Ab Initio Calibration Study of the Heat of Formation, Geometry, and Anharmonic Force Field of Fluoroacetylene

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The heat of formation, geometry, harmonic frequencies, and quartic force field of the fluoroacetylene (FCCH) molecule have been computed using coupled cluster methods and large basis sets. Inner-shell correlation was included explicitly, as were both cubic and quartic resonances. Our final force field, which does not involve any empirical adjustment, reproduces 36 vibrational band origins with a mean absolute error of 1.6 cm^{-1}. The bending anharmonicities exhibit a marked basis set sensitivity, due almost entirely to the CCF bend. Evidence was found for the existence of an additional quartic resonance, $\nu_2 \approx \nu_3 + 2\nu_4$. Our best estimates, with conservative uncertainties, for the heat of formation and the geometry are 25.3 ± 0.3 kcal/mol and r_e(CF) = 1.2768 ± 0.0005, r_e(CC) = 1.1964 ± 0.0005, and r_e(CH) = 1.0601 ± 0.0005 Å.

I. Introduction

The vibrational spectrum of monofluoroacetylene, FCCH, has recently generated considerable interest both theoretically and experimentally. A large amount of vibrational data are available, both in the low-energy range from the high-resolution Fourier transform infrared work of Holland et al.[1,2] and in the high-energy range from photoacoustic spectroscopy by Vaittinen et al.[3] Together these cover the entire spectrum from near-infrared through visible.

The theoretical interest is largely due to the complex resonance structure of the spectra. This includes cubic (Fermi) resonances such as[2,3] $\nu_1 \approx \nu_2 + \nu_3$, $2\nu_3 \approx \nu_2$, and $\nu_3 \approx 2\nu_4$, as well as a fairly important quartic resonance[4] $\nu_1 \approx \nu_2 + 2\nu_4$. An analytical expression for the "1−3" resonance constant $K_{1,244}$ in terms of the quartic normal coordinate force field has been derived by Borro, Mills, and Venuti (BMV),[5] while Lehmann[6] has considered an approximate treatment involving only the cubic force field.

As a result of these resonances, assignments in the high- or even medium-energy region become very difficult. This has made FCCH a test case for Lie-algebraic "vibron" models,[7] in which the dynamics of each chemical bond is described by the Lie algebra $u(4)$ associated with the Lie group $U(4)$. The choice of algebra is motivated by consideration of the atom−atom interactions leading to bonding.[7] For the case of an acyclic tetratomic molecule there are three bonds, and thus the complete dynamical problem involves the sum of three algebras. Representations are then constructed using subgroup chains: for the case of $u(4)\oplus u(4)\oplus u(4)$ the chain used is

$$u_1(4) \oplus u_2(4) \oplus u_3(4) \supset o_1(4) \oplus o_2(4) \oplus o_3(4) \supset o_{13}(4) \oplus o_2(4) \supset o_{132}(4) \supset o_{132}(3) \supset o_{132}(2) \quad (1)$$

The irreducible representations (irreps) of the respective $u_i(4)$ are indexed by three integers N_i: at each stage of the chain new indices arise for the subgroup irreps. The vibrational Hamiltonian is constructed as a linear combination of the Casimir operators of the chain of eq 1, and since the eigenvalues of the Casimir operators are known, an explicit form for the energies, for any values of the coefficients of the Casimir operators, can be obtained. This expression can be compared with the usual expression in terms of vibrational quantum numbers, and the latter can then be expressed in terms of the irrep indices. The complete correspondence is given by Bernardes, Hornos, and Hornos (BHH).[8] Values of the coefficients of the Casimir operators in the Hamiltonian are obtained by fitting, minimizing the least-squares difference between calculated and experimental energy levels.

This algebraic approach is phenomenological in nature, since the dynamical symmetries used do not (necessarily) reflect any underlying invariance properties of the system. It has nevertheless been successful in a number of cases (notably FCCH) in treating vibrational spectra even to very high degrees of excitation using a comparatively small set of parameters, and can thus provide valuable aid in the assignment of vibrational spectra in the high-energy region. A detailed derivation of the case of a linear tetratomic is given by Iachello and co-workers in ref 9, with acetylene as an example. Iachello et al.[10,11] applied algebraic models of various degrees of complexity to the FCCH spectrum. Independently, Bernardes et al.[12] achieved agreement to within 11 cm^{-1} (rms deviation) with 63 experimental states

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using a 10-parameter model: unlike the work of Iachello et al., these authors treat the u_4 irrep indices $\{N_1,N_2,N_3\}$ as adjustable (integer) parameters rather than fixing them at the approximate value (rounded to integer) $\omega_e/\omega_e x_e - 2$. In the very recent work presented in BHH these authors extend their analysis to higher energies and fit 170 states below 16 000 cm^{-1} to 6.8 cm^{-1} (rms deviation), still only using 10 parameters. The fit involved a modest number of reassignments of vibrational states compared to the original experimental assignments, but this is likely to arise for any model. FCCH is undoubtedly a very successful application of the algebraic approach.

There have been a number of ab initio studies of the anharmonic force field. Green et al.[13] combined a MP2/DZP (second-order many-body perturbation theory with a double-zeta plus polarization basis set) anharmonic force field with harmonic frequencies obtained at the MP2 level with a larger [5s4p2d1f] basis set. Botschwina[14] studied the stretching vibrations using an empirically corrected CEPA (coupled electron pair approximation[15]) potential. In a later contribution, Botschwina et al.[16] made a detailed study of the rotation−vibration coupling constants for several isotopomers of FCCH using coupled cluster methods and basis sets of [4s3p2d1f/3s2p] quality and proposed a revised equilibrium geometry. Finally, the Botschwina group published a further study[17] of the anharmonic stretching potential, including the dipole field, using the same force field with the diagonal quadratic terms adjusted for reproduction of the most recent experimentally derived values[4] of $\{\omega_1, \omega_2, \omega_3\}$.

In the present work, we will study the full quartic force field of FCCH using coupled cluster methods with basis sets including *g* functions, as well as special core correlation basis sets. We will demonstrate that, using an appropriately chosen "resonance polyad model", the fundamentals of FCCH can be reproduced to about 2 cm^{-1} and the rotational constants to four decimal places without any empirical correction. We believe that our best computed anharmonic force field is the best one presently available in the literature and definitely the best of those obtained entirely from first principles. Finally, benchmark calculations for the geometry and heat of formation of FCCH will be presented.

II. Computational Methods

All ab initio calculations were performed with the singles and doubles coupled cluster method with a perturbative correction for connected triples, CCSD(T) for short,[18−21] using either the MOLPRO 96.4 package[22] or the TITAN program interfaced to the MOLCAS-3 package.[23,24] The codes were run on four different platforms: a Cray C90 and an IBM RS/6000 model 591 at the San Diego Supercomputer Center, and a DEC AlphaStation 500/500 and an SGI Origin 2000 at the Weizmann Institute of Science. In most calculations the 1s electrons on F and C were not correlated, but some calculations with all electrons correlated were also performed in order to assess the effects of core correlation.

To establish the convergence of calculated properties with respect to the one-particle basis set, we performed calculations using a variety of basis sets. The basis sets used for valence correlation calculations were the cc-pV*n*Z (correlation consistent polarized *n*-tuple zeta, with n = D for double, T for triple, Q for quadruple, 5 for quintuple, etc.) basis sets by Dunning,[25] the aug-cc-pV*n*Z (augmented cc-pV*n*Z) basis sets by Dunning and co-workers,[26] and the atomic natural orbital (ANO)[27] basis sets by Widmark et al.[28] The contractions for the cc-pV*n*Z basis sets are as follows: cc-pVDZ [3s2p1d/2s1p], cc-pVTZ [4s3p2d1f/3s2p1d], cc-pVQZ [5s4p3d2f1g/4s3p2d1f], and cc-pV5Z [6s5p4d3f2g1h/5s4p3d2f1g]. The aug-cc-pV*n*Z basis sets correspond to the cc-pV*n*Z basis sets augmented with one diffuse function of each angular type. A combination of a regular cc-pV*n*Z basis set on hydrogen with an aug-cc-pV*n*Z basis set on the other elements is denoted aug′-cc-pV*n*Z following Del Bene.[29] Two contractions of the ANO basis sets were mainly used, [5s4p3d2f/4s3p2d] and [5s4p3d2f1g/4s3p2d1f], where the second contraction is augmented with one *g* function on F and C (exponents 1.536 and 0.600, respectively) and one *f* function on H (exponent 0.87312). For brevity, these two contractions are denoted ANO5432 and ANO54321, respectively. In addition, some exploratory calculations were carried out using smaller [4s3p2d/3s2p] and [4s3p2d1f/3s2p1d] contractions, or ANO432 and ANO4321 for short. The core correlated calculations employed the cc-pCVQZ (correlation consistent core−valence polarized valence quadruple zeta) basis set, again by Dunning et al.,[30] which for F and C is the cc-pVQZ basis set augmented to [8s7p5d3f1g] with functions describing core−core and core−valence correlation. For H the cc-pCVQZ and cc-pVQZ basis sets are identical. Spherical harmonic basis functions were used in all calculations, and only the C_{2v} subgroup of $C_{\infty v}$ was used for the linear symmetry calculations.

The equilibrium geometry was determined from iterative quadratic fits to 10 point grids in the three bond lengths: the final bond lengths were converged to about 10^{-5} a_0. The complete quartic force field was then determined in the curvilinear internal valence coordinates S_i, with $S_1 = r(\mathrm{FC})$, $S_2 = r(\mathrm{CC})$, $S_3 = r(\mathrm{CH})$, $S_{4x} = \theta_x(\mathrm{CCH})$, $S_{4y} = \theta_y(\mathrm{CCH})$, $S_{5x} = \theta_x(\mathrm{FCC})$, $S_{5y} = \theta_y(\mathrm{FCC})$, where θ represents a linear bend coordinate and the molecule lies on the *z*-axis. The force constants were obtained by repeated central differences using a step size of 0.01 Å for the stretch coordinates and 0.025 radian for the bends. We adopted the latter step size after numerical experimentation with the cc-pVDZ force field revealed that the off-diagonal bending constants were numerically ill-defined even when the energies were converged to 10^{-12} E_h. Some of the redundant quartic force constants such as $k_{4x4x4y4y}$, $k_{5x5x5y5y}$, and $k_{4x4y5x5y}$ were explicitly evaluated: the degree to which their numerical values satisfied the cylindrical symmetry relationships[31] served as a check on the numerical consistency of our calculated force field.

The geometry displacements and the transformation of the internal coordinate force field to Cartesian coordinates were performed using INTDER,[32] while the transformation from internal to normal coordinates and the initial spectroscopic analysis using second-order vibrational perturbation theory[33] were carried out using the SPECTRO package.[34,35] Resonance polyads were set up and diagonalized in Mathematica.[36]

To determine a quadratic force field required a total of 29 points (25 with C_{2v} symmetry and 4 with C_s symmetry), and to determine a quartic force field required a total of 247 points (129 C_{2v}, 108 C_s, and 10 C_1 symmetry).

III. Results and Discussion

Unless indicated otherwise, experimental vibrational data quoted below were taken from Table 2 in BHH, itself compiled from refs 1−3.

A. Harmonic and Vibrational Frequencies. In our initial model for the fundamental frequencies (Table 1), we only consider the strong Fermi type 1 resonance $\nu_2 \approx 2\nu_3$.

Thomas et al.[37] studied the harmonic frequencies of FCCH as part of a systematic study and found a very large difference

TABLE 1: CCSD(T) and Observed Fundamentals (cm^{-1})

	cc-pVDZ	cc-pVTZ	ANO5432	best estimate		expt
model	simple	simple	simple	simple	extended	ref 8
ν_1	3350.2	3356.9	3358.5	3360.3	3358.8	3356.972
ν_2	2219.9	2236.4	2227.8	2234.4	2237.3	2239.205
$2\nu_3$	2070.8	2108.6	2091.7	2104.7	2106.3	2108.131
ν_3	1042.3	1062.1	1053.3	1060.0	1059.7	1061.445
ν_4	535.8	576.7	577.0	583.2	583.2	583.704
ν_5	328.9	360.2	353.7	365.1	365.1	366.634

TABLE 2: CCSD(T) and Observed Harmonic Frequencies (cm^{-1})

	ω_1	ω_2	ω_3	ω_4	ω_5
TZ2P[a]	3467	2250	1042	559	342
TZ2Pf[a]	3515	2300	1069	666	412
cc-pVDZ	3487.1	2266.0	1052.4	576.6	357.2
cc-pVTZ	3493.7	2281.4	1073.2	585.0	366.7
b	3469.8	2263.0	1052.7	567.1	344.6
cc-pVQZ	3481.6	2281.1	1072.0	589.0	368.8
cc-pCVQZ[c]	3487.8	2289.2	1076.0	594.2	376.4
cc-pCVQZ	3482.3	2281.9	1072.4	589.3	368.6
aug-cc-pVTZ	3479.9	2270.6	1067.5	585.2	359.8
ANO432	3486.7	2256.2	1047.0	568.4	308.8
ANO4321	3487.8	2266.5	1061.4	576.4	331.8
ANO5432	3490.6	2273.1	1064.5	584.8	357.7
ANO54321	3485.6	2271.9	1066.8	585.8	361.2
best estimate	3491.1	2279.2	1070.4	590.7	369.0
expt[d]	3478.89	2283.062	1072.70	594.37	374.62

[a] Ref 37. All electrons correlated and Cartesian *d*, *f* functions used. [b] Ditto with *f* functions on C and F, and *d* functions on H, deleted. [c] All electrons correlated. [d] Ref 4. Error margin is quoted as "about 1 cm^{-1} ".

TABLE 3: Basis Set Convergence of CCSD(T) Anharmonic Corrections to Deperturbed Fundamentals (cm^{-1})

	cc-pVDZ	cc-pVTZ	ANO5432
$\nu_1-\omega_1$	136.841	136.396	132.112
$\nu_2^*-\omega_2$	52.041	52.096	52.263
$\nu_3-\omega_3$	10.143	11.019	11.151
$\nu_4-\omega_4$	40.838	8.095	7.791
$\nu_5-\omega_5$	28.332	6.935	3.951

(Table 2) between the bending harmonic frequencies computed at the CCSD(T) level with Huzinaga−Dunning[38,39] [5s3p2d/3s2p] (denoted TZ2P for triple-zeta plus two polarization) and [5s3p2d1f/3s2p1d] (denoted TZ2Pf for TZ2P plus an *f* function) basis sets. Specifically, they found that adding the *f* function increased ω_4, the CCH bend, by 107 cm^{-1} and ω_5, the CCF bend, by 70 cm^{-1}. By contrast, in the present work we find that CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ values for ω_4 and ω_5 differ by no more than 8 and 10 cm^{-1}, respectively. Selectively deleting the *f* functions from the cc-pVTZ basis set decreases ω_4 and ω_5 by only 18 and 22 cm^{-1} : the effects of deleting the *f* functions from the ANO4321 basis set are likewise much smaller (−8 and −23 cm^{-1}, respectively) than in the TZ2Pf case. It is also worth noting (Table 2) that the contribution of *f* functions to the stretching frequencies of FCCH is considerably smaller in the cc-pVTZ and particularly the ANO4321 basis sets than in the TZ2Pf basis set.

Perhaps the crucial difference between the TZ2Pf and cc-pVTZ basis sets, from our point of view, is that the former use d exponents on C (1.50; 0.375) and F (2.00; 0.50) which are quite different from the optimum values for atomic correlated calculations used in the cc-pVTZ basis set (C 1.097, 0.318; F 3.107, 0.855). Given a poor set of *d* exponents, it is conceivable that an exaggerated contribution of *f* functions would be found. We likewise found in previous work on C_2H_4,[40] C_6H_6,[41] and C_2H_2[42] that basis set effects on the "sensitive" modes of these molecules (the twisting vibration ω_8 for C_2H_4, the out-of-plane bending modes ω_4 and ω_5 in the case of C_6H_6, and the bending vibrations of acetylene) exhibit much smaller basis set unsaturation effects in correlation-consistent and particularly ANO basis sets than in Huzinaga−Dunning basis sets. The present example further confirms our observation and suggests that not only basis set balance but also exponent optimization are important in achieving basis set convergence for bending and out-of-plane modes involving multiply bonded atoms.

In the past, we have generally (e.g., ref 40) found CCSD(T)/cc-pVDZ fundamentals to be in fairly good agreement with experiment despite the small basis set, in part because of an error compensation between harmonic frequencies and anharmonicities. This rule of thumb is violated in the present case: the bending anharmonicities are clearly nonsensical even though the harmonic frequencies (Table 2) appear to be good, and the stretching anharmonicities (Table 3) are in quite good agreement with those obtained using larger basis sets. A very strong basis set dependence of the bending anharmonicities has been observed for the acetylene molecule,[42] as we discussed above; in the present case the phenomenon is weaker since even improving the basis set to cc-pVTZ—still woefully inadequate in the case of C_2H_2—appears to remedy the problem. A more detailed understanding can be obtained by considering the results in Table 5, where we can immediately identify the FCC bend, S_5, as the culprit. Every bending force constant except perhaps for the diagonal CCH quartic is affected, with a particularly large effect on the diagonal FCC quartic as well as the $f_{4x4x4x5x}$ coupling constant. As a result, all the normal coordinate quartics that appear in the anharmonicity constants are significantly affected. Since in addition the X_{ij} involve a balance between large cubic and quartic terms of opposite sign, X_{44}, X_{45}, and X_{55} are all affected, as are, to a lesser extent, G_{44} and G_{55}. Since G_{45} has only cubic terms at this level of approximation, it is not affected; a clear effect is seen on R_{45}, though, which depends on $\phi_{4x4y5x5y} = (\phi_{4x4x5x5x} - \phi_{4x4x5y5y})/2$. Finally, we note that none of the stretch or even stretch-bend anharmonicities (not given in Table 5) are affected to any appreciable degree by this basis set issue, which appears to be strictly related to the bending quartics.

Further extension of the basis set from cc-pVTZ to cc-pVQZ affects ω_1 (the CH stretch) and ω_4 (the CCH bend) significantly (−12 and +4 cm^{-1}, respectively). Addition of diffuse functions to the cc-pVTZ basis set lowers all harmonic frequencies except ω_4: the effects are −14, −11, −6, +0.2, and −7 cm^{-1}. It should be noted that there will be significant coupling between this addition and the expansion of the underlying basis set to cc-pVQZ since the latter's outermost functions are already fairly diffuse themselves. Given both the polar nature of the molecule and the known importance of diffuse functions for the bending frequencies of acetylene, it was decided that an atomic natural orbital (ANO) basis set—with a primitive exponent range that includes more diffuse functions—would be a better choice. It was previously found[41] that, while the ω_4 and ω_5 out-of-plane bending frequencies of benzene were in error by as much as 50 cm^{-1} with a cc-pVTZ basis set, they were found in excellent agreement with experiment using a [4s3p2d1f/4s2p] ANO basis set instead.

Harmonic frequencies at the CCSD(T)/ANO54321 level differ appreciably from their CCSD(T)/cc-pVQZ counterparts (+4, −9, −5, +1, and −8 cm^{-1}); the effect of deleting the *g* functions on the heavy atoms and the *f* function on hydrogen is noticeable

TABLE 4: CCSD(T)/ANO5432 Quartic Force Field in Simple Internal Coordinates. Units Are Consistent with aJ for Energy, Å for Distance, and Radians for Angles

f_{11}	8.491 80	f_{21}	0.152 20	f_{22}	16.623 60
f_{31}	−0.040 62	f_{32}	−0.123 93	f_{33}	6.483 13
f_{44}	0.372 96	f_{64}	0.158 09	f_{66}	0.196 93
f_{111}	−54.873 07	f_{211}	−1.359 64	f_{221}	−0.756 24
f_{222}	−97.377 30	f_{311}	0.055 07	f_{321}	−0.075 23
f_{322}	−0.106 98	f_{331}	0.029 77	f_{332}	0.356 35
f_{333}	−36.800 22	f_{441}	−0.805 52	f_{551}	0.117 67
f_{442}	−1.502 36	f_{552}	−0.958 28	f_{443}	−0.040 21
f_{553}	−0.136 93	f_{541}	−0.104 00	f_{542}	0.424 32
f_{543}	−0.006 52				
f_{1111}	310.206 11	f_{2111}	4.909 93	f_{2211}	1.851 15
f_{2221}	−0.554 58	f_{2222}	473.915 11	f_{3111}	−0.095 93
f_{3211}	−0.019 64	f_{3221}	0.179 18	f_{3222}	−0.510 11
f_{3311}	−0.031 81	f_{3321}	−0.145 62	f_{3322}	−1.822 80
f_{3331}	−0.016 16	f_{3332}	−1.549 48	f_{3333}	187.371 56
f_{4411}	1.739 99	f_{4421}	1.222 26	f_{4422}	−0.201 45
f_{4431}	0.030 97	f_{4432}	−0.125 70	f_{4433}	−0.030 83
f_{5511}	−0.526 94	f_{5521}	0.029 16	f_{5522}	−0.271 35
f_{5531}	−0.008 65	f_{5532}	0.125 70	f_{5533}	−0.019 95
f_{5411}	0.329 81	f_{5421}	−0.107 98	f_{5422}	0.443 37
f_{5431}	−0.002 37	f_{5432}	0.065 43	f_{5433}	−0.050 92
f_{4444}	0.852 59	f_{5444}	−0.264 92	f_{5554}	−0.221 19
f_{5555}	0.183 20	$f_{5x5x4x4x}$	0.085 23	$f_{5y5y4x4x}$	0.122 15

TABLE 5: Basis Set Convergence at the CCSD(T) Level for Quartic Bending Force Constants in Internal and Normal Coordinates, as Well as Anharmonicity Constants. Units for Internal Coordinate Force Constants Are Consistent with aJ for Energy, Å for Length, and Dimensionless sin α for Linear Bending Angles. All Other Quantities Are in cm^{-1} [a]

	cc-pVDZ	cc-pVTZ	ANO5432
$f_{4x4x4x4x}$	2.084 66	2.171 25	2.344 25
$f_{4x4x4x5x}$	0.018 29	−0.099 28	−0.106 81
$f_{4x4x5x5x}$	0.023 48	0.062 52	0.085 23
$f_{4x4x5y5y}$	0.055 94	0.102 95	0.122 15
$f_{4x4y5x5y}$	−0.016 23	−0.020 21	−0.018 46
$f_{4x5x5x5x}$	0.084 74	−0.075 21	−0.063 09
$f_{5x5x5x5x}$	0.233 28	0.993 29	0.970 87
$\phi_{4x4x4x4x}$	2477.353	2710.592	2724.827
$\phi_{4x4x5x5x}$	29.730	103.359	100.762
$\phi_{4x4x5y5y}$	−13.631	15.563	16.866
$\phi_{4x4y5x5y}$	21.677	43.900	41.950
$\phi_{5x5x5x5x}$	77.786	131.858	149.695
X_{44}	−8.050	−0.287	−0.516
X_{45}	−9.768	2.346	2.455
X_{55}	−3.289	0.258	1.237
G_{44}	6.694	4.418	4.581
G_{45}	0.390	0.411	0.400
G_{55}	2.134	0.931	0.537
R_{45}	−8.648	2.364	2.018

[a] Simultaneous positive displacements in the *x* components of ν_4 and ν_5 lead to a trans structure. This convention affects the signs of $f_{4x4x4x5x}$ and $f_{4x5x5x5x}$.

(+5, +1, −2, −1, −4 cm^{-1}) but smaller and is not expected to affect the anharmonicities appreciably. Therefore, as a compromise between convergence and computational cost, we have selected CCSD(T)/ANO5432 as the level of theory for our best computation of the quartic force field. The entire force field in internal coordinates is reported in Table 4.

As seen in Table 5, X_{55} and, to a lesser extent, X_{44} and R_{45} are mildly affected by the basis set expansion from cc-pVTZ to ANO5432: nevertheless, the effect is small enough to justify considering the CCSD(T)/ANO5432 values to be essentially converged.

The main additional effect on the harmonic frequencies is expected to be that of inner-shell correlation. This was evaluated by carrying out CCSD(T)/cc-pCVQZ calculations with and without correlation from the 1s-like orbitals admitted. As expected, the valence correlation-only CCSD(T)/cc-pCVQZ results are essentially identical to those obtained at the CCSD(T)/cc-pVQZ level. The differential effect of inner-shell correlation is found to be +5.5, +7.3, +3.6, +4.9, and +7.8 cm^{-1} for the five harmonic frequencies, so that the greatest relative effect is seen for ω_5.

We now obtain our best estimate of the harmonic frequencies as follows:

$$\omega_i(\text{best}) = \omega_i(\text{CCSD(T)/ANO[5s4p3d2f1g/4s3p2d1f], valence}) + \omega_i(\text{CCSD(T)/cc-pCVQZ, core+valence}) - \omega_i(\text{CCSD(T)/cc-pCVQZ, valence}) \quad (2)$$

and similarly for the geometry. In conjunction with the CCSD(T)/ANO5432 cubic and quartic force field, we obtain the fundamentals given in Table 1. Especially for the lower three fundamentals, the agreement with experiment is excellent: deviations from experiment are somewhat larger for the CC and CH stretching fundamentals, as well as the FC stretching overtone, which is in resonance with the former. However, the full accuracy of the present force field is only reflected when a more detailed vibrational model is used, which we shall consider below.

B. Refined Vibrational Model. In our final model, we use the CCSD(T)/ANO[5s4p3d2f/4s3p2d] quartic force field together with the best estimate geometry and harmonic frequencies in the second-order perturbation theory analysis. Aside from $2\nu_3 \approx \nu_2$, the weaker first-order resonant interactions $\nu_2 + \nu_3 \approx \nu_1$ and $2\nu_4 \approx \nu_3$ were deleted from the contact transformation. (The even weaker interaction between $\nu_4 + \nu_5$ and ν_3, considered by BHH, was not treated as a resonance.) In addition the second-order resonances $\nu_1 \approx \nu_2 + 2\nu_4$ and $\nu_2 \approx \nu_3 + 2\nu_4$ are included. A comprehensive discussion of all the resonance polyads in the complicated spectrum of this molecule is beyond the scope of the present work: we shall limit ourselves to those polyads involving fundamentals.

The parameters required, apart from the deperturbed band origins, are $k_{233} = 59.991$, $k_{123} = 43.723$, and $k_{344} = 17.766$ cm^{-1} for the first-order resonances and $K^*_{1;244} = 16.544$ and $K^*_{2;344} = 12.147$ cm^{-1} for the second-order resonance constants. The asterisks indicate that terms with near-singular denominators related to the resonances $\nu_2 + \nu_3 \approx \nu_1$ in $K_{1,244}$ were deleted following the recommendation of BMV,[5] and analogously for the terms affected by $2\nu_3 \approx \nu_2$ in $K_{2,344}$. (The uncorrected constants are 13.799 and 22.794 cm^{-1}, respectively.)

For ν_3 we have a simple 2 × 2 resonance matrix:

$$\begin{pmatrix} |0002^00^0\rangle* & k_{344}/\sqrt{8} \\ k_{344}/\sqrt{8} & |0010^00^0\rangle* \end{pmatrix} = \begin{pmatrix} 1154.069 & 12.562 \\ 12.562 & 1061.409 \end{pmatrix} \tag{3}$$

with eigenvalues $|0010^00^0\rangle = 1059.7$ and $|0002^00^0\rangle = 1155.7$ cm^{-1}, in excellent agreement with the observed values 1061.445 and 1155.592 cm^{-1}.

The resonant interactions listed above lead to ν_2 being involved in a tetrad:

$$\begin{pmatrix} |0020^00^0\rangle* & k_{344}/\sqrt{2} & k_{233}/2 & 0 \\ k_{344}/\sqrt{2} & |0012^00\rangle* & K^*_{2;344}/2 & k_{344}/\sqrt{3/2} \\ k_{233}/2 & K^*_{2;344}/2 & |0100^00^0\rangle* & 0 \\ 0 & k_{344}/\sqrt{3/2} & 0 & |0004^00^0\rangle* \end{pmatrix} = \begin{pmatrix} 2114.871 & 12.563 & 29.995 & 0 \\ 12.563 & 2213.718 & 6.074 & 21.759 \\ 29.995 & 6.074 & 2227.062 & 0 \\ 0 & 21.759 & 0 & 2299.986 \end{pmatrix} \tag{4}$$

which has the eigenvalues, in left-to-right order, 2106.3, 2206.9, 2237.3, and 2305.3 cm^{-1}, in excellent agreement with the experimentally observed transitions 2108.131, 2211.614, 2239.205, and 2303.480 cm^{-1}. The eigenvectors have the structure (columns in same order as eigenvalues)

$$\begin{pmatrix} -0.971 & 0.026 & 0.235 & 0.020 \\ 0.098 & 0.920 & 0.283 & 0.254 \\ 0.216 & -0.314 & 0.924 & 0.024 \\ -0.011 & -0.235 & -0.102 & 0.967 \end{pmatrix} \tag{5}$$

The polyad involving ν_1 requires, for consistency, no less than seven states:

$$\begin{pmatrix} |0030^00^0\rangle* & k_{344}\sqrt{3/2} & k_{233}\sqrt{3/4} & 0 & \approx 0 & 0 & 0 \\ k_{344}\sqrt{3/2} & |0022^00^0\rangle* & 0 & k_{344}\sqrt{3} & 0 & k_{233}/2 & 0 \\ k_{233}\sqrt{3/4} & 0 & |0110^00^0\rangle* & 0 & k_{123}/\sqrt{8} & k_{344}/2 & 0 \\ 0 & k_{344}\sqrt{3} & 0 & |0014^00^0\rangle* & 0 & 0 & k_{344}\sqrt{15}/2 \\ \approx 0 & 0 & k_{123}/\sqrt{8} & 0 & |1000^00^0\rangle* & K^*_{1;244}/2 & 0 \\ 0 & k_{233}/2 & k_{344}/2 & 0 & K^*_{1;244}/2 & |0102^00\rangle* & 0 \\ 0 & 0 & 0 & k_{344}\sqrt{15}/2 & 0 & 0 & |0006^00^0\rangle \end{pmatrix} = \begin{pmatrix} 3160.384 & 21.759 & 51.953 & 0 & 0 & 0 & 0 \\ 21.759 & 3265.418 & 0 & 30.772 & 0 & 29.995 & 0 \\ 51.953 & 0 & 3281.024 & 0 & 15.458 & 8.883 & 0 \\ 0 & 30.772 & 0 & 3357.874 & 0 & 0 & 34.404 \\ 0 & 0 & 15.458 & 0 & 3358.564 & 8.272 & 0 \\ 0 & 29.995 & 8.883 & 0 & 8.272 & 3366.666 & 0 \\ 0 & 0 & 0 & 34.404 & 0 & 0 & 3437.751 \end{pmatrix} \tag{6}$$

which has the eigenvalues (ordered left to right) 3137.3, 3251.4, 3296.8, 3349.8, 3358.8, 3382.3, and 3451.2 cm^{-1}, which compare very well with the available experimental ones: 3142.611, –, 3300.529, 3351.731, 3356.972, 3384.760, and – cm^{-1}. It should be noted that eliminating even a single band from this matrix leads to a significant error in at least one of the remaining bands: a balanced treatment of resonances affecting ν_1 requires that all seven states be included.

The structure of the eigenvectors, in the same order, is

$$\begin{pmatrix} 0.929 & 0.114 & -0.174 & -0.302 & 0.012 & 0.052 & 0.003 \\ 0.024 & -0.829 & 0.247 & -0.427 & -0.124 & -0.226 & -0.035 \\ -0.003 & 0.398 & 0.827 & -0.334 & 0.208 & -0.042 & 0.022 \\ -0.364 & 0.184 & -0.399 & -0.771 & 0.047 & 0.279 & 0.024 \\ -0.003 & 0.167 & 0.147 & -0.040 & -0.898 & 0.167 & -0.339 \\ 0.065 & -0.273 & 0.207 & 0.136 & 0.081 & 0.908 & 0.171 \\ -0.005 & 0.066 & 0.016 & -0.027 & -0.355 & -0.122 & 0.924 \end{pmatrix} \tag{7}$$

Together with the two remaining fundamentals ν_4 and ν_5 (calculated 583.2 and 365.0; observed 583.704 and 366.639 cm^{-1}) we thus find a mean absolute error for 13 states of 2.3 cm^{-1}. For the fundamentals and $2\nu_3$, the mean absolute error for six states is actually only 1.5 cm^{-1} : the two largest errors are associated with the three-quantum states $|0012^00^0\rangle$ and $|0030^00^0\rangle$. The reliability of our predicted band origins for the missing $|0022^00^0\rangle$ and $|0006^00^0\rangle$ states involved in the ν_1 heptad is hard to quantify, but we expect the observed values to lie within a few cm^{-1} of our computed band origins, 3251.4 and 3451.2 cm^{-1}. The former compares quite well with the band origin, 3253.18 cm^{-1}, predicted by Iachello et al.,[11] while the latter is considerably higher in energy than their prediction of 3436.42 cm^{-1}. It should be pointed out that the Iachello et al. values differ themselves considerably from those with the Holland et al. model, 3267.0 and 3432.7 cm^{-1}. We believe that our computed force field will be very useful as a starting point for more extensive vibrational analysis of the spectrum of FCCH.

This point is made more emphatically by considering a larger number of vibrational states. As seen in Table 6, the mean absolute error of the present model for 36 band origins from ν_5 to the range around ν_1 is only 1.6 cm^{-1}, confirming that the excellent agreement found for the fundamentals is not fortuitous and reflects the actual quality of the force field. For the same set of 36 band origins the mean absolute error of the algebraic approach of BHH is 5.6 cm^{-1} for the BHH model. This is a very respectable performance from a model with only 10 adjustable parameters, compared to 9 quadratic, 19 cubic, and 39 quartic distinct constants in the present force field. Indeed, what is even more impressive is that the BHH model yields results of similar quality for almost 5 times this number of states, up to a total energy of almost 16 000 cm^{-1}. It would be very valuable to explore up to this energy range with our own force field, but this is probably beyond the capabilities of second-order vibrational perturbation theory for the vibrational problem and would require a variational treatment of some sort (e.g., refs 43, 44). Unfortunately, no such method for linear tetratomics is available to us.

For the stretching modes, very good agreement is found with the mixed empirical ab initio force field of Botschwina et al.[17] which gives $2\nu_3 = 2107.1$, $3\nu_3 = 3137.8$, and $\nu_2 + \nu_3 = 3299.4$ cm^{-1}. (The harmonic stretching frequencies in that force field were taken from Borro, Mills, and Mose (BMM),[4] while the stretch−bend coupling was adjusted for the computed and observed fundamentals to coincide. The anharmonic part of the potential was calculated at the CCSD(T)/cc-pVTZ level, with the *d* functions omitted on H.)

As can be seen in Table 8, there is clearly a large difference between the presently computed anharmonicity constants and the experimentally derived set of Holland et al.[1] The more recent set due to BMM[4] agrees rather better, with X_{12} being the principal exception. BMM note that the spectrum in the $\nu_1 + \nu_2$ region is very complicated and that their X_{12} value of −13.0 cm^{-1} may require substantial revision. The most striking difference for the harmonic frequencies is in ω_1: we would be

TABLE 6: Comparison of Observed Band Origins (cm^{-1}) with Computed Values Using the Present Best ab Initio Force Field and the BHH Algebraic Model

expt[1,2]	this work	BHH	assignment
366.639	365.044	368.201	$\|00001\rangle$
583.704	583.171	582.147	$\|00010\rangle$
732.080	731.084	733.762	$\|00002\rangle(\Sigma^+)$
735.579	733.716	738.609	$\|00002\rangle(\Delta)$
949.028	948.283	945.570	$\|00011\rangle(\Sigma^-)$
951.203	951.106	950.216	$\|00011\rangle(\Delta)$
952.670	952.241	945.570	$\|00011\rangle(\Sigma^+)$
1061.445	1061.412	1068.392	$\|00100\rangle$
1155.592	1154.098	1159.516	$\|00020\rangle(\Sigma^+)$
1175.182	1174.510	1164.162	$\|00020\rangle(\Delta)$
1315.600	1317.109	1311.038	$\|00012\rangle(\Pi(\mathrm{I}))$
1322.240	1322.985	1311.239	$\|00012\rangle(\Pi(\mathrm{II}))$
1431.337	1430.457	1436.155	$\|00101\rangle$
1523.440	1523.668	1522.846	$\|00101\rangle(\Pi(\mathrm{I}))$
1543.425	1544.020	1522.846	$\|00021\rangle(\Pi(\mathrm{II}))$
1642.769	1643.703	1645.668	$\|00110\rangle$
1735.372	1733.193	1736.792	$\|00030\rangle(\Pi)$
1466.830	1471.256	1466.639	$\|00004\rangle(\Sigma^+)$
1799.720	1800.458	1801.269	$\|00102\rangle(\Sigma^+)$
1803.431	1803.090	1806.131	$\|00102\rangle(\Delta)$
2011.301	2012.796	2008.732	$\|00111\rangle(\Sigma^-)$
2013.517	2015.619	2013.220	$\|00111\rangle(\Delta)$
2014.953	2016.754	2008.732	$\|00111\rangle(\Sigma^+)$
2100.420	2101.224	2095.423	$\|00031\rangle(\Sigma^-)$
2104.480	2106.026	2099.911	$\|00031\rangle(\Delta)$
2108.131	2106.3	2119.576	$\|00200\rangle$
2108.668	2109.140	2095.423	$\|00031\rangle(\Sigma^+)$
2211.614	2206.9	2218.245	$\|00120\rangle(\Sigma^+)$
2231.909	2234.162	2222.733	$\|00120\rangle(\Delta)$
2239.205	2237.3	2240.918	$\|01000\rangle$
2303.480	2305.3	2309.369	$\|00040\rangle(\Sigma^+)$
3142.611	3137.3	3153.553	$\|00300\rangle$
3300.529	3296.8	3299.647	$\|01100\rangle$
3351.731	3349.8	3358.435	$\|00140\rangle(\Sigma^+)$
3356.972	3358.8	3339.469	$\|10000\rangle$
3384.760	3382.3	3390.771	$\|01020\rangle(\Sigma^+)$
	1.58	5.57	mean absolute error

TABLE 7: Comparison of Assignments for Some Disputed Bands

experimental frequency cm^{-1}	band assignments				
	Holland et al.[a]	BHH[b]	BMM[c]	this work	
2687.342	$\|00041\rangle$	$\|00210\rangle$	$\|00210\rangle$	$\|00210\rangle$	Π
2937.768	$\|01002\rangle$	$\|00122\rangle$		$\|01002\rangle$	Σ^+
2940.485	$\|01002\rangle$	$\|00122\rangle$		$\|01002\rangle$	Δ
3518.640	$\|01012\rangle$	$\|00301\rangle$	$\|00301\rangle$	$\|00301\rangle$	Π
3718.700	$\|00141\rangle$	$\|00141\rangle$	$\|00310\rangle$	$\|00310\rangle$	Π
3725.031	$\|00141\rangle$	$\|00310\rangle$	$\|00141\rangle$	$\|00141\rangle$	Π
4646.869	$\|01032\rangle$	$\|10012\rangle$		$\|10012\rangle$	Π
4774.540	$\|00241\rangle$	$\|10101\rangle$	$\|10101\rangle$	$\|10101\rangle$	Π
5579.134	$\|10040\rangle$	$\|11000\rangle$	$\|10040\rangle$	$\|10040\rangle$	Σ^+
5587.233	$\|11000\rangle$	$\|01140\rangle$	$\|11000\rangle$	$\|11000\rangle$	Σ^+

[a] Ref 2. [b] Ref 8. [c] Ref 5.

TABLE 8: Computed and Experimentally Derived Anharmonicity and Resonance Constants (cm^{-1})

	MP2[a] ref 13	this work[b]	expt ref 1	expt ref 4
X_{11}	−54.8	−53.871	−52.000	−48.12*
X_{21}	−5.9	−7.864*	−11.165	−13.00*[c]
X_{22}	−8.6	−8.439	−7.790	−8.006
X_{31}	0.8	−0.836*	−3.869	−2.445*
X_{32}	−9.3	−7.447*	−0.118	−5.932*
X_{33}	−3.8	−3.974*	−6.850	−4.063*
X_{41}	−12.5	−15.940	−22.261	−19.35
X_{42}	−7.7	−7.232	−6.727	−6.563
X_{43}	−2.2	−0.880*	−2.380	−1.204*
X_{44}	−0.9	−1.019*	−1.101	−1.095*
X_{51}	−3.8	−4.504	−8.981	−4.617
X_{52}	−19.6	−20.374	−16.630	−19.405
X_{53}	3.5	3.979	3.253	3.369
X_{54}	0.2	2.436	0.684	0.718
X_{55}	1.1	1.136	0.281	0.276
G_{44}	4.8	5.103	4.898	5.409
G_{45}	0.4	0.422	0.177	0.177
G_{55}	0.5	0.658	0.879	0.857
R_{45}	1.227	2.005	1.821	1.821
$K_{1;244}$		16.544*		7.500* ± 3.0
$K_{2;344}$		13.905*		
k_{123}		43.723		47.88 ± 3.0
k_{233}	61.9	59.991		58.95 ± 3.0
k_{344}		17.766		13.78 ± 3.0
ω_1	3526.5	3491.1	3499.722	3478.89
ω_2	2274.5	2279.2	2283.781	2283.06
ω_3	1078.9	1070.4	1076.266	1072.70
ω_4	593.3	590.7	596.836	594.37
ω_5	375.9	369.0	375.411	374.62

[a] MP2/TZ2P+f harmonics combined with MP2/DZP anharmonicities. [b] Best estimate. [c] Authors note that "spectrum in $\nu_1 + \nu_2$ region is complicated, and this value may need revision". Constants marked with an asterisk have been "deperturbed"; that is, they have had near-singular terms removed.

TABLE 9: CCSD(T) and Experimentally Derived Bond Distances (Å)

	r_e(FC)	r_e(CC)	r_e(CH)
cc-pVDZ	1.294 19	1.220 73	1.076 09
cc-pVTZ	1.281 75	1.202 79	1.061 02
cc-pVQZ	1.279 10	1.199 48	1.061 12
cc-pVTZ+aug(F)	1.303 85	1.220 68	1.077 01
cc-pVTZ+aug(F)	1.284 36	1.202 64	1.061 67
cc-pVQZ+aug(F)	1.280 06	1.199 52	1.061 29
cc-pV∞Z+aug(F)[c]	1.278 83	1.198 87	1.061 28
best estimate[d]	1.276 81	1.196 43	1.060 09
cc-pCVQZ[a]	1.276 84	1.196 78	1.059 91
cc-pCVQZ	1.278 86	1.199 22	1.061 10
aug-cc-pVTZ	1.283 18	1.203 10	1.061 60
ANO4321	1.284 61	1.208 53	1.062 14
ANO5432	1.281 25	1.201 32	1.060 37
ANO54321	1.280 50	1.201 74	1.061 19
from best estimate force field	1.278 48	1.199 30	1.060 00
adjusted final geometry	1.276 44	1.196 50	1.059 58
Borro et al.[4]	1.2781(8)	1.1955(8)	1.0555(15)
ibid. with $K_{1;244} = 7.5$ cm^{-1}	1.2764(8)	1.1962(8)	1.0603(15)
best estimate[16]	1.2765(2)	1.1961(2)	1.0591(5)
CCSD(T)/cc-pVQZ[a,b] [16]	1.2762	1.1969	1.0586

[a] All electrons correlated. [b] Omitting *f* functions on hydrogen. [c] Geometric extrapolation from previous three values. [d] considering core correlation additive to cc-pV∞Z+aug(F).

TABLE 10: Computed and Observed Rotational and Rovibrational Coupling Constants (cm^{-1})

	calculated	adjusted	ref 4	ref 2
B_e	0.323 329	0.324 537	0.324 600[a]	0.324 517[a]
B_0	0.322 560	0.323 763		0.323 763 3
α_1	0.000 866	0.000 871	0.000 872	0.000 723
α_2	0.001 991	0.002 001	0.001 980	0.001 983
α_3	0.001 267	0.001 273	0.001 263	0.001 238
α_4	−0.000 324	−0.000 326	−0.000 298	−0.000 295
α_5	−0.000 968	−0.000 973	−0.000 923	−0.000 923
q_4	0.000 412	0.000 416		0.000 428
q_5	0.000 637	0.000 641		0.000 646

[a] Derived from B_0 in ref 2 and the rovibrational coupling constants in this column.

inclined to argue that the presently computed harmonic frequencies are more reliable than the experimentally derived ones.

Agreement between the present calculations and the work of BMM for the Fermi resonance constants is generally good. No experimental value for the quartic resonance constant $K_{2;344}$ is available; the BMM[4] value for $K_{1;244}$, 7.5 ± 3 cm^{-1}, is much lower than both the presently computed value of 16.54 cm^{-1} and the value calculated earlier by BMV[5] from cubic force constants by Botschwina et al.[16] and estimated quartic force constants.

We have already noted that there are significant differences in the vibrational assignments between the work of BHH and BMM, as well as the work of Holland and co-workers.[2] We have investigated 10 bands for which differences exist, in the energy range up to about 6000 cm^{-1}. The assignments are compared in Table 7. Given the close correspondence between our calculated spectroscopic constants and the experimentally derived values of BMM, it is not surprising that the seven available BMM assignments agree with those obtained in the present work. Of the three remaining ones, the {2937.768, 2940.485} doublet clearly belongs to the $|01002\rangle$ (Σ) and $|01002\rangle$ (Δ) states, while for the 4646.869 cm^{-1} band, both the sextuplet generated by the $|01032\rangle$ (Π) and $|00232\rangle$ (Π) bands (three components each) and the $|10012\rangle - |02012\rangle$ doublet contain bands close to the experimental value. On the basis of Occam's razor, we prefer the $|10012\rangle$ assignment. In short, we agree with BHH in only four out of 10 cases, and with Holland et al. in five out of 10 cases. It should be noted that, for example, the $|11000\rangle$ state is part of a resonance polyad of order 11 in the present model, and even more elaborate polyads will be required for states at higher energy. Clearly, an accurate variational treatment of the vibrational Schrödinger equation of FCCH would be highly desirable.

C. Geometry and Rotational Constants. Computed and experimentally derived geometries are given in Table 9, and rotational and rovibrational coupling constants are given in Table 10. An initial attempt at a "best estimate" was obtained in the same way as for the vibrational force field, i.e., combining the core correlation contribution obtained at the CCSD(T)/cc-pCVQZ level with the CCSD(T)/ANO54321 results. However, this leads to computed rotational constants that are clearly too small and bond distances that are somewhat too long. On the other hand, using the CCSD(T)/cc-pCVQZ geometry directly together with the best estimate force field leads to $B_0 = 0.323\,607$ cm^{-1}, in excellent agreement with the best experimental value[2] of 0.323 763 cm^{-1}. It should be noted that, while the CCSD(T)/cc-pCVQZ (valence only) r_e(CH) is essentially identical to the CCSD(T)/cc-pVQZ values, the other two bond distances are 0.0003 and 0.0004 Å shorter, respectively, suggesting that these distances are not completely converged yet as a function of valence basis set.

An alternative approach is to use experimental data to correct for systematic errors in our results. Accurate experimental B_0 values are available[45] for six isotopomers: FCCH, FCCD, $F^{13}CCH$, $FC^{13}CH$, $F^{13}CCD$, and $FC^{13}CD$. If we calculate B_0 from our best force field combined with the CCSD(T)/cc-pCVQZ geometry for these isotopomers, we find that all the

B_0 values are systematically underestimated by a factor of 1.000 48. This factor can be constant across the isotopomers only if there are no significant differences between the errors in the individual bond distances, so it would seem that all bond distances are more or less equally overestimated, and a simple scaling of all bond distances by the ratio $\sqrt{B_0(\mathrm{calc})/B_0(\mathrm{obs})}$ would be reasonable. Since of course doing so affects the $B_e - B_0$ difference in turn, one more iteration of this kind was necessary. Our final geometry is then r_e(CH) = 1.059 58, r_e(CC) = 1.196 50, r_e(CF) = 1.276 44 Å, to which we conservatively assign an uncertainty of 0.0005 Å from remaining errors in the quantum-chemical treatment.

Another "best estimate" geometry can be obtained as follows. Using the geometric extrapolation $A + B/C^n$ first proposed by Feller,[46] one could use CCSD(T)/cc-pV*n*Z (n = 2, 3, 4) bond distances to extrapolate to the valence correlation limit and simply add in the core correlation contribution to obtain a "best estimate" geometry, along the lines of studies on C_2H_4[40] and C_2H_2.[42] In the present case, unfortunately, this extrapolation diverges. However, no such problem occurs with an extrapolation based on CCSD(T)/cc-pV*n*Z+aug(F) results, that is, in which the aug-cc-pV*n*Z basis set is used on the highly electronegative F atom and the regular cc-pV*n*Z basis on all other atoms. This yields us a valence correlation-only basis set limit of r(CF) = 1.2788, r(CC) = 1.1989, and r(CH) = 1.0613 Å. After adding the core correlation contributions we therefore obtain r_e(CF) = 1.2768, r_e(CC) = 1.1964, r_e(CH) = 1.0601 Å. The B_e corresponding to this geometry, 0.324 44 cm^{-1}, is within 0.0001 cm^{-1} of the B_e derived from the experimental[2] B_0 and α_i.

Both of our computed geometries agree to within overlapping of uncertainties with the best estimate geometry of Botschwina et al.[16] and suggest that their r_e(CH) and r_e(CC) are slightly too short. Our calculations also confirm that the second of the two geometries proposed by Borro et al.[4]—which accounts for quartic resonance perturbation of the rotational constants in deriving the α_i—is the one to be preferred. Both of our computed geometries lie well within the error bars of the Borro et al. geometry. Since there is little to choose between our two computed geometries, and the latter of the two has the aesthetic advantage of avoiding empirical corrections, we choose r_e(CF) = 1.2768, r_e(CC) = 1.1964, r_e(CH) = 1.0601 Å as our recommended geometry, with an uncertainty of 0.0005 Å.

D. Heat of Formation. The FCCH heat of formation listed in the JANAF tables,[48] $\Delta H_f^\circ = 30 \pm 15$ kcal/mol, is no more than a crude estimate derived from heats of formation of CF and CH, plus the assumption that the CC bond strength is the average of that in C_2H_2 and C_2F_2.

Ochterski, Petersson, and Wiberg (OPW)[49] report FCCH heats of formation obtained using the empirically corrected model known as Gaussian-2 (G2),[50] a simplified version known as G2(MP2),[51] and two variants of a hybrid extrapolation/empirical correction scheme known as the complete basis set (CBS) method[52,53] as part of a general comparison of these methods. All methods arrived at substantially larger values, ranging from 24.7 kcal/mol for CBS-Q (the value of 27.5 kcal/mol given in OPW is a misprint) to 25.3 kcal/mol for CBS-4. Very recently, a family of simple basis set extrapolations was proposed[54] based on the asymptotic convergence behavior in terms of the angular momentum l of the two-electron cusp.[55−57] One variant thereof was recently shown[58] to yield total atomization energies (TAEs) of a number of small polyatomics with a mean absolute error of 0.12 kcal/mol without any empirical correction. Since this sample included HF, F_2, and C_2H_2, there is no a priori reason why similar accuracy could not be obtained for the total atomization energy, and hence the heat of formation, of FCCH.

Following the procedure described in ref 58, we have performed CCSD(T)/aug′-cc-pVTZ, CCSD(T)/aug′-cc-pVQZ, and CCSD(T)/aug′-cc-pV5Z calculations of the atomization energy and carried out separate extrapolations to the basis set limit for the SCF and correlation energy components. The aug′-cc-pV5Z calculation involved 436 basis functions and required about 24 GB of temporary disk space on the Origin 2000. The CCSD(T)/cc-pVQZ+aug(F) geometry was used as the reference geometry for all three calculations.

The SCF component of the TAE, following ref 58, was extrapolated from the largest two calculations using the expression $A + B/(l + 1/2)^5$. This yields an SCF limit TAE of 276.41 kcal/mol, only 0.09 kcal/mol larger than the directly computed SCF/aug′-cc-pV5Z results. This is consistent with previous findings[58,59] that the SCF level TAE is essentially converged at this level of one-particle basis set. The valence correlation energy limit is then obtained by a three-point extrapolation using the expression $A + B/(l + 1/2)^\alpha$. From the present results we find α = 4.58 and a valence correlation limit of 118.84 kcal/mol. The extrapolation itself accounts for 1.05 kcal/mol of that value.

We thus obtain a valence correlation limit TAE of 395.25 kcal/mol. From the present results with the cc-pCVQZ basis set, with and without 1s correlation included, we find that the core correlation contribution to TAE is significant, at 2.43 kcal/mol, leading us to $\mathrm{TAE}_{e,\mathrm{NR}}$ = 397.68 kcal/mol, with the subscript "NR" standing for "nonrelativistic".

To bring this on the same scale as the experimental heats of formation, we should include the effect of spin-orbit splitting on the C and F atomic energies (see, for example, refs 60, 61 for details), which amounts to −0.47 kcal/mol, from which the TAE_e = 397.21 kcal/mol. Subtracting our best computed zero-point energy, 12.40 kcal/mol, we finally obtain TAE_0 = 384.81 kcal/mol.

Combining this with the heats of formation of the F, C, and H atoms from the JANAF tables, which add up to 410.06 ± 0.29 kcal/mol, we finally obtain ΔH_f° = 25.25 kcal/mol, which we would suggest is the most accurate heat of formation available for this compound.

The value obtained with the relatively simple CBS-4 model[49] appears to be (fortuitously) the closest to this result. It should however be remembered that none of the values in OPW include a spin−orbit correction: after applying it, the CBS-Q model appears to be the closest to the present computed value. We also find that the more recent CBS-QCI/APNO model,[53] as implemented in Gaussian 94,[62] yields a heat of formation of 25.5 kcal/mol.

We may consider the performance here of the three-parameter empirical correction method due to Martin.[63−65] In that model, a correction

$$\Delta E = a_\sigma \Delta n_\sigma + b_\pi \Delta n_\pi + c_{\mathrm{pair}} \Delta n_{\mathrm{pair}} \quad (8)$$

is applied, with the coefficients a, b, and c specific for the basis set and electron correlation method. (n_σ, n_π, and n_{pair} are the number of σ bonds, π bonds, and closed-shell electron pairs, respectively.) In the present case, $n_\sigma = n_{\mathrm{pair}} = 3$ and $n_\pi = 2$; coefficients appropriate for the aug′-cc-pV*n*Z (n = T, Q, 5) basis sets are found in ref 65. Using the "implicit core correlation" parameters (i.e., where it was attempted to absorb the core correlation effects into the empirical parametrization) yields spin−orbit-corrected TAE_0 values of 383.90, 384.69, and 384.82 kcal/mol from the CCSD(T)/aug′-cc-pV*n*Z (n = T, Q, 5) results, respectively; correcting only the valence energy and adding in the core correlation term explicitly leads to the slightly higher values 384.03, 384.82, and 384.95 kcal/mol. It is seen that from the aug′-cc-pVQZ basis set on, the empirically corrected result is in excellent agreement with our best value.

IV. Conclusions

We have carried out large basis set coupled cluster calculations on the geometry, harmonic frequencies, vibrational anharmonicity, and heat of formation of fluoroacetylene, FCCH.

Our best computed geometry includes the effects of inner-shell correlation and reproduces the experimental B_e to 0.0001 cm^{-1} : bond lengths are $r_e(\text{CF}) = 1.2768$, $r_e(\text{CC}) = 1.1964$, $r_e(\text{CH}) = 1.0601$ Å, with an estimated uncertainty of 0.0005 Å.

Our best computed harmonic frequencies, which also include effects of inner-shell correlation, suggest some revision of the accepted experimental values. In combination with CCSD(T)/[5s4p3d2f/4s3p2d] anharmonicities and a vibrational resonance polyad model involving the cubic resonances $\nu_3 + \nu_2 \approx \nu_1$, $2\nu_3 \approx \nu_2$, and $2\nu_4 \approx \nu_3$, as well as the quartic resonances $K_{1;244}$ and $K_{2;344}$, we obtain a mean absolute error of 1.6 cm^{-1} for 36 vibrational states. A consistent treatment of ν_1 and ν_2 requires the use of vibrational resonance matrices of dimension 7 and 4, respectively. A strong basis set dependence was noted in the bending anharmonicities, which is almost entirely related to the CCF bend.

Our best computed heat of formation at 0 K, 25.25 kcal/mol, was obtained using an *l*-extrapolation method that ordinarily yields a mean absolute error of 0.12 kcal/mol. The computed value explicitly includes inner-shell correlation, anharmonic zero-point energy, and atomic spin−orbit coupling effects. We conservatively assign an uncertainty of 0.3 kcal/mol.

Finally, we emphasize that none of the computed properties involve empirical adjustment of any kind and that therefore the results are purely ab initio. Nevertheless, the work of BHH shows that empirical methods for solving the vibrational problem can produce results of not much lower accuracy for a wide range of energies in FCCH.

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Supporting Information Available: The CCSD(T)/ANO5432 computed quartic force field in Cartesian, internal, and normal coordinate representations is available in machine-readable form on the Internet World Wide Web (WWW) at the Uniform Resource Locator (URL) http://theochem.weizmann.ac.il/web/papers/fcch.html Interested parties without WWW access can request the material by e-mail to comartin@wicc.weizmann.ac.il.

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