

Electron Affinity of *trans*-2-C₄F₈ from Electron Attachment–Detachment Kinetics[†]Jane M. Van Doren,^{*,a} Laura R. Condon, and Antonet DeSouza-Goding

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Electron attachment and detachment kinetics of 2-C₄F₈ were studied over the temperature range 298–487 K with a flowing-afterglow Langmuir-probe apparatus. Only parent anions were formed in the attachment process throughout this temperature range. At the highest temperatures, thermal electron detachment of the parent anions is important. Analysis of the 2-C₄F₈ gas showed an 82/18 mixture of *trans*/*cis* isomers. The kinetic data at the higher temperatures were used to determine the electron affinity EA(*trans*-2-C₄F₈) = 0.79 ± 0.06 eV after making some reasonable assumptions. The same quantity was calculated using the G3(MP2) compound method, yielding 0.74 eV. The kinetic data were not sufficient to establish a reliable value for EA(*cis*-2-C₄F₈), but G3(MP2) calculations give a value 0.017 eV greater than that for *trans*-2-C₄F₈. MP2 and density functional theory were used to study the structural properties of the neutral and anion isomers.

I. Introduction

Saturated perfluorocompounds have unique properties that have led to a suite of industrial processes and applications such as dry etching, solid foams, and electrical insulation. Unfortunately, most of these compounds also have large global warming potentials (GWP). Recent attention has focused on finding alternatives. Several studies investigated the potential of unsaturated perfluorocarbon compounds such as 2-C₄F₈ to meet etching, foam, and insulation needs.^{1–3} Our research focused on determining key properties of 2-C₄F₈ including electron attachment and detachment kinetics and electron affinity.

Several previous studies have examined electron attachment to 2-C₄F₈ at room temperature and found the reaction to be nondissociative and relatively efficient.^{4–10} Our data support these findings and extend them, providing information about the temperature dependence of electron attachment to 2-C₄F₈ and detachment from 2-C₄F₈[−] at higher temperatures. The *cis*/*trans* composition of the 2-C₄F₈ gas sample studied in previous electron attachment work was never mentioned, but we assume that it was a mixture. In the present study, we explicitly measured the *cis*/*trans* isomeric distribution of our C₄F₈ sample. We have also explored the structure, energies, and properties of the individual neutral and anionic isomers computationally to learn how the molecular properties are changed upon attachment of an electron. The compositional and computational data also enable us to determine the electron affinity (EA) of the major isomer from the experimental measurements, i.e., from the data revealing the kinetic competition between attachment and detachment. Our data analysis assumes that both *cis*- and *trans*-isomers undergo electron attachment and detachment and

neither neutral nor anionic isomers isomerize during the experiment. One additional assumption is required to complete our analysis. We explore two different reasonable assumptions: (1) the attachment rate constant for both isomers is the same and (2) the difference of the isomer EA values is known/fixed (by computation or estimated from experiments in the literature). We show that each leads to essentially the same value for EA(*trans*-2-C₄F₈). Computations provide electron affinity values for both isomers and indicate that their values are similar, with that of *trans*-2-C₄F₈ being slightly smaller than that of the *cis*-isomer. The electron affinities of *trans*- or *cis*-2-C₄F₈ have not been measured or computed previously, aside from a report of charge transfer reactions that gave limits for the EA of “2-C₄F₈”.¹¹

II. Experimental Method

A. Analysis of 2-C₄F₈ Isomeric Distribution. The 2-C₄F₈ sample available from the manufacturer noted overall purity (98%) but no characterization of the relative concentrations of the *cis*- and *trans*-isomers.¹² Relative concentrations of these isomers were determined from analysis of the mid-infrared (IR) spectrum of a dilute mixture of the sample in ultrahigh-purity (UHP) helium, using a multipass gas cell and a Nicolet Magna-IR 750 Spectrometer Series II with a mercury–cadmium–telluride detector. Features unique to each isomer and the relative strengths of these features were determined from the work of Heicklen et al.¹³ Strong isolated *cis* features included peaks at 1350, 1117, and 955 cm^{−1} with absorptivities of 21.3, 14.4, and 16.4 atm^{−1} cm^{−1}, respectively. One strong isolated *trans* feature appeared at 1291 cm^{−1} with an absorptivity of 28.8 atm^{−1} cm^{−1}. The infrared spectrum of a dilute mixture of the 2-C₄F₈ sample with UHP helium is shown in Figure 1. On the basis of the relative peak heights of the *cis*- and *trans*-features, we determined that the sample contained an 18/82 mixture of *cis*- and *trans*-2-C₄F₈, respectively, with an uncertainty of two percentage points. This relative concentration of isomers is essentially the same as a 300 K equilibrium mixture, calculated from the

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14. ABSTRACT Electron attachment and detachment kinetics of 2-C ₄ F ₈ were studied over the temperature range 298-487 K with a flowing-afterglow Langmuir-probe apparatus. Only parent anions were formed in the attachment process throughout this temperature range. At the highest temperatures, thermal electron detachment of the parent anions is important. Analysis of the 2-C ₄ F ₈ gas showed an 82/18 mixture of trans/cis isomers. The kinetic data at the higher temperatures were used to determine the electron affinity EA(trans-2-C ₄ F ₈) = 0.79 ± 0.06 eV after making some reasonable assumptions. The same quantity was calculated using the G3(MP2) compound method, yielding 0.74 eV. The kinetic data were not sufficient to establish a reliable value for EA(cis-2-C ₄ F ₈), but G3(MP2) calculations give a value 0.017 eV greater than that for trans-2-C ₄ F ₈ . MP2 and density functional theory were used to study the structural properties of the neutral and anion isomers.						
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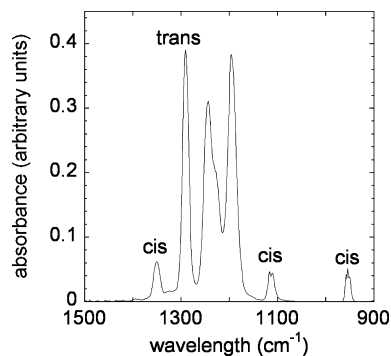


Figure 1. Mid-IR spectrum of a dilute mixture of the 2-C₄F₈ sample in UHP helium from which the sample composition of 18% *cis*-perfluoro-2-butene and 82% *trans*-perfluoro-2-butene was obtained. The peaks labeled are unique to the isomer indicated (from ref 13) and were used in sample analysis.

isomerization enthalpy and entropy experimentally determined near 740 K by Schlag and Kaiser.¹⁴

Schlag and Kaiser also measured the isomerization rate constant as a function of temperature, thereby determining the *trans*–*cis* isomerization activation energy, E_a , and Arrhenius A factor.¹⁴ Their data ($E_a = 2.45$ eV, $A = 10^{13.5}$) indicate that interconversion of the neutral isomers is negligible over the temperature range employed in the present study.

B. Kinetics Experiments. A flowing-afterglow Langmuir-probe (FALP) apparatus was used for this work at the Air Force Research Laboratory. The FALP method¹⁵ and this particular apparatus¹⁶ have been well described in the literature and will not be detailed here. The reader is also referred to our work with *c*-C₄F₈.¹⁷ The measurements were carried out in a flowing weak plasma created in He gas with a small amount of Ar gas added downstream of a microwave discharge. The He number density was generally maintained at 3.22×10^{16} cm⁻³ throughout the temperature range (133 Pa at 300 K). The 2-C₄F₈ isomeric mixture was introduced into the flow tube at a concentration of typically 1 ppm by volume. The electron density as a function of distance along the flow tube axis was obtained using a movable Langmuir probe. The plasma flow velocity (~ 100 m/s) was measured at each temperature to provide the time scale for the reaction. The ambipolar diffusion rate constant was determined from the decrease in electron density with distance/time in the absence of an electron attaching gas C₄F₈. At long times in the presence of an attaching gas, the

ambipolar diffusion rate constant will decrease a little due to the conversion of Ar⁺ to much larger positive ions,¹⁸ the major ionic product of the reaction of Ar⁺ with 2-C₄F₈ is C₄F₇⁺. This decrease was determined from electron density data at very long times.

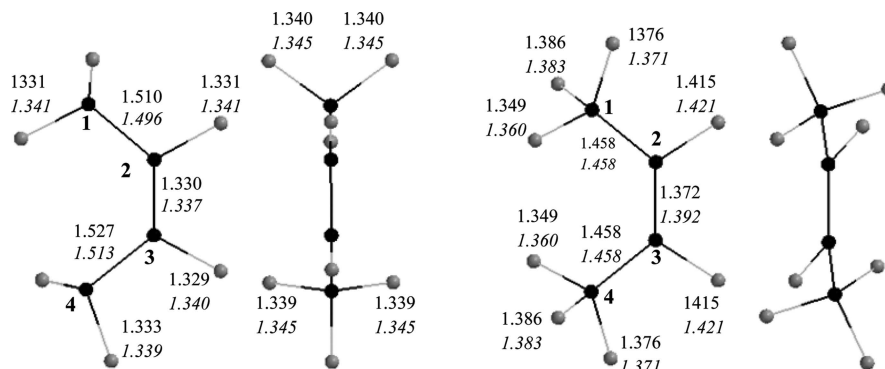
III. Computations

Electronic structure calculations were carried out using the GAUSSIAN-03 program package¹⁹ on a personal computer and on an IBM SP/RS6000 computer at the Maui High Performance Computing Center. Density functional theory (DFT) was utilized primarily to generate entropies and heat capacities needed to interpret the attachment and detachment data in terms of EAs, with the functional B3LYP^{20,21} and basis set 6-311+G(3df).²² The G3 method with reduced Møller–Plesset orders,²³ denoted by G3(MP2), was also applied to obtain accurate calculated EAs. DFT should yield more accurate entropies and heat capacities since a much larger basis set is feasible to use with DFT than with perturbation theory. But the G3(MP2) method will give a more accurate EA because of empirical corrections tied to experimental ionization energies, electron affinities, and heats of formation. For a large number of molecules with accurately known properties, the G3(MP2) method proved accurate within 56 meV, on average.²³ Molecular vibrational frequencies, polarizabilities, dipole moments, and atomic charges within each species were determined at the B3LYP/6-311+G(3df) level of theory, as preferable to the Hartree–Fock quantities used in the standard G3(MP2) method. A natural population analysis was used to determine atomic charges.²⁴

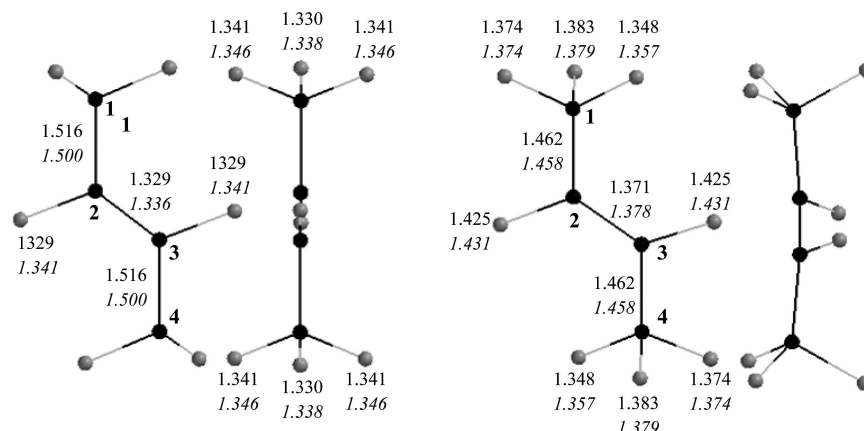
Computational results for the structures²⁵ of isomers of 2-C₄F₈ are shown in Charts 1 and 2. The structures of the neutral isomers agree quite well with previous calculations by Lindner and Lemal who used HF/6-31+G(d,p)//6-31+G(d,p) level of theory.²⁶

As expected, attachment of an electron to these molecules lengthens the C2–C3 and C2–F and C3–F bonds significantly. All other C–F bonds increase in length to a smaller extent while the C1–C2 and C3–C4 bonds decrease in length somewhat. Natural population analysis indicates that the extra charge is distributed throughout the molecule but most concentrated on C2, C3, and associated fluorine atoms ($\sim 65\%$), consistent with the bond changes. The remainder of the extra charge is spread throughout the molecule, shared in part by each of the atoms

CHART 1: Structures Calculated for *cis*-C₄F₈ Neutral (C_s Symmetry, Left) and Anion (C₂ Symmetry, Right)^a



^a Both are shown facing the average plane of the carbon atoms, and to the side of that plane. Bond lengths from DFT B3LYP/6-311+G(3df) optimization are given in plain type, and those from the MP2(Full)/6-31G(d) optimization used in the G3(MP2) calculations are given in italics. The angle $\angle C1-C2-C3$ is 130.0° (DFT) and 129.4° (MP2) for the neutral, and 129.3° (DFT) and 125.3° (MP2) for the anion. The corresponding numbers for the angle $\angle C2-C3-C4$ are 128.8° , 128.1° , 129.3° , and 125.3° . The dihedral angle $\angle C1-C2-C3-C4$ is 0.0° for the neutral (i.e., planar carbons for both DFT and MP2), and 11.9° (DFT) and -14.4° (MP2) for the anion.

CHART 2: Structures Calculated for *trans*-C₄F₈ Neutral (C_{2h} Symmetry, Left) and Anion (C₂ Symmetry, Right)^a

^a Both are shown facing the average plane of the carbon atoms, and to the side of that plane. Bond lengths from DFT B3LYP/6-311+G(3df) optimization are given in plain type, and those from the MP2(Full)/6-31G(d) optimization used in the G3(MP2) calculations are given in italics. The angle $\angle C1-C2-C3$ is 127.5° (DFT) and 127.4° (MP2) for the neutral, and 125.1° (DFT) and 122.3° (MP2) for the anion. The corresponding numbers for the angle $\angle C2-C3-C4$ are the same. The dihedral angle $\angle C1-C2-C3-C4$ is 180.0° for the neutral (i.e., planar carbons for both DFT and MP2), and 168.7° (DFT) and -178.8° (MP2) for the anion.

TABLE 1: Results of Møller–Plesset and Density Functional Calculations for C_s (¹A₁) *cis*-C₄F₈ and C₂ (²A) *cis*-C₄F₈[−]

quantity	G3(MP2)		DFT	
	<i>cis</i> -C ₄ F ₈	<i>cis</i> -C ₄ F ₈ [−]	<i>cis</i> -C ₄ F ₈	<i>cis</i> -C ₄ F ₈ [−]
zero-point energy ^a	0.04663	0.04281	0.04575	0.04132
total energy (0 K) ^b	−950.21334	−950.24109	−951.43231	−951.47386
EA (eV) ^c	0.755		1.13	
S ^o (meV K ^{−1}) ^a				
447 K	5.350	5.438	5.412	5.722
457 K	5.396	5.486	5.458	5.771
467 K	5.442	5.533	5.505	5.820
477 K	5.487	5.580	5.550	5.868
487 K	5.532	5.626	5.593	5.915
<i>f</i> C _p dT (meV) ^a				
447 K	561.6	583.6	562.1	620.1
457 K	581.6	604.4	582.2	641.6
467 K	601.9	625.3	602.7	663.3
477 K	622.3	646.5	623.3	685.2
487 K	643.0	667.9	644.1	707.2

^a Hartree units; HF/6-31G(d) level of theory, with frequencies scaled by 0.8929, for G3(MP2) results; B3LYP/6-31+G(3df) level of theory, with frequencies scaled by 0.989, for DFT results.

^b Hartree units; G3(MP2) formalism and B3LYP/6-31+G(3df)//B3LYP/6-31+G(3df) + ZPE for DFT results. ^c Difference between the anion total energy at 0 K and that of the neutral.

in the molecule. Small changes in bond angles further reduce electron–electron repulsion, particularly between fluorine atoms.²⁶

Energies, entropies, and integrated specific heats of the neutral and anionic species are given in Tables 1 and 2.²⁵ Earlier tests have shown that the calculated entropies and heat capacities are of sufficient accuracy as to affect the EAs deduced from the experimental data by less than 1 meV, mainly because these corrections to the measured free energy of attachment are small to begin with.²⁷

The DFT calculations find that the molecular polarizabilities of the two isomers are nearly identical (within 1%) with a value of ~ 8.5 Å³ while the dipole moments differ (0 and 0.321 D, for *trans*- and *cis*-C₄F₈, respectively), as expected.

The G3(MP2) calculations place *trans*-C₄F₈ 16 meV lower in energy than the *cis*-C₄F₈ isomer (at 0 K). Schlag and Kaiser¹⁴ also found the *trans*-isomer to be more stable than the *cis*-isomer. We can directly compare the computational results with their

TABLE 2: Results of Møller–Plesset and Density Functional Calculations for C_{2h} (¹A_g) *trans*-C₄F₈ and C₂ (²B) *trans*-C₄F₈[−]

quantity	G3(MP2)		DFT	
	<i>trans</i> -C ₄ F ₈	<i>trans</i> -C ₄ F ₈ [−]	<i>trans</i> -C ₄ F ₈	<i>trans</i> -C ₄ F ₈ [−]
zero-point energy ^a	0.04658	0.04237	0.04566	0.04076
total energy (0 K) ^b	−950.21394	−950.24106	−951.43378	−951.47394
EA (eV) ^c	0.738		1.09	
S ^o (meV K ^{−1}) ^a				
447 K	5.324	5.490	5.321	5.529
457 K	5.371	5.538	5.368	5.578
467 K	5.416	5.585	5.414	5.626
477 K	5.462	5.632	5.459	5.674
487 K	5.504	5.678	5.504	5.721
<i>f</i> C _p dT (meV) ^a				
447 K	563.7	590.5	564.1	598.9
457 K	583.7	611.4	584.3	620.1
467 K	604.0	632.5	604.7	641.6
477 K	624.4	653.8	625.3	663.3
487 K	645.0	675.2	646.1	685.2

^a Hartree units; HF/6-31G(d) level of theory, with frequencies scaled by 0.8929, for G3(MP2) results; B3LYP/6-31+G(3df) level of theory, with frequencies scaled by 0.989, for DFT results.

^b Hartree units; G3(MP2) formalism and B3LYP/6-31+G(3df)//B3LYP/6-31+G(3df) + ZPE for DFT results. ^c Difference between the anion total energy at 0 K and that of the neutral.

experimental results by calculating the isomerization enthalpy in the temperature range of their equilibrium experiments (700–780 K). This leads to a G3(MP2) enthalpy value of 14 meV as compared with the experimental value of 35 ± 2 meV, well within the accuracy of G3(MP2).²³ The G3(MP2) results place the *trans*- and *cis*- anions at the same energy (within 0.8 meV at 0 K).

Of particular interest to this study is the difference in energy between the neutral and anionic structures of each isomer. G3(MP2) provides the best estimate yielding (*trans*-C₄F₈) = 0.738 eV and EA(*cis*-C₄F₈) = 0.755 eV. DFT calculations of electron affinities also find that the EA(*cis*-C₄F₈) is slightly larger than EA(*trans*-C₄F₈) with values of 1.13 and 1.09 eV, respectively. However, DFT EA determinations are less accurate; our experience with the particular application of DFT used here is that it will overestimate the EA by ~ 0.25 eV when the neutral is a singlet,^{27–29} as in the present case, though not always.³⁰

TABLE 3: Rate Constants for Electron Attachment, k_a , to a Cis/Trans Composite Molecule 2-C₄F₈ and Electron Detachment, k_d , from 2-C₄F₈^{-a}

T (K)	k_a (10^{-8} cm ³ s ⁻¹) ^b	k_d (s ⁻¹) ^c	ν_D (s ⁻¹) ^d	EA (meV) ^e
296	4.8		346	
297	4.8		339	
299	4.8		349	
	5.4		349	
303	4.6		353	
	5.2		353	
	4.8		353	
341	4.7		385	
	4.8		385	
	4.7		385	
364	4.4		399	
	4.5		399	
	4.5		399	
447	3.6	350	495	780
	3.4	420	495	786
457	4.0	765	508	788
	3.7	775	508	784
467	3.3	850	502 ^f	793
	3.3	1050	701 ^f	785
477	2.7	1120	507 ^f	791
	3.0	1270	723 ^f	790
487	2.4	1320	509	796
	2.7	1490	509	796

^a The data were fit assuming that the 2-C₄F₈ mixture was composed of a single species, the average 2-C₄F₈ molecule in the mixture. ^b The k_a values are accurate to $\pm 30\%$. ^c The k_d values are accurate to $\pm 35\%$. No k_d values are given for temperatures where the detachment rate is smaller than the ambipolar diffusion rate. ^d For comparison with k_d , the measured ambipolar diffusion decay constant ν_D is given for the electron-(He⁺, Ar⁺) plasma at 133 Pa pressure and ~ 100 m s⁻¹ plasma velocity. ^e The EA values utilize a weighted average entropy and integrated specific heat values for the 2-C₄F₈ mixture, i.e., average values calculated from the computational (DFT) entropy and integrated specific heat values given in Tables 1 and 2 weighted by the relative concentration of each isomer in the mixture. ^f The two ambipolar diffusion decay constant ν_D values reported at 467 and 477 K differ because the flow tube pressures differed. One data run at both temperatures was carried out at 133 Pa (higher diffusion rate) instead of 208 Pa (467 K) and 213 Pa (477 K) as a test of pressure independence.

IV. Electron Attachment and Detachment Kinetics

Electron attachment at room temperature is moderately efficient with an apparent attachment rate constant (k_a) for the mixture (primarily composed of *trans*-2-C₄F₈) of 4.9×10^{-8} cm³ s⁻¹ at 300 K. This value can be compared with the calculated collision rate³¹ of 3.0×10^{-7} cm³ s⁻¹ (decreasing to 2.6×10^{-8} cm³ s⁻¹ by 500 K) for either isomer. This attachment rate constant agrees well with other values measured only at 300 K for “2-C₄F₈” by Bansal and Fessenden (4.9×10^{-8} cm³ s⁻¹),⁵ Christodoulides et al. (4.9×10^{-8} cm³ s⁻¹),⁷ Christophorou et al. (4.7×10^{-8} cm³ s⁻¹),⁸ and Mayhew et al. (4.2 ± 0.2) $\times 10^{-8}$ cm³ s⁻¹.⁹ The previous reports did not characterize the isomeric distribution of the perfluoro-2-butene but it is likely that it was similar to the mixture used in this report if the synthesis used to form the perfluoro-species was the same. Table 3 shows the apparent attachment rate constant, k_a , as a function of temperature. k_a decreases with increasing temperature over the experimental range of 300–487 K.

Above ~ 450 K, the signature of thermal electron detachment is apparent in the kinetic data, namely, a change in the slope of the decay with time, approaching a diffusion-limited steady state at long times, Figure 2. Data such as these can be fit to determine k_a and k_d as described in refs 32 and 33. Values for the apparent

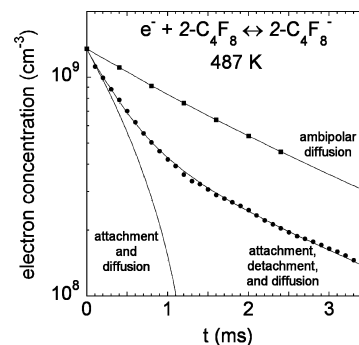


Figure 2. Example of the FALP data for 2-C₄F₈ at 487 K, with a concentration of 2-C₄F₈ (82/18 mixture of *trans*/*cis*) of 4.69×10^{10} cm⁻³. The topmost line was obtained without 2-C₄F₈ present and gave a diffusion decay constant $\nu_D = 509$ s⁻¹. The fit to the lower data set assuming the sample contains a single molecular species, “2-C₄F₈”, yields $k_a = 2.4 \times 10^{-8}$ cm³ s⁻¹, $k_d = 1320$ s⁻¹, and EA(2-C₄F₈ “average” molecule) = 0.796 eV.

detachment rate constant as a function of temperature are listed in Table 3. As expected, k_d increases with increasing temperature.

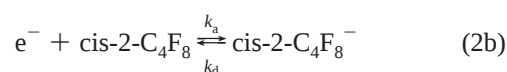
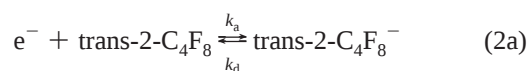
The ratio of the detachment and attachment rate constants can be used to determine the free energy change upon attachment of an electron. The electron affinity can be determined from the free energy using calculated values for the entropy change and thermal energy correction.

$$k_d/k_a = L_0(273.15/T) \exp[\Delta G^0/kT]$$

$$\Delta G^0 = -EA - T\Delta S^0 - (H_T - H_0) \quad (1)$$

In eq 1, k is Boltzmann’s constant, L_0 is Loschmidt’s number, EA is the electron affinity (at 0 K, by definition), ΔS^0 is the entropy change due to electron attachment at temperature T , and $H_T - H_0$ is a thermal energy correction (determined from the integrated specific heat) for the reaction. The entropy and thermal energy terms in the free energy expression are small; their sum is typically only a few percent of the electron affinity, for the range of electron affinities accessible by this technique (~ 0.4 – 0.9 eV). Thus, the ratio of experimental rate constants k_d/k_a essentially determines the electron affinity. Using weighted average values for the entropy and thermal energy in eq 1 and the rate constants in Table 3, we determined an apparent electron affinity value for our 2-C₄F₈ mixture for each data set over the temperature range where detachment was significant. Most accurate values are obtained from kinetic data where detachment is much faster than diffusion (e.g., 487 K in these experiments), but all the data in Table 3 indicate the EA of the average 2-C₄F₈ in the mixture is ~ 0.79 eV.

To obtain a measure of the electron affinity for each individual isomer, we must include the kinetic equations for reactions of both isomers in our analysis.



The related kinetic equations are

$$\begin{aligned} \frac{d[e^-]}{dt} &= -\frac{[C_4F_8^-]_{trans}}{dt} - \frac{[C_4F_8^-]_{cis}}{dt} - \frac{d[P^+]}{dt} \\ &= -0.82k_{a,trans}[C_4F_8] - 0.18k_{a,cis}[C_4F_8] - \\ &\quad k_{diffusion}[P^+] + k_{d,trans}[C_4F_8^-]_{trans} + k_{d,cis}[C_4F_8^-]_{cis} \end{aligned} \quad (3a)$$

$$\frac{d[P^+]}{dt} = -k_{diffusion}[P^+] \quad (3b)$$

$$\frac{d[e^-]}{dt} + \frac{[C_4F_8^-]_{trans}}{dt} + \frac{[C_4F_8^-]_{cis}}{dt} = \frac{d[P^+]}{dt} \quad (3c)$$

where the concentrations of each isomer is expressed as the product of the concentration of C_4F_8 times the isomeric fraction determined experimentally (II.A) and ambipolar diffusion of electrons and positive ions is included. $[P^+]$ is the concentration of positive ions (mostly Ar^+) in the plasma. The positive ion diffusive loss is balanced by the loss of electrons; effectively no negative ions are lost until the electron density is much smaller than the negative ion density (which does not occur in these FALP kinetic experiments).

The ratio of the detachment and attachment rate constants for each isomer are related to the EA value for each:

$$\begin{aligned} k_{d,trans}/k_{a,trans} &= L_0(273.15/T) \exp[\Delta G_{trans}^0/kT] \\ \Delta G_{trans}^0 &= -EA_{trans} - \Delta S_{trans}^0 - (H_T - H_0)_{trans} \end{aligned} \quad (4a)$$

$$\begin{aligned} k_{d,cis}/k_{a,cis} &= L_0(273.15/T) \exp[\Delta G_{cis}^0/kT] \\ \Delta G_{cis}^0 &= -EA_{cis} - T\Delta S_{cis}^0 - (H_T - H_0)_{cis} \end{aligned} \quad (4b)$$

where the entropy and thermal energy corrections are determined from computation (DFT), as described above.

In the analysis that follows, we make two major assumptions: (1) all four electron attachment and detachment processes are operative as described by eq 2a and 2b, and (2) the isomers (neutral and anion) do not isomerize. The similarity of neutral and anion structures, properties, and changes in properties upon attachment of an electron, as determined by our calculations, supports the first assumption. Furthermore, our kinetic data illustrate that if both species attach, both detach, because the electron-positive ion plasma does not collapse to an ion-ion plasma at long times. The second assumption is supported by the experimental data of Schlag and Kaiser,¹⁴ which established that interconversion of the neutrals is negligible over the temperature range and time scale explored in these experiments because of a large (2.45 eV) barrier to isomerization. While it is likely that the barrier to isomerization of the anions is reduced somewhat as compared to their neutral counterparts because of the lengthening of the C2–C3 bonds, we assume that the barrier is large enough that the rate of isomerization for the anions is also negligible for $T \leq 487$ K over the 3–4 ms time scale of our experiments. These assumptions do not reduce the dimensionality of the problem but establish the framework upon which our analysis stands.

Analysis of the kinetic data at temperatures where detachment is significant requires one additional assumption to reduce the number of unknowns in the kinetic equations. We explore two reasonable assumptions and demonstrate that each, independently, leads to essentially the same limits for the EA for the major isomer in our mixture, $EA(trans-C_4F_8)$.

The first approach assumes that the attachment rate constants for the neutral isomers are the same, as might be expected from their similar properties and collision rate constants. The attachment rate constant and range of detachment rate constants that

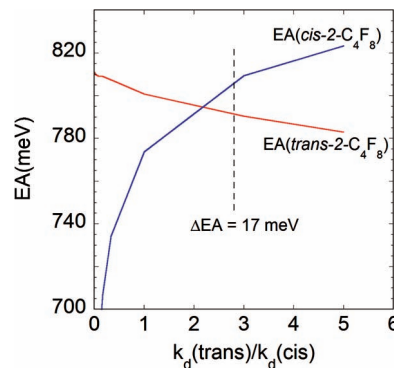


Figure 3. EAs resulting from fits to one set of 487-K electron attachment–detachment kinetic data under the assumption that $k_a = 2.7 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ is the same for both *cis*- and *trans*-2- C_4F_8 . $EA(trans-2-C_4F_8)$ shows much less variation than does $EA(cis-2-C_4F_8)$ because *trans*-2- C_4F_8 constitutes 82% of the gas. The EAs plotted at $k_{d,trans}/k_{d,cis} = 2.9$ correspond to $EA(cis-2-C_4F_8) = 17$ meV higher than $EA(trans-2-C_4F_8)$, as given by G3(MP2) calculations.

fit the kinetic data were determined. It was simplest to explore this range by varying the relative values of the detachment rate constants, particularly because this ratio is related to the difference in isomer EAs.

The kinetic data at 487 K could be fit to the kinetic equations (eqs 3a–3c) with an attachment rate constant of $2.70 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ and a wide range of detachment rate constant ratios shown in Figure 3. The actual value of $k_{d,trans}$ found in these fits varied from 1200 to 2300 s^{-1} with best fits when $0 < k_{d,trans}/k_{d,cis} < 5$.

Inserting the rate constant values determined from the kinetic data together with the computed entropy and thermal energy corrections into eqs 4a and 4b, we can determine the EA value for each isomer. Results are shown in Figure 3. The much narrower EA range for *trans*-2- C_4F_8 as compared with the *cis*-isomer arises from the much larger concentration of the *trans*-isomer in the neutral mixture.

A second approach to modeling the data assumes that the difference in electron affinities is known, either from the G3(MP2) calculations Schlag (17 meV) or, alternatively, from the experimental equilibrium measurements of Schlag and Kaiser¹⁴ (35 meV; assuming the anion energies are the same, as determined in this work (G3(MP2))). Combining eqs 4a and 4b we find

$$\begin{aligned} (k_d/k_a)_{trans}/(k_d/k_a)_{cis} &= \exp\{[-(EA_{trans} - EA_{cis}) - \\ &\quad T(\Delta S_{trans}^0 - \Delta S_{cis}^0) - ((H_T - H_0)_{trans} - \\ &\quad (H_T - H_0)_{cis})]/kT\} \end{aligned} \quad (5)$$

which reduces to

$$(k_{a,cis}/k_{a,trans})(k_{a,trans}/k_{d,cis}) = 2.9, \quad \text{at 487 K and } \Delta EA = 17 \text{ meV} \quad (6)$$

when we insert the computed values for entropy and thermal energy (Tables 1 and 2) and fix the isomer EA difference to 17 meV. Using the alternative value $\Delta EA = 35$ meV leads to a rate constant ratio value of 4.4 in eq 6.

The range of attachment and detachment rate constants that fit the kinetic data (constrained by a fixed EA difference) was explored by varying the attachment rate ratio. EA values resulting from fits with $\Delta EA = 17$ meV and k_a ratios from 0 to 10 are shown in Figure 4. Nearly identical ranges are found for the case where $\Delta EA = 35$ eV.

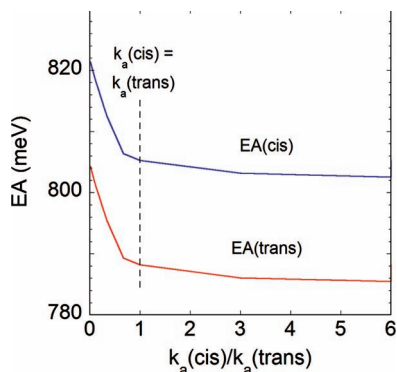


Figure 4. EA(*trans*-2-C₄F₈) values resulting from fits to one set of 487 K electron attachment–detachment kinetic data under the assumption that the difference in EAs for *cis*- and *trans*-2-C₄F₈ is 17 meV (G3(MP2) value, eq 6). The EA value of 788 meV corresponds to the case when the attachment rate constants for the two isomers are equal, $k_{a,cis}/k_{a,trans} = 1$.

TABLE 4: Electron Affinity of *trans*-2-C₄F₈

method	EA(<i>trans</i> -2-C ₄ F ₈) (eV)
computation (G3(MP2))	0.738
kinetic ($k_{a,trans} = k_{a,cis}$) ^a	0.78–0.81
hybrid (17 meV ≤ EA ≤ 35 meV) ^b	0.77–0.83

^aEA derived from a kinetic analysis of the electron density kinetic data at 487 K, assuming the rate constants for *cis*- and *trans*-2-C₄F₈ are equal, both anions can detach, and no interconversion between isomeric species takes place. ^bEA derived from a kinetic analysis of the electron density kinetic data at 487 K, assuming the difference in EAs for *cis*- and *trans*-2-C₄F₈ is between 17 and 35 meV (the computationally derived EA difference and the experimentally determined energy difference between neutral isomer energies (ref 14)), both isomeric neutrals attach and their respective anions detach, and no interconversion between isomeric species takes place.

A summary of the full range of EA(*trans*-2-C₄F₈) values determined from both approaches is presented in Table 4. “Kinetic” results arise from fits of kinetic data using the assumption that the attachment rate constants of the two isomers are equal, such as shown in Figure 3. “Hybrid” results arise from fits using the assumption that the difference in EA values for the isomers is known (constraint 5) and is in the range 17–35 meV, such as shown in Figure 4. Uncertainty in the relative concentrations of the isomers was explored and has only a minor effect on the EA values determined (± 2 meV). The kinetic and hybrid results are strikingly similar and lead to a best value of 0.79 ± 0.06 eV. The above analysis does not provide a precise estimate of EA(*cis*-2-C₄F₈) because it was only a minor constituent of the C₄F₈ mixture, but the computations suggest that the value is slightly larger than EA(*trans*-2-C₄F₈).

Only one previous study attempted to place limits on the electron affinity of these perfluorocompounds. Lifshitz, Tiernan, and Hughes investigated ion–molecule charge-transfer reactions involving “2-C₄F₈”,¹¹ which we presume contained a mixture of isomers. Their experiments yielded estimates of ≥ 1.2 eV based on charge transfer from O[−] (0.3 eV KE) and ≥ 0.7 eV based on the endothermic charge transfer threshold from S[−].¹¹ There is no reason to expect the results from the exothermic charge transfer and endothermic threshold experiments arose from reaction with different isomers because the computations presented here indicate that the properties and electron affinities of isomers are very similar. The experimentally and computationally derived electron affinity values determined in this work agree with the threshold experiments and therefore suggest that

the O[−] charge transfer portion of that experiment was misinterpreted, possibly because of the broad energy distribution of reactant ions.

The electron affinity values determined in this work for *cis*- and *trans*-2-C₄F₈ can be compared with that found for the cyclic C₄F₈ isomer. G3(MP2) computations indicate the electron affinity of the cyclic isomer is 143–160 meV smaller than that of either linear 2-C₄F₈ isomer, i.e., EA(*c*-C₄F₈) = 0.595 eV.¹⁷ Comparison of the experimentally derived EAs gives the same result; EA(*c*-C₄F₈)¹⁷ $\sim$ EA(*trans*-2-C₄F₈) − 160 meV. The smaller electron affinity of *c*-C₄F₈ as compared with the linear isomers presumably arises from the decreased stability of the anion caused by increased electron–electron repulsion in the cyclic structure.

V. Conclusions

Electron attachment to 2-C₄F₈ (82/18 mixture of *trans*/*cis* isomers) is associative in the temperature range 298–487 K. Above ~ 450 K, electron detachment from the parent anions begins to compete with attachment. Kinetic data from this competition were used to determine the electron affinity of the detaching species after making some reasonable assumptions. These data establish EA(*trans*-2-C₄F₈) = 0.79 ± 0.06 eV. The data are not sufficient to place narrow limits on the EA of the *cis*-isomer. G3(MP2) calculations provide an independent measure of EA values, yielding EA(*trans*-2-C₄F₈) = 0.74 eV and EA(*cis*-2-C₄F₈) = 0.76 eV. Indeed, the calculations reveal that the total energy of the *trans*- and *cis*-2-C₄F₈ anions are the same, and those of the neutral isomers are nearly so. Density functional theory computations reveal that the structural changes arising from attachment of an electron to the *trans*- and *cis*-isomers are also similar.

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angle within 0.02° of C_s symmetry. But forcing C_s symmetry yields an imaginary frequency of 6i cm^{−1}, which corresponds to rotation of the trifluoromethyl groups about the C–C axes. A HF/6-31G(d) or MP2(Full)/6-31G(d) frequency analysis does not have this problem; thus we are confident in giving C_s symmetry for *cis*-C₄F₈. The energy and entropy uncertainty caused by the 6i cm^{−1} frequency is too small (sub-millielectronvolt) to affect the present results. The second point is that we usually find that the entropy and internal energy corrections do not require high-level calculation. For *cis*-C₄F₈[−], however, the entropy results were unusually dependent on the size of the basis set. Some indication of this problem may be seen by comparing the HF/6-31G(d) entropies and integrated specific heats given in Tables 1 and 2 with those from B3LYP/6-311+G(3df) calculations. Good agreement is seen except for the *cis* anion. Differences in certain bond lengths (and thus especially the low frequencies relevant for the entropy) appear to be at the heart of this basis set dependence.

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