-CISD results, both the (T,Q) and the (Q,5) extrapolated barrier heights decrease from 65 to 45 μE_h and from 71 to 51 μE_h , respectively. Furthermore, by applying the MR-AQCC method with (T,Q)- and (Q,5)-based extrapolations, E_{barrier} lowers further to 36 and 33 μE_h , respectively. It is noteworthy

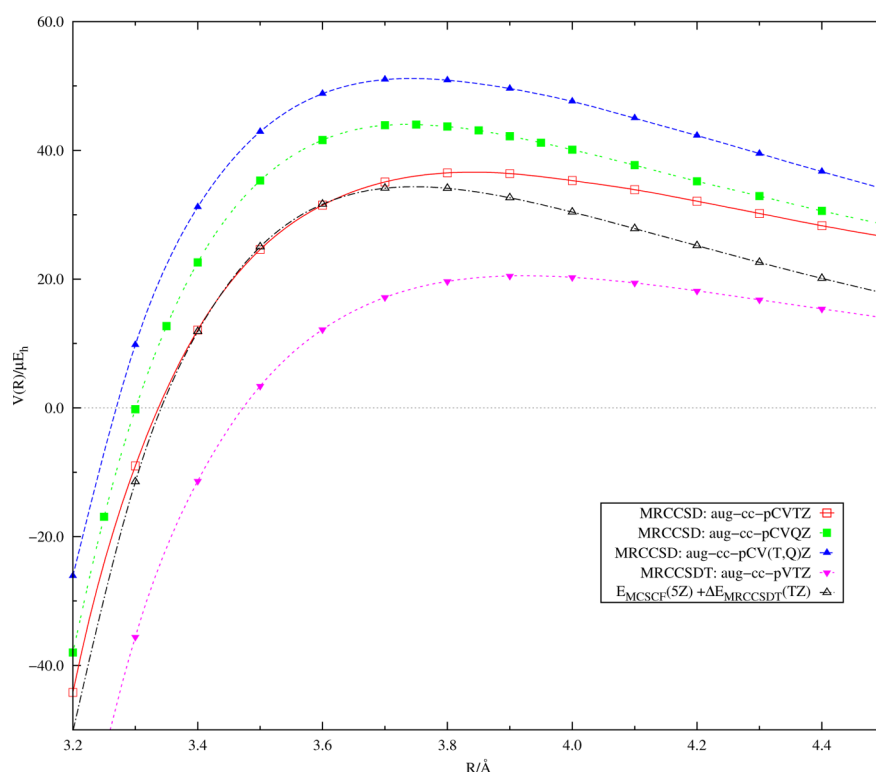


Figure 2. Barrier along the dissociation curve calculated with the SRMRCCSD and SRMRCCSDT methods using the aug-cc-pCV(T,Q)Z basis sets.

that the (T,Q)-based MR-AQCC result slightly overestimates E_{barrier} whereas the (Q,5) extrapolated value essentially coincides with that obtained with the pure pentuple- ζ basis set. The origin of these observations is due to the convergence properties of the correlation energy. In particular, the difference between the correlation energies obtained with the triple- ζ and quadruple- ζ basis sets, $\Delta E_{\text{MR-AQCC}}^{\text{TZ}}$ and $\Delta E_{\text{MR-AQCC}}^{\text{QZ}}$, respectively, is much larger than the difference between the corresponding $\Delta E_{\text{MR-AQCC}}^{\text{QZ}}$ and $\Delta E_{\text{MR-AQCC}}^{\text{5Z}}$ results. This fact clearly indicates the inadequate convergence of the MR-AQCC results obtained with the triple- ζ basis set.

In the case of the MR-ACPF method, convergence problems occurred when all reference symmetries were allowed during the selection of the configuration space. Our calculations at the MR-CISD(+Q) and the MR-AQCC levels set forth that the inclusion of all configurations to the reference space increases E_{barrier} by approximately 5–10 μE_h . Because of this large difference, the MR-ACPF results were not considered during the evaluation of the final E_{barrier} and R_{barrier} .

Effects of the BSSE on the barrier height were also studied with the aid of the MR- N techniques. CP corrections were calculated at R_{barrier} obtained with the corresponding MR- N method. As can be expected, BSSE decreases rapidly as the cardinal number of the basis set increases and completely vanishes at the basis set limit at both the CASSCF and the MR- N levels of theory and, consequently, BSSE has no effect on our E_{barrier} values.

As mentioned above, no barrier was found with the rigorously size-consistent SS-MRCCSD method based on CASSCF(2,2) reference orbitals.⁴⁷ Using the same (2,2) active space, a similar result was obtained in this study at the SRMRCCSD level; i.e., there was no trace of barrier with this small active space. Nevertheless, by expanding the CAS in the CASSCF and SRMRCCSD treatments to include all core and

valence electrons, the barrier appears, and the resulting E_{barrier} and R_{barrier} are in excellent agreement with those obtained with the MR- N methods. Therefore, the straightforward conclusion can be drawn that a small CAS(2,2) reference is not enough to properly recover the effects being responsible for the appearance of the barrier.

Inclusion of triple excitations in the correlation treatment by utilizing SRMRCCSDT/aug-cc-pCVT(Z) calculations decreases the barrier height to the value of 20 μE_h . Taking the sum of the pentuple- ζ CASSCF energy and the triple- ζ SRMRCCSDT correlation contribution, according to eq 5, yields $E_{\text{barrier}} = 34 \mu E_h$ at $R_{\text{barrier}} = 3.70 \text{ \AA}$. These results show very good agreement with those obtained by the MR-AQCC model, and they are in line with the MR-CISD+Q and SRMRCCSD values as well.

For R_{barrier} and E_{barrier} our best estimates $3.80 \pm 0.20 \text{ \AA}$ and $42 \pm 10 \mu E_h$ ($0.11 \pm 0.03 \text{ kJ/mol}$), respectively, were obtained by averaging the (Q,5) extrapolated MR-CISD+Q and MR-AQCC results, the (T,Q) extrapolated SRMRCCSD values, and the results taken from the SRMRCCSDT calculations. These findings are in good agreement with those published by Bytautas et al.⁴⁶ and they expressly support the existence of the barrier.

4. CONCLUDING REMARKS

The present study tried to resolve the discrepancies between the most recently published experimental results for both $D_0(\text{F}_2)$ and $\Delta_f H_0^\circ(\text{F})$. To this end, a highly accurate ab initio model chemistry was applied including higher, up to pentuple, excitations in coupled-cluster theory as well as contributions beyond the Born–Oppenheimer and nonrelativistic approximations. On the other hand, the existence of a barrier along the dissociation curve of F_2 was confirmed by means of various multireference techniques. The most accurate theoretical values for $D_0(\text{F}_2)$, $\Delta_f H_0^\circ(\text{F})$, and the height of the barrier calculated in

this study are 154.95 ± 0.48 , 77.48 ± 0.24 , and 0.11 ± 0.03 kJ/mol, respectively. Due to overlapping error bars, none of the experimental findings can be ruled out on the basis of our best estimates; however, the results obtained by the ion-pair dissociation of fluorine,^{13,14} $D_0(\text{F}_2) = 154.92 \pm 0.10$ kJ/mol, $\Delta_f H_0^\circ(\text{F}) = 77.46 \pm 0.05$ kJ/mol, almost precisely agree with our results. Furthermore, the barrier on the dissociation curve implies that the uncertainties in the experimental values of $D_0(\text{F}_2) = 154.52 \pm 0.12$ kJ/mol and $\Delta_f H_0^\circ(\text{F}) = 77.26 \pm 0.06$ kJ/mol, which depend on the long-range region of the dissociation curve,^{15,16,111} should be increased.

■ ASSOCIATED CONTENT

● Supporting Information

Total energies in E_h , relative energies in μE_h along the dissociation curve, and basis sets. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jcsontos@mail.bme.hu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are indebted to Professors Péter G. Szalay, Attila G. Császár, and Lucas Visscher for useful discussions. The authors also thank the reviewers for their valuable comments and suggestions. Financial support has been provided by the European Research Council (ERC) under the European Community's Seventh Framework Programme (FP7/2007-2013), ERC Grant Agreement No. 200639. B.N. thanks New Széchenyi Plan TÁMOP-4.2.2/B-10/1-2010-0009 project for financial support. The higher-order parallelized coupled-cluster and some parts of the multireference CI and CC calculations were run on the Hungarian HPC infrastructure (NIIF Institute, Hungary).

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