Microwave Spectrum, Structure and Dipole Moment of 3-fluorophenylacetylene (3FPA)

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Abstract

The 6-18 GHz rotational spectrum of 3-fluorophenylacetylene (3FPA) was measured by chirped-pulse Fourier-transform microwave (CP-FTMW) spectroscopy. Rotational constants and quartic centrifugal distortion constants based on a Watson-A reduction were determined with 89 transitions; $A = 3383.73821(33)$ MHz, $B = 1180.97617(16)$ MHz, $C = 875.26172(12)$ MHz, $\Delta_J = 0.0382(13)$ kHz, $\Delta_K = 1.316(21)$ kHz, $\delta_J = 13.93(56)$ Hz, and $\delta_K = 180.3(60)$ Hz. An additional 12-13 transitions for each of eight ^{13}C isotopic species and Stark effect to determine dipole moment components were observed by Balle-Flygare FTMW spectroscopy. Gas phase molecular structures of 3FPA were derived via the least-square fitting (r_0) and substitution (r_s) methods using the moments of inertia of the isotopic species. The ring geometry is discussed and compared with previous studies of structures of monosubstituted benzene and crystalline solid structures of 3FPA.

Keywords

3-fluorophenylacetylene

Rotational spectrum

Chirped-pulse microwave spectroscopy

Structure

1. Introduction

The changes in ring geometry of benzene derivatives have been studied in detail from microwave [1–7] or electron diffraction [8–10] investigations. Fluorine is one of electronegative and electron withdrawing substituents. It has been reported that fluorine tends to shorten the C-C bonds and increase the angle between them according to so-called hybridization effects [1,2], which assume the electronegative fluorine atom attract more of the p character in the hybrid orbital towards itself with increasing s character in the other two hybrid orbitals. Otherwise, another electron withdrawing substituent, the acetylenic group ($\text{C}\equiv\text{C}$) slightly changes the ring parameters at the substituent carrying carbon in phenylacetylene (PA) [3,4]. Those two different impacts of substituents on ring geometry invokes interest in fluorine substituted PA. It is expected that the effect of fluorine would be similar to the one in fluorine substituted benzene.

There are three structural isomers of fluorophenylacetylene (FPA), depending on the location of fluorine. Shivatare et al.[11] studied the active vibrations of FPAs in the electronically excited and cationic states, and showed the fluorine location relative to the acetylenic group make a slight difference in the transition energy and molecular vibration. It was found that 3-fluorophenylacetylene (3FPA) has largest adiabatic ionization energy among them. The present microwave study gives a structural

determination and the dipole moment components for 3FPA. To the best of our knowledge, information about microwave spectrum of 3FPA is still not available in the literature. Recent crystal structure studies [12], however, provide several structures of the fluorophenylacetylenes (2FPA, 3FPA, and 4FPA) determined by in situ cryo-crystallization. In the case of 3FPA, there were two polymorphic forms as the solid phase structures, and three and one molecular structures were discovered in each form.

In this report, the rotational transitions of 3FPA and single substituted eight ^{13}C isotopic species (in natural abundance) were measured to determine a gas phase molecular structure of 3FPA, using chirped-pulse (CP) [13] and resonant cavity [14] Fourier-transform microwave (FTMW) spectroscopy. The dipole moments of 3FPA were also studied by measuring the Stark effect of the parent molecule.

2. Experimental

The 3-fluorophenylacetylene (98%, 3FPA), which is a liquid at ambient conditions, was procured from SynQuest Labs., and used directly. To measure the microwave spectrum, He/Ne carrier gas (17.5%, 82.5%; B.O.C. gases) was flowed over a small amount of liquid sample held in a Teflon tube and delivered directly to a General Valve Series 9 solenoid valve at a pressure of ~ 2.5 bar. Initially, the full 6-18 GHz spectrum of 3FPA was measured (with 5 free induction decays recorded for each gas pulse and 400 gas pulses per frequency step, giving final spectra of 2000 averages) using the 480 MHz bandwidth CP-FTMW spectrometer at Eastern Illinois University (EIU) [15]. A few transitions of ^{13}C isotopic species were also observed with low intensities, and they were utilized for the initial assignments of the species. Additional measurement for the isotopic species with a higher resolution and sensitivity, and Stark effect measurements, were performed using a standard Balle-Flygare type resonant cavity instrument [16,17].

All spectroscopic fits followed the SPCAT and SPFIT packages of Pickett [18] and Kisiel's AABS package [19]. The rotational constants and centrifugal distortion parameters were determined according to a Watson A-reduction Hamiltonian in the I' representation [20]. Initial spectroscopic parameters for fitting were obtained from *ab initio* optimization and energy calculation results at the MP2/6-31+G(d,p) level of Gaussian 03 [21]. For ^{13}C isotopic species, the rotational constants were initially estimated from experimental rotational constants of the parent by subtracting differences between calculated constants of the parent (above) and the isotopic species. The calculated rotational constants of each ^{13}C isotopomer were obtained by a single point energy calculation at simpler level as HF/6-31G, using the optimized MP2 structure of the parent.

3. Results

3.1. Rotational spectra

The full 6-18 GHz spectrum of 3FPA including a few peaks of ^{13}C isotopic species in natural abundance were measured by 480 MHz bandwidth CP-FTMW spectrometer, with signal to noise (S/N) ratios of up to 100. As the first input file for fitting, the results from optimization and energy calculation of Gaussian 03 shown in Table 1 were used. The results at the MP2/6-31+G(d,p) level were utilized for initial fitting, and additional calculations were done at MP2/6-311++G(2d,2p) for comparison. The theoretical quartic centrifugal distortion constants were obtained by anharmonic frequency calculations at MP2/6-31G level for the structure optimized at MP2/6-31+G(d,p) and at MP2/3-21G after optimization at MP2/6-311++G(2d,2p).

Table 2 shows the rotational constants, the centrifugal distortion constants, and the planar moments of the parent and eight ^{13}C isotopic species. All transition frequencies are listed in Tables 3-4. To the best of our knowledge, this work is the first time to study microwave spectrum and to determine the spectroscopic parameters of 3FPA.

For the normal isotopologue (with all ^{12}C atoms), a total of 89 transitions were assigned, giving an overall root-mean-square deviation of 3.9 kHz, including *a*-type and *b*-type *R*-branch ($J' = J'' + 1$) and *Q*-branch ($J' = J''$) transitions. Rotational constants are $A = 3383.73821(33)$ MHz, $B = 1180.97617(16)$ MHz, and $C = 875.26172(12)$ MHz. Compared to the results of *ab initio* calculations, these values are much closer to the constants from MP2/6-311++G(2d,2p) basis set than from MP2/6-31+G(d,p). Ray's asymmetry parameter [22], $\kappa = (2B - A - C)/(A - C)$, is -0.75625 , which is close to so-called near-prolate asymmetric top ($\kappa \approx -1$) [23]. Four quartic centrifugal distortion constants of 3FPA were fitted from the Watson A-reduction. A small and negative value of about -0.2 kHz for Δ_{JK} was derived in the *ab initio* anharmonic frequency calculation but experimentally Δ_{JK} was poorly determined, so it was excluded in our fit.

For the isotopic species, four transitions were identified in the CP-FTMW spectrum for initial assignment to obtain frequency information of other transitions. Additional measurements were done using a resonant cavity microwave spectrometer. Rotational constants shown in Table 2 were determined for each species with 12-13 transitions. The distortion constants were fixed to the values of the parent isotopomer. It was hard to measure several peaks of $^{13}\text{C}_2$ isotopologue, because they were very close to the parent's strong peaks.

The planar moments were defined as $P_{aa} = \sum_i m_i a_i^2 = \frac{1}{2}(I_b + I_c - I_a)$; P_{bb} and P_{cc} were also obtained by similar permutations. The P_{cc} value close to zero suggests that the molecule has a planar and rigid structure. The moments of the isotopic species helps to confirm each ^{13}C carbon atom was assigned correctly, giving some additional structural information. For example, the off-axis ^{13}C substitutions have larger P_{aa} values than those where ^{13}C lies on the *b*-axis. In this molecule, C3 & C4 (right side of Fig. 1) and C7 & C8 (left side of Fig. 1) in Table 2 are confirmed as the off-axis carbon atoms by their larger P_{aa} values, (over $429.8 \text{ u}\text{\AA}^2$) while $^{13}\text{C}_2$ isotopomer shows the lowest P_{aa} value ($428.0 \text{ u}\text{\AA}^2$) which means it is located very close to *b*-axis. Likewise, C5, whose isotopologue has the largest value of P_{bb} ($152.8 \text{ u}\text{\AA}^2$), would be the furthest atom from *a*-axis, with the small distance to C6 ($P_{bb} = 151.5 \text{ u}\text{\AA}^2$). The normal isotopologue and other ^{13}C substitutions show P_{bb} values in the range of $149\text{-}150 \text{ u}\text{\AA}^2$.

3.2. Structure

It was expected that 3-fluorophenylacetylene (3FPA) has a planar structure in gas phase because the z -coordinates of *ab initio* calculation results were zero for all atoms. Planar structure has only two independent moments of inertia. In this work, carbon atom structures were studied via two approaches, r_0 and r_s structure, with a total of eighteen moments of inertia from normal and eight ^{13}C isotopic species of 3FPA ($\text{C}_8\text{H}_5\text{F}$). Since spectroscopic data directly related to hydrogen and fluorine atoms was absent, it was impossible to determine a full structure.

Kisiel's KRA program [24] can derive the Cartesian coordinates of each atom (as an absolute value) from the changes in moments of inertia between parent and isotopic species of the atom, based on Kraitchman's substitution equations [25]. The coordinates except for C1 and C2 atom are very consistent with the *ab initio* optimized coordinates, within 0.0001-0.01 Å (see Table 5). The location of C2 atom on the b -axis of the molecule caused large uncertainties [26, 27] of its a -coordinate shown as a complex number. It also could give rise to unexpected uncertainties on the r_s structural parameters including this atom. So, when the structural parameters were estimated, the a -coordinate of C2 was modified to the coordinate from *ab initio* calculation and Costain's error was applied in order to obtain more realistic structure. Similarly, b -coordinate of C1 atom which lies on a -axis of the molecule slightly differs from the optimized coordinate. Atom C1 lies very close to the center of mass and so these differences between experimental and *ab initio* results are reasonable. Table 6 shows structural parameters derived from different sources. The variation trends on bond lengths and angles in Kraitchman's structure agrees very well with that of *ab initio* optimized structure (r_e), though some values including C1 atom seem to be quite different. For example, fluorine substituted carbon angle (C2-C3-C4) is largest and two adjacent angles are smaller than other angles in benzene ring.

Inertial fit (r_0 structure) was obtained by least-squares fitting of experimental moments of inertia for the parent and ^{13}C species using the STRFITQ program [28]. Note that all parameters related to fluorine and hydrogen atoms were fixed as the optimized values from *ab initio* calculation. For the structural determination, second moments, P_{aa} and P_{bb} , for the normal and 8 isotopic species were fit to obtain all carbon bond lengths and angles. All these atoms are in the ab symmetry plane. The best fit shows a planar carbon ring and reasonable structure compared to r_e structure. Bond lengths are consistent within 0.01 Å, and bond angle within 0.8° (see Table 6). Comparison of all structures for 3FPA is available in Figure 2.

3.3. Dipole moments

Dipole moment components of 3FPA were determined by measuring Stark effects and were fitted using QSTARK [29], based on initial assignment of patterns predicted from Stark coefficients obtained using second order perturbation theory as implemented in the ASYSPEC program [30] and *ab initio* dipole moment components. Stark effect measurements were made using the Balle-Flygare Fourier-transform microwave spectrometer. As an example, observed Stark shifts for the $4_{04}-3_{13}$ transitions are plotted in Figure 3. The results of fitting the dipole moment components for the parent isotopomer (fixing rotational constants and distortion constants at the values listed in Table 2) are given in Table 7. The values of μ_a and μ_b were directly determined from a least-squares fit of 44 frequencies corresponding to a total of 11 M components from 5 distinct rotational transitions, using applied fields

up to 270 V cm⁻¹. The resulting dipole moment components are $\mu_a = 0.6422(14)$ D, $\mu_b = 1.2021(15)$ D, with μ_c fixed to zero, and the resulting standard deviation of observed–calculated transition frequency values (6.0 kHz) is within the expected precision of this type of measurement. For many transitions, one or more M components were poorly resolved or had small frequency shifts, leading to spectral congestion that reduced the number of lines that could justifiably be fitted; however, even for these lines, observed patterns were quantitatively consistent with expected shifts, confirming assignment of the reported M values in Table 7. In addition, plots of $\Delta\nu$ vs. E^2 (for example, Fig. 3) that were constructed during measurements to facilitate tracking of individual M components, were used to obtain experimental Stark coefficients that were then least-squares fitted using the DIPOLE program [31] to obtain dipole moment components from second order perturbation theory (Table 8). These values are in good agreement with the fitted dipole moment components from QSTARK. The experimental dipole moment components are in close agreement with MP2/6-311++G(2d,2p) *ab initio* values (Table 1).

4. Discussion

3-fluorophenylacetylene (3FPA) is a benzene derivative which has two substituents, a fluorine atom and an acetylenic group. As a strong electron withdrawing substituent, fluorine has had impact on distortion of benzene ring geometry. Doraiswamy and Sharma [2] studied variation of the ring geometry in fluorobenzene. When they assumed a bond length of 1.3974 Å and bond angle of 120° in a benzene ring, 0.014 Å shortening on the C–C bond adjacent to the C–F bond and 3.4° increasing on the *ipso* position carbon angle were observed in monofluorobenzene. The angle of *ortho* position was decreased by 2° but at *meta* position, it was increased by about 0.5° and slightly decreased at *para* position. On the other hand, in the microwave study for phenylacetylene done by Cox et. al.[3], 0.009 Å shortening of bond length and 0.8° increasing of bond angle were described. Both substituents have caused angle opening at *ipso* position and bond shortening where adjacent to the substituent carrying carbon in monosubstituted benzene, though one has large effect but the other affect slightly. In this paper, we studied carbon frame structure of 3FPA including benzene ring via a rotational microwave study of the parent and eight ¹³C isotopic species. Since there were angle opening at *ipso* and *meta* position of fluorobenzene and also at *ipso* position of phenylacetylene, it was expected that angle opening at both substituent carbon would occur in 3FPA, such as in each monosubstituted molecule.

Prior to analysis of the microwave spectrum, an equilibrium molecular structure (r_e) was obtained by *ab initio* calculation using Gaussian 03. Then, two kinds of methods, least-square fitting (r_0) and substitution (r_s), were used to determine the structure of 3FPA in the gas phase. Though the equilibrium structure is not directly comparable to a gas phase molecular structure, it gave clues to confirm reasonable structures. In r_0 structure, bond lengths (C2–C3 and C3–C4) involving fluorine substituent carbon atom are shorter than 1.3974 Å of benzene by about 0.02 Å, and bond angle (C2–C3–C4) is larger than 120° of benzene by 3.5°. These variations of ring geometry correspond to the distortion observed in monofluorobenzene very well. Unexpectedly, increasing bond lengths (C6–C1 and C1–C2) and a decreasing bond angle (C6–C1–C2) were observed for acetylenic group. Those trends, however, are consistent with trends in the *ab initio* optimized structure. The bond angle of *meta* position (C5) from both substituent carbons is increased as *meta* position of fluorobenzene does. Another two angles (C1–C2–C3 and C3–C4–C5) show clearly smaller values than other carbon angles. Kraitichman's structure (r_s) shows consistent values with inertial structure (r_0) and *ab initio* structure (r_e) on the whole. Note again that the a -coordinate of C2 was replaced by the *ab initio* coordinate in order to reduce

uncertainties of its imaginary value from the substitution structure. Since the *b*-coordinate of C1 was a little different from that of the *r_e* structure, some parameters including C1 atom show dissimilar results. It is unfortunate that C1 atom related to acetylenic group lies on the *a*-axis, since it has caused large uncertainties in Kraitchman's *b*-coordinates.

To the author's knowledge, this is the first microwave study for 3FPA and only one paper related to the structure of the molecule has been found. Dikundwar et al. [12] studied crystalline polymorphism of three fluorophenylacetylenes. Microwave studies for gas phase molecules can improve understanding about the impact of intermolecular interaction on their structure, giving experimental standards for a single molecule. There were two kinds of polymorphic forms of 3FPA which is a liquid in ambient condition. They quenched it suddenly with liquid nitrogen (Form1) and recrystallized it at 90 K (Form2) after quenching and melting it again. There are three independent molecular structures in Form1 and one structure in Form2. The three structures in Form1 were drawn using three RGB colors in the original paper [12], and in this paper they are referred as to Form1-1(green), Form1-2(blue), and Form1-3(red). Reanalyzed structural parameters of the crystallographic information files (.cif) using Diamond software [31] are listed in Table 6. All four structures are also visualized in Figure 2 for comparison with our microwave and *ab initio* results.

The three molecules in Form1 have complex interaction along all possible hydrogen bonding. Form 1-2 and 1-3 make a tetramer structure with hydrogen bonding between $\equiv \text{C} - \text{H}$ (Form1-2) and F (Form1-3), in addition to $\text{C5} - \text{H}$ (Form1-2) and F (Form1-3). Different directions of hydrogen bonding to fluorine might result in larger angle ($\text{C2}-\text{C3}-\text{C4}$) and symmetrically shorter bond lengths ($\text{C2}-\text{C3}$ and $\text{C3}-\text{C4}$) in Form1-3 than those values from microwave structures. Likewise, the H-bond interactions pull the groups and then slightly decrease the bond angles ($\text{C6}-\text{C1}-\text{C2}$ and $\text{C4}-\text{C5}-\text{C6}$) of Form 1-2. The other tetramer structure composed of hydrogen bonding such as (Form1-1) $\equiv \text{C} - \text{H} \cdots \pi(\text{C} \equiv \text{C})$ (Form1-3) and (Form1-3) $\text{C5} - \text{H} \cdots \pi(\text{C} \equiv \text{C})$ (Form1-1) does not show significant change. The $\text{C4} - \text{H}$ of Form1-1, which acts as H-bond donor, interacts with fluorine of Form1-2. It seems that hydrogen bonding reduces the p character of fluorine atom, which is the reason why fluorine has increased the bond angle of the substituent carbon atom of the benzene. This is consistent with a slight decrease in the internal angle of fluorine substituent carbon (C3) of Form1-2 for the crystal structure. Similar effect of the hydrogen bonding also appears in the decreasing $\text{C2}-\text{C3}-\text{C4}$ angle of Form1-1 where fluorine acts as H-bond acceptor from $\text{C2} - \text{H}$ of Form1-3.

The distortion affected by H-bond is more clearly apparent in Form2. In Form2, the crystal packing consists of only one molecular structure with hydrogen bonding of $\equiv \text{C} - \text{H} \cdots \pi(\text{C} \equiv \text{C})$ and $\text{C4} - \text{H} \cdots \text{F}$. It might be because of simpler packing structure than Form1, which enhance the impact of direct interaction. The $\text{C4} - \text{H} \cdots \text{F}$ bonding could reduce the p character of fluorine, consistent with the decreasing $\text{C2}-\text{C3}-\text{C4}$ angle. Slightly smaller $\text{C3}-\text{C4}-\text{C5}$ angle is also shown as the interaction pulls each other. The other H-bond making lattice, which is $\equiv \text{C} - \text{H} \cdots \pi(\text{C} \equiv \text{C})$, also reduces the internal angle of C1 substituted with acetylenic group. The tension in C1 and C3 also affects opening of the angle $\text{C1}-\text{C2}-\text{C3}$ and shortening of the bond length $\text{C1}-\text{C2}$ and $\text{C2}-\text{C3}$.

5. Conclusion

A microwave spectrum of 3FPA in the gas phase was measured using chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer and 89 transitions were fitted to determine rotational constants and quartic centrifugal distortion constants of 3FPA, and compared to *ab initio* results at the level of MP2/6-311++G (2d,2p) and MP2/6-31+G (d,p). Using ^{13}C isotopic species, a single molecular structure (r_0 and r_s structure) was defined. The geometry of benzene ring is discussed by comparing to fluorobenzene and phenylacetylene. The structural study gives possibility as the experimental standards to analyze how hydrogen bonding affects structural distortion in solid crystal structures. In addition, dipole moment components of 3FPA were derived by performing Stark effect measurements.

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Table 1. *Ab initio* rotational constants, dipole moment components and zero-point energy for the 3-fluorophenylacetylene.

	MP2/6-31+G (d,p)	MP2/6-311++G (2d,2p)
A (MHz)	3356.00 ^a	3378.10
B (MHz)	1170.39 ^a	1177.21
C (MHz)	867.76 ^a	872.99
Δ_J (kHz)	0.063991 ^b	0.054649 ^c
Δ_{JK} (kHz)	-0.223347 ^b	-0.161595 ^c
Δ_K (kHz)	3.214204 ^b	2.595158 ^c
δ_J (Hz)	26.226 ^b	21.737 ^c
δ_K (Hz)	279.637 ^b	234.789 ^c
P_{aa} (uÅ ²)	431.00461	429.30187
P_{bb} (uÅ ²)	150.59035	149.60402
P_{cc} (uÅ ²)	-0.00064	0.00051
μ_a (Debye)	-0.8917371 ^a	-0.6912413
μ_b (Debye)	-1.3305352 ^a	-1.2199738
μ_c (Debye)	0 ^a	0
μ_{total} (Debye)	1.6017237	1.4021949
E (kcal/mole)	-255060.6215	-255209.149

^a These values were used to make initial input files of fitting experimental rotational constants.

^b The results from anharmonic frequency calculation at the MP2/6-31G level.

^c The results from anharmonic frequency calculation at the MP2/3-21G level.

Figure 1. The principal axes and numbering for carbon atoms of 3-fluorophenylacetylene

Table 2. Spectroscopic parameters for the normal and all eight ^{13}C isotopologues of 3-fluorophenylacetylene. See Fig.1 for atom numbering.

	Parent	$^{13}\text{C1}$	$^{13}\text{C2}$	$^{13}\text{C3}$	$^{13}\text{C4}$	$^{13}\text{C5}$	$^{13}\text{C6}$	$^{13}\text{C7}$	$^{13}\text{C8}$
A (MHz)	3383.73821(33)	3383.70275(64)	3366.16853(65)	3379.48259(64)	3365.83739(76)	3309.02290(64)	3337.88206(64)	3381.00736(76)	3373.04419(73)
B (MHz)	1180.97617(16)	1178.50813(40)	1181.00953(45)	1175.80550(43)	1172.85844(42)	1179.65450(42)	1179.85387(41)	1166.29124(42)	1148.55970(39)
C (MHz)	875.26172(12)	873.90378(16)	874.10212(16)	872.13529(19)	869.60536(17)	869.45896(16)	871.54806(16)	866.99083(17)	856.63527(16)
Δ_J (kHz) ^a	0.0382(13)	0.0382	0.0382	0.0382	0.0382	0.0382	0.0382	0.0382	0.0382
Δ_{JK} (kHz) ^a	-	-	-	-	-	-	-	-	-
Δ_K (kHz) ^a	1.316(21)	1.316	1.316	1.316	1.316	1.316	1.316	1.316	1.316
δ_J (Hz) ^a	13.93(56)	13.93	13.93	13.93	13.93	13.93	13.93	13.93	13.93
δ_K (Hz) ^a	180.3(60)	180.3	180.3	180.3	180.3	180.3	180.3	180.3	180.3
P_{aa} (uÅ ²) ^b	427.99071	428.88663	427.97789	429.87254	430.95234	428.47106	428.39847	433.37848	440.07031
P_{bb} (uÅ ²) ^b	149.41264	149.41394	150.19146	149.60068	150.20674	152.78587	151.46519	149.53317	149.88795
P_{cc} (uÅ ²) ^b	-0.05739	-0.05713	-0.05666	-0.05736	-0.05716	-0.05829	-0.05809	-0.05699	-0.05918
N ^c	89	13	12	12	13	13	13	12	12
Δv_{rms} (kHz) ^d	39	3.5	2.3	2.7	2.6	2.7	2.5	1.2	3.2

^a For the ^{13}C isotopic species, the distortion constants were fixed to the values from the most abundant isotopic species.

^b Planar moments, defined as $P_{aa} = \sum_i m_i a_i^2 = \frac{1}{2} (I_b + I_c - I_a)$ and similar permutations for P_{bb} and P_{cc} .

^c N is the number of transitions in the fit.

^d Root-mean-square deviation: $\Delta v_{rms} = [\sum (v_{obs} - v_{calc})^2 / N]^{1/2}$

Table 3. Microwave frequencies of 3-fluorophenylacetylene (parent isotopologue).

Parents	J'	K ₋₁ '	K ₊₁	J''	K ₋₁ ''	K ₊₁ ''	Obs. freq.	Obs.-calc.
	3	1	2	2	1	1	6607.7500	-0.0008
	2	2	0	2	1	1	6637.9338	0.0026
	6	1	5	6	0	6	6820.4144	-0.0009
	8	2	6	8	1	7	6968.4824	0.0033
	2	2	1	2	1	2	7525.4086	0.0005
	4	1	4	3	1	3	7559.2420	0.0006
	3	1	3	2	0	2	7619.1334	0.0005
	4	0	4	3	0	3	7943.7353	0.0000
	3	2	2	3	1	3	8001.6962	0.0003
	9	2	7	9	1	8	8026.8974	-0.0038
	6	1	5	5	2	4	8046.6314	0.0024
	4	2	3	3	2	2	8201.8212	0.0037
	4	3	2	3	3	1	8279.2176	-0.0007
	4	3	1	3	3	0	8290.0066	0.0009
	4	2	2	3	2	1	8482.9341	0.0016
	7	1	6	7	0	7	8546.6320	-0.0007
	5	0	5	4	1	4	8574.2090	0.0028
	4	2	3	4	1	4	8644.2711	-0.0008
	4	1	3	3	1	2	8771.3020	0.0003
	4	1	4	3	0	3	9126.5080	0.0015
	5	1	5	4	1	4	9404.6440	0.0037
	5	2	4	5	1	5	9454.9402	0.0002
10	2	8	10	1	9	9	9457.1321	0.0013
8	3	5	8	2	6	6	9530.8431	-0.0019
5	0	5	4	0	4	4	9756.9775	0.0000
7	3	4	7	2	5	5	10084.3835	0.0009
5	2	4	4	2	3	3	10215.3068	-0.0015
5	4	2	4	4	4	1	10347.0358	0.0033
5	4	1	4	4	4	0	10347.7656	0.0045
5	3	3	4	3	2	2	10365.5050	0.0057
5	3	2	4	3	1	1	10402.7620	0.0038
6	2	5	6	1	6	6	10431.2772	0.0002
8	1	7	8	0	8	8	10464.6206	-0.0005
5	1	5	4	0	4	4	10587.4137	0.0023
6	3	3	6	2	4	4	10646.4201	0.0045
6	0	6	5	1	5	5	10681.1555	0.0018
5	2	3	4	2	2	2	10738.7747	0.0022
7	1	6	6	2	5	5	10805.1802	0.0020
5	1	4	4	1	3	3	10895.9338	0.0020
2	2	1	1	1	0	0	11026.4573	0.0015
5	3	2	5	2	3	3	11122.0962	0.0037
6	1	6	5	1	5	5	11228.4594	0.0040
2	2	0	1	1	1	1	11361.8359	0.0032
4	3	1	4	2	2	2	11458.1104	0.0037
6	0	6	5	0	5	5	11511.5901	0.0025
7	2	6	7	1	7	7	11565.2549	-0.0028
3	3	0	3	2	1	1	11651.0375	0.0039
4	3	2	4	2	3	3	11873.1333	0.0030
5	3	3	5	2	4	4	12023.3224	0.0012
6	1	6	5	0	5	5	12058.8899	0.0006
6	2	5	5	2	4	4	12204.7927	0.0003
6	3	4	6	2	5	5	12273.2879	0.0164
6	4	3	5	4	2	2	12437.2203	-0.0115
6	4	2	5	4	1	1	12440.4838	-0.0031
6	3	4	5	3	3	3	12454.7432	0.0005
9	1	8	9	0	9	9	12480.5590	0.0057
6	3	3	5	3	2	2	12551.6660	-0.0010
7	3	5	7	2	6	6	12648.0130	-0.0009
7	0	7	6	1	6	6	12689.8250	0.0025
3	2	2	2	1	1	1	12776.9763	-0.0012
8	2	7	8	1	8	8	12843.0056	-0.0022
6	1	5	5	1	4	4	12965.7445	-0.0033
6	2	4	5	2	3	3	13027.3488	0.0049
7	1	7	6	1	6	6	13032.6066	0.0045
8	3	6	8	2	7	7	13168.2464	-0.0011
7	0	7	6	0	6	6	13237.1219	-0.0023

8	1	7	7	2	6	13513.2446	0.0037
7	1	7	6	0	6	13579.9026	-0.0012
3	2	1	2	1	2	13840.6218	-0.0008
9	3	7	9	2	8	13848.4925	-0.0051
7	2	6	6	2	5	14166.5788	-0.0040
4	2	3	3	1	2	14371.0377	-0.0064
8	0	8	7	1	7	14613.8731	-0.0044
8	1	8	7	1	7	14820.3432	-0.0040
8	0	8	7	0	7	14956.6567	-0.0003
7	1	6	6	1	5	14963.3346	-0.0071
8	1	8	7	0	7	15163.1260	-0.0008
7	2	5	6	2	4	15312.3402	-0.0083
5	2	4	4	1	3	15815.0504	-0.0002
5	4	2	5	3	3	16421.7618	-0.0050
4	4	0	4	3	1	16427.7252	-0.0032
8	4	5	8	3	6	16428.4660	0.0050
4	4	1	4	3	2	16440.2336	0.0001
9	0	9	8	1	8	16474.7125	0.0059
4	2	2	3	1	3	16631.1314	-0.0020
9	1	9	8	0	8	16801.9265	0.0012
6	2	5	5	1	4	17123.9108	-0.0004
3	3	1	2	2	0	17934.7704	-0.0053
3	3	0	2	2	1	17966.2370	-0.0111

Table 4. Transition frequencies of carbon-13 isotopomers of 3-fluorophenylacetylene (See Figure 1 for atom numbering).

¹³ C1	J'	K ₋₁ '	K ₊₁	J''	K ₋₁ ''	K ₊₁ ''	Obs. freq.	Obs.-calc.
	3	1	3	2	0	2	7612.7594	-0.0045
	3	2	2	3	1	3	8003.8628	0.0034
	5	0	5	4	1	4	8554.0828	-0.0072
	4	1	4	3	0	3	9118.0219	-0.0033
	5	0	5	4	0	4	9741.5588	0.0052
	5	1	5	4	0	4	10576.5792	0.0006
	6	0	6	5	1	5	10658.9316	0.0040
	5	1	4	4	1	3	10875.3121	-0.0004
	2	2	1	1	1	0	11024.9912	-0.0003
	2	2	0	1	1	1	11359.0170	-0.0036
	6	0	6	5	0	5	11493.9556	0.0030
	6	1	6	5	0	5	12045.2166	-0.0005
	3	2	2	2	1	1	12772.7988	0.0015

¹³ C2	J'	K ₋₁ '	K ₊₁	J''	K ₋₁ ''	K ₊₁ ''	Obs. freq.	Obs.-calc.
	3	1	3	2	0	2	7595.3613	0.0041
	3	2	2	3	1	3	7954.5130	-0.0008
	5	0	5	4	1	4	8579.8643	0.0029
	4	1	4	3	0	3	9100.1771	0.0020
	5	0	5	4	0	4	9744.7264	0.0008
	5	1	5	4	0	4	10559.3761	-0.0036
	5	1	4	4	1	3	10890.7981	-0.0029
	2	2	1	1	1	0	10972.5897	0.0025
	2	2	0	1	1	1	11309.6042	0.0000
	6	0	6	5	0	5	11495.7330	0.0003
	6	1	6	5	0	5	12030.3308	-0.0014
	3	2	2	2	1	1	12720.7881	-0.0016

¹³ C3	J'	K ₋₁ '	K ₊₁	J''	K ₋₁ ''	K ₊₁ ''	Obs. freq.	Obs.-calc.
	3	1	3	2	0	2	7600.1034	-0.0008
	3	2	2	3	1	3	7995.0102	-0.0020
	5	0	5	4	1	4	8533.3537	0.0024
	4	1	4	3	0	3	9102.4273	-0.0056
	5	0	5	4	0	4	9721.6954	-0.0012
	5	1	5	4	0	4	10557.9921	-0.0007
	6	0	6	5	1	5	10634.5090	-0.0009
	5	1	4	4	1	3	10851.4441	-0.0030
	2	2	1	1	1	0	11010.5626	0.0000

	2	2	0	1	1	1	11343.5041	0.0017
	6	0	6	5	0	5	11470.8111	0.0051
	3	2	2	2	1	1	12754.8341	0.0027
¹³ C4	J'	K ₋₁ '	K ₊₁	J''	K ₋₁ ''	K ₊₁ ''	Obs. freq.	Obs.-calc.
	3	1	3	2	0	2	7574.0449	0.0024
	3	1	3	2	0	2	7574.0473	0.0049
	5	0	5	4	1	4	8513.6042	0.0002
	4	1	4	3	0	3	9071.8407	-0.0071
	5	0	5	4	0	4	9693.7031	0.0005
	5	1	5	4	0	4	10523.2485	0.0010
	6	0	6	5	1	5	10607.8186	0.0003
	5	1	4	4	1	3	10822.6783	-0.0004
	2	2	1	1	1	0	10967.0984	0.0014
	2	2	0	1	1	1	11299.6722	-0.0023
	6	0	6	5	0	5	11437.3628	-0.0003
	6	1	6	5	0	5	11984.7921	0.0000
	3	2	2	2	1	1	12706.3066	0.0006
¹³ C5	J'	K ₋₁ '	K ₊₁	J''	K ₋₁ ''	K ₊₁ ''	Obs. freq.	Obs.-calc.
	3	1	3	2	0	2	7513.9375	0.0060
	3	2	2	3	1	3	7802.7260	-0.0035
	5	0	5	4	1	4	8585.0903	-0.0003
	4	1	4	3	0	3	9009.1048	-0.0012
	5	0	5	4	0	4	9694.7929	-0.0012
	5	1	5	4	0	4	10461.4154	-0.0037
	6	0	6	5	1	5	10666.0396	0.0011
	2	2	1	1	1	0	10796.5047	-0.0024
	5	1	4	4	1	3	10861.3668	-0.0005
	2	2	0	1	1	1	11138.1874	0.0045
	6	0	6	5	0	5	11432.6627	-0.0007
	6	1	6	5	0	5	11929.0743	0.0009
	3	2	2	2	1	1	12535.4243	0.0010
¹³ C6	J'	K ₋₁ '	K ₊₁	J''	K ₋₁ ''	K ₊₁ ''	Obs. freq.	Obs.-calc.
	3	1	3	2	0	2	7553.8603	-0.0030
	3	2	2	3	1	3	7879.7669	-0.0046
	5	0	5	4	1	4	8578.7492	-0.0010
	4	1	4	3	0	3	9053.4977	-0.0017
	5	0	5	4	0	4	9717.1631	-0.0004
	5	1	5	4	0	4	10508.8132	0.0016
	6	0	6	5	1	5	10669.6000	0.0001
	5	1	4	4	1	3	10872.2862	-0.0003
	2	2	1	1	1	0	10885.1736	-0.0002
	2	2	0	1	1	1	11224.2122	0.0038
	6	0	6	5	0	5	11461.2514	0.0034
	6	1	6	5	0	5	11977.5388	-0.0033
	3	2	2	2	1	1	12628.2704	0.0023
¹³ C7	J'	K ₋₁ '	K ₊₁	J''	K ₋₁ ''	K ₊₁ ''	Obs. freq.	Obs.-calc.
	3	1	3	2	0	2	7577.7001	-0.0006
	5	0	5	4	1	4	8454.8945	0.0021
	4	1	4	3	0	3	9072.1063	-0.0010
	5	0	5	4	0	4	9663.1098	0.0003
	5	1	5	4	0	4	10518.7813	0.0010
	6	0	6	5	1	5	10548.3290	-0.0013
	5	1	4	4	1	3	10772.3044	-0.0005
	2	2	1	1	1	0	11009.9906	-0.0018
	2	2	0	1	1	1	11337.6240	0.0013
	6	0	6	5	0	5	11403.9998	-0.0013
	6	1	6	5	0	5	11973.3134	0.0008
	3	2	2	2	1	1	12743.9731	0.0008
¹³ C8	J'	K ₋₁ '	K ₊₁	J''	K ₋₁ ''	K ₊₁ ''	Obs. freq.	Obs.-calc.
	3	1	3	2	0	2	7521.0551	0.0059
	3	2	2	3	1	3	8003.1812	-0.0029
	5	0	5	4	1	4	8311.2153	-0.0027

	4	1	4	3	0	3	8999.0443	-0.0005
	5	0	5	4	0	4	9545.6593	0.0043
	6	0	6	5	1	5	10386.4637	-0.0010
	5	1	5	4	0	4	10428.1026	0.0000
	5	1	4	4	1	3	10621.1691	0.0039
	6	0	6	5	0	5	11268.9064	-0.0059
	2	2	0	1	1	1	11294.5580	0.0004
	6	1	6	5	0	5	11862.1150	-0.0005
	3	2	2	2	1	1	12689.0162	0.0001

Table 5. Kraitchman coordinates of 3-fluorophenylacetylene and a comparison with the principal axis *ab initio* coordinates.

	Kraitchman		<i>Ab initio</i> ^a	
	a	b	a	b
C1	0.94902(8)	0.03972(41)	-0.9601	-0.0738
C2	0.11006i(79)	0.88511(2)	0.0682	0.8813
C3	1.37476(6)	0.43622(4)	1.3817	0.4416
C4	1.72283(5)	0.89821(2)	1.7227	-0.9038
C5	0.68993(12)	1.84255(1)	0.6922	-1.8452
C6	0.63724(13)	1.43705(1)	-0.6408	-1.4410
C7	2.32652(4)	0.35154(5)	-2.3264	0.3502
C8	3.48101(2)	0.70464(3)	-3.4897	0.7100

^a Performed at MP2/6-311++G (2d,2p) level.

Table 6. Summary of structural parameters obtained from microwave structures, *ab initio* calculation, and crystal structures for 3-fluorophenylacetylene. See Fig 2 for atom numbering.

Parameter	Inertial fit	Kraitchman ^a	<i>Ab initio</i> ^b	Form1-1 ^c	Form1-2 ^c	Form1-3 ^c	Form2 ^c
R(C1-C2) (Å)	1.412(20)	1.375(27)	1.403	1.390(4)	1.392(4)	1.394(4)	1.387(6)
R(C2-C3) (Å)	1.377(19)	1.381(13)	1.385	1.367(4)	1.375(4)	1.360(5)	1.349(7)
R(C3-C4) (Å)	1.380(4)	1.379(4)	1.388	1.388(5)	1.378(5)	1.364(4)	1.398(6)
R(C4-C5) (Å)	1.396(2)	1.400(2)	1.396	1.382(4)	1.383(4)	1.384(5)	1.393(7)
R(C5-C6) (Å)	1.402(3)	1.388(3)	1.393	1.373(4)	1.378(4)	1.380(6)	1.384(7)
R(C6-C1) (Å)	1.400(19)	1.432(37)	1.404	1.395(5)	1.394(5)	1.390(4)	1.395(6)
R(C1-C7) (Å)	1.426(6)	1.432(11)	1.431	1.448(4)	1.444(4)	1.435(5)	1.433(8)
R(C7-C8) (Å)	1.218 ^d	1.207(2)	1.218	1.188(4)	1.184(4)	1.184(5)	1.191(7)
∠(C6-C1-C2) (°)	119.78(69)	119.70(93)	119.74	119.97(26)	119.21(26)	119.44(26)	118.22(36)
∠(C1-C2-C3) (°)	118.29(68)	118.76(120)	118.61	118.40(26)	118.52(26)	118.41(27)	120.64(38)
∠(C2-C3-C4) (°)	123.51(34)	123.58(27)	122.74	122.88(27)	123.00(28)	123.64(28)	122.21(40)
∠(C3-C4-C5) (°)	117.95(11)	117.82(11)	118.19	117.79(27)	118.13(28)	117.90(27)	117.80(41)
∠(C4-C5-C6) (°)	120.77(10)	120.57(10)	120.72	121.00(27)	120.37(27)	120.54(31)	119.88(39)
∠(C5-C6-C1) (°)	119.70(23)	119.57(36)	120.01	119.95(27)	120.76(27)	120.06(29)	121.20(38)
∠(C2-C1-C7) (°)	119.92(146)	121.87(265)	119.88	119.46(25)	120.10(25)	119.14(27)	120.74(37)
∠(C6-C1-C7) (°)	120.29(96)	118.43(179)	120.38	120.56(26)	120.68(27)	121.42(27)	120.98(36)
∠(C1-C7-C8) (°)	179.95 ^d	178.85(150)	179.95	178.67(31)	179.69(31)	178.40(34)	179.63(46)

^a The a-coordinate of C2 atom use the *ab initio* result rather than original imaginary value.

^b Performed at MP2/6-311++G (2d,2p) level.

^c Structural parameters in crystal structure from ref. [12]

^d Fixed to the *ab initio* values.

Figure 2. Comparison of (a) microwave r_0 structure, (b) microwave r_s structure, (c) ab initio (MP2/6-311++G(2d,2p)) structure, (d) ab initio (MP2/6-31+G(d,p)) structure, (e-h) crystal structures from Ref. [12]; (e) Form1-1, (f) Form1-2, (g) Form1-3, (h) Form2 of 3-fluorophenylacetylene.

Figure 3. Stark effect data for the $4_{04}-3_{13}$ transition.

Table 7. Stark effect transition frequencies for the 3-fluorophenylacetylene taken from the last iteration of QSTARK.

J'	K ₁	K ₂	J''	K ₁	K ₂	M	E ²	Obs. freq. ^a	Obs.-calc.
3	2	2	2	1	1	1	0	12776.9796	0.0021 ^b
3	2	2	2	1	1	1	4857.329	12776.8425	0.0140
3	2	2	2	1	1	1	10438.311	12776.6684	0.0108
3	2	2	2	1	1	1	18120.838	12776.4326	0.0098
3	2	2	2	1	1	1	27904.910	12776.1238	-0.0008
3	2	2	2	1	1	1	39790.527	12775.7525	-0.0111
3	2	1	2	1	2	0	0	13840.6212	-0.0015 ^b
3	2	1	2	1	2	0	4857.329	13840.6748	0.0034
3	2	1	2	1	2	0	10438.311	13840.7235	-0.0040
3	2	1	2	1	2	0	18120.838	13840.8003	-0.0043
3	2	1	2	1	2	0	39790.527	13841.0230	0.0010
3	2	1	2	1	2	0	53777.689	13841.1620	-0.0002
3	2	1	2	1	2	0	69866.396	13841.3293	0.0059
3	2	1	2	1	2	1	4857.329	13840.7935	-0.0071
3	2	1	2	1	2	1	10438.311	13840.9929	-0.0118
3	2	1	2	1	2	1	27904.910	13841.6436	0.0021
4	1	4	3	0	3	0	0	9126.5067	0.0002 ^b
4	1	4	3	0	3	0	4857.329	9126.4363	0.0008
4	1	4	3	0	3	1	4857.329	9126.4617	0.0038
4	1	4	3	0	3	1	10438.311	9126.4034	0.0012
4	1	4	3	0	3	1	18120.838	9126.3200	-0.0054
4	1	4	3	0	3	1	27904.910	9126.2134	-0.0143
4	1	4	3	0	3	1	39790.527	9126.1115	0.0025
4	1	4	3	0	3	1	53777.689	9125.9702	0.0009
4	1	4	3	0	3	1	69866.396	9125.8023	-0.0064
4	1	4	3	0	3	2	4857.329	9126.5303	0.0049
4	1	4	3	0	3	2	10438.311	9126.5516	0.0046
4	1	4	3	0	3	2	18120.838	9126.5776	0.0007
4	1	4	3	0	3	2	27904.910	9126.6158	0.0010
4	1	4	3	0	3	2	39790.527	9126.6635	0.0026
4	1	4	3	0	3	2	53777.689	9126.7159	0.0008
4	1	4	3	0	3	2	69866.396	9126.7792	0.0019
4	1	4	3	0	3	3	4857.329	9126.6391	0.0014
4	1	4	3	0	3	3	18120.838	9126.9860	-0.0100
4	1	4	3	0	3	3	27904.910	9127.2527	-0.0075
5	1	5	4	0	4	3	0	10587.4115	0.0000 ^b
5	1	5	4	0	4	3	39790.527	10588.3000	0.0015
5	1	5	4	0	4	4	10438.311	10587.6984	-0.0073
6	0	6	5	1	5	3	0	10681.1552	0.0015 ^b
6	0	6	5	1	5	3	18120.838	10680.9805	0.0024
6	0	6	5	1	5	3	27904.910	10680.8837	0.0005
6	0	6	5	1	5	3	39790.527	10680.7722	0.0043
6	0	6	5	1	5	3	69866.396	10680.4709	-0.0048
6	0	6	5	1	5	4	10438.311	10681.1032	0.0028

^a Only Stark components that are well resolved from each other and from the zero-field frequency are included in the QSTARK fit. Approximate measurements of poorly resolved components are consistent with the predicted shifts based on the fitted dipole moment components.

^b The zero-field transitions were not included in a list of fitting.

Table 8. Observed and calculated Stark coefficients^a and derived dipole moment components for the 3-fluorophenylacetylene.

	$10^5 \times (\Delta\nu/E^2)$ obs.	$10^5 \times (\Delta\nu/E^2)$ calc.
$3_{21} \leftarrow 2_{12} M = 0$	1.0096	1.0008
$3_{21} \leftarrow 2_{12} M = 1$	3.6485	3.6531
$3_{22} \leftarrow 2_{11} M = 1$	-3.0655	-3.0603
$4_{14} \leftarrow 3_{03} M = 0$ ^b	-1.4494	-1.4571
$4_{14} \leftarrow 3_{03} M = 1$	-1.0065	0.9960
$4_{14} \leftarrow 3_{03} M = 2$	0.3911	0.3873
$4_{14} \leftarrow 3_{03} M = 3$	2.6662	2.6929
$5_{15} \leftarrow 4_{04} M = 3$ ^b	2.2329	2.2207
$5_{15} \leftarrow 4_{04} M = 4$ ^b	2.8203	2.8084
$6_{06} \leftarrow 5_{15} M = 3$	-0.9684	-0.9652
$6_{06} \leftarrow 5_{15} M = 4$	-0.5062	-0.5078
$\mu_a = 0.6412(13)$ D		
$\mu_b = 1.2000(14)$ D		
$\mu_c = 0$ D		
$\mu_{\text{total}} = 1.3606(14)$ D		

^a Stark coefficients are in units of MHz V⁻² cm².

^b The number of applied fields in the fit for these transitions was 1.