Electron Affinity of trans-2-C$_4$F$_8$ from Electron Attachment—Detachment Kinetics$^\dagger$

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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.

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-C$_4$F$_8$ to meet etching, foam, and insulation needs.1–3 Our research focused on determining key properties of 2-C$_4$F$_8$ including electron attachment and detachment kinetics and electron affinity.

Several previous studies have examined electron attachment to 2-C$_4$F$_8$ 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-C$_4$F$_8$ and detachment from 2-C$_4$F$_8^-$ at higher temperatures. The cis/trans composition of the 2-C$_4$F$_8$ 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 C$_4$F$_8$ 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-C$_4$F$_8$). Computations provide electron affinity values for both isomers and indicate that their values are similar, with that of trans-2-C$_4$F$_8$ being slightly smaller than that of the cis-isomer. The electron affinities of trans- or cis-2-C$_4$F$_8$ have not been measured or computed previously, aside from a report of charge transfer reactions that gave limits for the EA of “2-C$_4$F$_8$.”11

II. Experimental Method

A. Analysis of 2-C$_4$F$_8$ Isomeric Distribution. The 2-C$_4$F$_8$ 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-C$_4$F$_8$ 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-C$_4$F$_8$, 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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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 $EA(\text{trans-}2$-$\text{C}_4\text{F}_8) = 0.79 \pm 0.06 \text{ eV}$ 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 $EA(\text{cis-}2$-$\text{C}_4\text{F}_8)$, but G3(MP2) calculations give a value 0.017 eV greater than that for $\text{trans-}2$-$\text{C}_4\text{F}_8$.

MP2 and density functional theory were used to study the structural properties of the neutral and anion isomers.

<table>
<thead>
<tr>
<th>Electron attachment</th>
<th>Cyclic $\text{C}_4\text{F}_8$</th>
<th>Rate constant</th>
<th>Temperature dependence</th>
<th>Electron affinity</th>
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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 ($E_a = 2.45 \text{ eV}$, $A = 10^{13.5}$) 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 $3.22 \times 10^{16} \text{ cm}^{-3}$ 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 C2F8. At long times in the presence of an attaching gas, the ambipolar diffusion rate constant will decrease a little due to the conversion of $\text{Ar}^+$ to much larger positive ions;18 the major ionic product of the reaction of $\text{Ar}^+$ 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 B3LYP20,21 and basis set 6-311+G(3df).22 The G3 method with reduced Möller–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(d,p) 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 (~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.

**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.

**Chart 1:** Structures Calculated for cis-C4F8 Neutral (C, Symmetry, Left) and Anion (C2 Symmetry, Right)

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.
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 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 14.78 eV 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- ions 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) = 0.758 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

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**TABLE 1: Results of Møller–Plesset and Density Functional Calculations for C₁, (¹A₁) cis-C₄F₈ and C₂ (²A) cis-C₄F₈**

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<thead>
<tr>
<th>quantity</th>
<th>G3(MP2)</th>
<th>DFT</th>
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<tr>
<td>zero-point energy (eV)</td>
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<td>0.04281</td>
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<tr>
<td>total energy (0 K) (meV K⁻¹)</td>
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<td>1.13</td>
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<td>EA (eV)</td>
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<td>S° (meV K⁻¹)</td>
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<td>S° (meV K⁻¹)</td>
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**TABLE 2: Results of Møller–Plesset and Density Functional Calculations for C₁, (¹A₁) trans-C₄F₈ and C₂ (²B) trans-C₄F₈**

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<td>0.04573</td>
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</tr>
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* 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.

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

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**CHART 2: Structures Calculated for trans-C₄F₈ Neutral (C₂ᵥ Symmetry, Left) and Anion (C₂ Symmetry, Right)**

- 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 ∠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 ∠C₂–C₃–C₄ are the same. The dihedral 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.
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-C$_4$F$_8$) of $4.9 \times 10^{-8}$ cm$^3$ s$^{-1}$ at 300 K. This value can be compared with the calculated collision rate\(^a\) of $3.0 \times 10^{-7}$ cm$^3$ s$^{-1}$ (decreasing to $2.6 \times 10^{-8}$ cm$^3$ s$^{-1}$ at 500 K) for either isomer. This attachment rate constant agrees well with other values measured only at 300 K for "2-C$_4$F$_8"$ by Bansal and Fessenden (4.9 \times 10^{-8}$ cm$^3$ s$^{-1}$),\(^5\) Christodoulides et al. (4.9 \times 10^{-8}$ cm$^3$ s$^{-1}$),\(^7\) Christophorou et al. (4.7 \times 10^{-8}$ cm$^3$ s$^{-1}$),\(^8\) and Mayhew et al. (4.2 \pm 0.2) \times 10^{-8}$ cm$^3$ 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 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.

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

$$\Delta G^o = -EA - T\Delta S^o - (H_f - H_o) \quad (1)$$

In eq 1, $k$ is Boltzmann’s constant, $L_o$ is Loschmidt’s number, $EA$ is the electron affinity (at 0 K, by definition), $\Delta S^o$ is the entropy change due to electron attachment at temperature $T$, and $H_f - H_o$ 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 for our 2-C$_4$F$_8$ mixture for each data set over the temperature range where detachment was significant. Most accurate values are obtained form 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-C$_4$F$_8$ 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.

$$\text{e}^- + \text{trans-2-C}_4\text{F}_8 \overset{k_a}{\rightarrow} \text{trans-2-C}_4\text{F}_8^- \quad (2a)$$

$$\text{e}^- + \text{cis-2-C}_4\text{F}_8 \overset{k_a}{\rightarrow} \text{cis-2-C}_4\text{F}_8^- \quad (2b)$$

The related kinetic equations are
where the concentrations of each isomer is expressed as the product of the concentration of C4F8 times the isomeric fraction determined experimentally (II.A) and ambipolar diffusion of electrons and positive ions is included. [Pdetermined experimentally (II.A) and ambipolar diffusion 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 is related to the EA value for each:

$$\frac{k_{d,trans}}{k_{a,trans}} = \frac{L_0(273.15/T) \exp[\Delta G^o_{trans}/kT]}{\Delta G^o_{trans} = -EA_{trans} - \Delta S^o_{trans} - (H_T - H_0)_{trans} \text{ (4a)}}$$

$$\frac{k_{d,cis}}{k_{a,cis}} = \frac{L_0(273.15/T) \exp[\Delta G^o_{cis}/kT]}{\Delta G^o_{cis} = -EA - T\Delta S^o_{cis} - (H_T - H_0)_{cis} \text{ (4b)}}$$

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 ≤ 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, EATD(CF). 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 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 × 10^{-8} cm^3 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 \(0 < k_{d,trans}/k_{a,cis} < 5\).

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-CF 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 Kaiser15 (35 meV); assuming the anion energies are the same, as determined in this work (G3(MP2)). Combining eqs 4a and 4b we find

$$\frac{(k_d/k_a)_{trans}/(k_d/k_a)_{cis}}{\exp[(-EA_{trans} - EA_{cis}) - T(\Delta S^o_{trans} - \Delta S^o_{cis} - ((H_T - H_0)_{trans} - (H_T - H_0)_{cis}))]/kT]}$$

which reduces to

$$(k_a,cis/k_a,trans)/(k_d,trans/k_d,cis) = 2.9,$$

at 487 K and ∆EA = 17 meV (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 ∆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 ∆EA = 17 meV and k_d ratios from 0 to 10 are shown in Figure 4. Nearly identical ranges are found for the case where ∆EA = 35 eV.
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) calculations indicate the electron affinity of the cyclic isomer is 143−160 meV smaller than that of either linear 2-C₄F₈ isomer, i.e., EA(cis-C₄F₈) = 0.595 eV.¹⁷ Comparison of the experimentally derived EAs gives the same result; EA(cis-C₄F₈) = 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 detachment 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-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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References and Notes
(2) Tran-Quinn, T.; Lakritz, M. ASMC 2008; pp 37−42.
(12) 2-C₄F₈ gas was purchased from SynQuest Labs (Lot# QSB-110, Assay 98% min). The negative-ion mass spectra obtained in the present work showed only the expected 200 amu mass peak.
(13) Heicklen, J.; Wachi, F.; Knight, V. The Infrared Spectra of perfluorocyclopropane and cis- and trans-perfluorobutene-2. SSD-TDR-64-

### Table 4: Electron Affinity of trans-2-C₄F₈

<table>
<thead>
<tr>
<th>Method</th>
<th>EA(trans-2-C₄F₈) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>computation (G3(MP2))</td>
<td>0.738</td>
</tr>
<tr>
<td>kinetic (kₐ,trans = kₐ,cis)p</td>
<td>0.78−0.81</td>
</tr>
<tr>
<td>hybrid (17 meV ≤ EA ≤ 35 meV)p</td>
<td>0.77−0.83</td>
</tr>
</tbody>
</table>

a EA 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. b EA 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 affect 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.

![Figure 4](image.png)


(17) Miller, T. M.; Friedman, J. F.; Viggiano, A. A. J. Chem. Phys. 2004, 120, 7024. There is a misprint in Table II of this paper: the C–F bond lengths in c-C4F8 are all 1.410 Å for the G3(MP2) method, which uses a MP2(Full)/6-31G(d) geometry optimization. Also, the typical concentration of c-C4F8 vapor in the flow tube was misstated; it should read 4 ppmv.


(25) Two details deserve a footnote. Unconstrained B3LYP/6-31+G(3df) optimization yields a cis-C4F8 geometry that has a C1–C2–C3–C4 dihedral angle within 0.02° of C5 symmetry. But forcing C5 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 C5 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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