Microwave Spectrum, Structure and Dipole Moment of 4-fluorophenylacetylene (4FPA)

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Abstract

Using a chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer, a 6-18 GHz spectrum of 4-fluorophenylacetylene (4FPA) was measured and only *a*-type *R*-branch transitions were observed up to $J = 9$. Rotational constants and quartic centrifugal distortion constants for the normal isotopic species were determined based on Watson-S reduction: $A = 5652.812(22)$ MHz, $B = 966.92885(11)$ MHz, $C = 825.67680(11)$ MHz, $D_J = 0.01377(60)$ kHz, and $D_{JK} = 0.2468(61)$ kHz, with other three distortion constants fixed as $D_K = 0.6629$ kHz, $d_1 = 2.386$ Hz, and $d_2 = 0.989$ Hz from *ab initio* results. For six kinds of carbon-13 isotopic species, 10-15 transitions were detected by a resonant cavity FTMW spectrometer in natural abundance, and rotational constants of each species were also determined by fitting transition frequencies. Gaseous molecular structures of 4FPA were derived via the least-squares fitting (r_0) and substitution (r_s) methods, and *ab initio* optimization (r_e). They were compared to the structures of benzene derivatives having fluorine and the acetylenic group as substituents. In addition, dipole moment component of 4FPA was also determined to be $\mu_a = \mu_{\text{total}} = 0.8935(9)$ D from Stark effect measurements.

Keywords

4-fluorophenylacetylene

Rotational spectrum

Chirped-pulse microwave spectroscopy

Ab initio structure

Dipole moments

1. Introduction

Fluorophenylacetylenes have invoked our interest in ring geometry of benzene derivatives with the different influences on ring distortion of their two substituents, fluorine and the acetylenic group, being worth attention. There are three isomers of fluorophenylacetylenes that differ in the fluorine position relative to the acetylenic group: 2-fluorophenylacetylene (2FPA), 3-fluorophenylacetylene (3FPA), and 4-fluorophenylacetylene (4FPA). The meta-substituted compound, 3FPA, was already reported by our group using microwave spectroscopy [1]. The paper includes its spectrum, structure and dipole moment components. As expected, angle opening in an endocyclic angle at the carbon substituted by fluorine was found, whereas the other endocyclic angle at the carbon adjacent to the acetylenic group decreased slightly. In this work, by analyzing its rotational spectrum, structure and dipole moment components, 4FPA has been studied in a similar fashion.

Mono-substituted compounds, fluorobenzene [2-4] and phenylacetylene (ethynylbenzene) [5-8], have been studied using microwave and electron diffraction study, whereas this microwave study is the first investigation of dipole moment components and structure for 4FPA, to the author's knowledge. Maity [9-10] investigated water complexes of fluorophenylacetylenes (2FPA and 4FPA) using IR-UV double resonance spectroscopy and *ab initio* calculation. Though fluorination does not change the intermolecular structure, it enhances the interaction of water to the acetylenic triple bond by about 1.5 times, compared to phenylacetylene. It indicates that fluorination at *ortho*- and *para*-position would affect electron density of the acetylenic group in the molecule. A recent paper [11] about structural trends in mono-, di-, and pentafluorobenzonitriles also helped us to interpret structural changes in 4FPA because a $\text{--C}\equiv\text{N}$ functional group is expected to have structural properties similar to the $\text{--C}\equiv\text{CH}$ functional group with a triple bond, although the previous study does not include 4-fluorobenzonitrile.

In this work, the measurement of a rotational spectrum for 4FPA, via a chirped-pulse Fourier transform microwave spectrometer (CP-FTMW) and a resonant cavity FTMW, leads to determination of spectroscopic parameters such as rotational constants, centrifugal distortion constants, and second moments. Analyzing transitions for the six carbon-13 singly substituted isotopic species (in natural abundance) enabled heavy atom molecular structures in gas phase to be obtained and compared to the equilibrium structure given by *ab initio* calculation. Structural changes compared to benzene and other substituted benzenes will be discussed in Section 4. In addition, observing Stark shifts of rotational transitions under electric fields allows determination of the dipole moment components of 4FPA.

2. Experimental

A sample of 4-fluorophenylacetylene (4FPA, 98%) was purchased from SYNQUEST Labs and used without further purification. The vapor pressure of the solid compound was enough to do spectroscopic experiments without heating since its melting point (27-28°C) is close to ambient temperature.

The broadband spectrum of 4FPA was obtained by the 480 MHz bandwidth CP-FTMW spectrometer at Eastern Illinois University (EIU) [12] in the range of 6 to 18 GHz. A carrier gas composed of 82.5% Ne and 17.5% He (BOC Gases) was continuously flowed over the solid at a

pressure of ~ 2.5 bar and then expanded into the vacuum chamber via a General Valve Series 9 solenoid valve with 400 gas pulses with 5 FID collected per gas pulse to give a total of 2000 free induction decays averaged per frequency step. The separate spectra were stored as 0-240 MHz offsets from each center frequency, and then compiled into a full spectrum using a LabVIEW program.

Subsequent high resolution measurements were performed by a standard Balle-Flygare type resonant cavity instrument at EIU [13-14]. Rotational transitions of the parent species at frequencies lower than 6 GHz, and of each ^{13}C singly substituted isotopologue in natural abundance were collected. Stark effects of the parent transitions under applied electric fields were also measured using the cavity FTMW with the electric field calibrated using OCS, and assuming a dipole moment of $0.71519(3)\text{D}$ [15].

All recorded transition frequencies except for Stark effects measurements were fitted following Pickett's SPCAT/SPFIT packages [16] and Kisiel's AABS packages, ASCP and SVIEW [17]. The rotational constants and quartic centrifugal distortion constants were determined based on the I^r representation of the Watson S-reduction Hamiltonian [18]. The *ab initio* rotational constants of an optimized structure at the MP2/6-311++G(2d,2p) level of Gaussian 03 [19] were used as initial parameters. The centrifugal distortion constants of the equilibrium structure (r_e) were also obtained by *anharmonic* frequency calculation at the MP2/3-21G level for comparison.

Substitution (r_s) and ground state (r_0) structures were determined by the difference of rotational constants between the parent and minor isotopic species using KRA/EVAL [20] and STRFITQ [21] programs, respectively. To derive dipole moment components of the parent species from the Stark effect, QSTARK [22] and ASYSPEC/DIPOLE [23] were utilized; by least-squares fitting, experimental Stark coefficients ($\Delta\nu/E^2$) were compared with calculated ones based on second order perturbation theory.

3. Results

3.1. Rotational spectra

Using the 480 MHz bandwidth chirped-pulse FTMW, the 6-18 GHz spectrum of 4FPA was initially recorded. As it has C_{2v} symmetry, a smaller number of transitions was observed than for the previously studied 3FPA (3-fluorophenylacetylene) [1]. Further transitions out of the range of the CP-FTMW spectrometer for the normal isotopic species, and for all minor isotopic species, were measured by a standard resonant cavity FTMW. Although there are eight different carbon atoms in 4FPA, transitions for only six ^{13}C isotopic species were observable due to the C_{2v} symmetry. Figure 1 represents the atom numbering of the carbons and the principal axes of the *ab initio* results. With the experiment, the equilibrium structure ($^{12}\text{C}_8\text{H}_5\text{F}$) was optimized at the MP2/6-311++G(2d,2p) level, and its energy was also calculated at the same level using Gaussian03 [19]. In addition, *anharmonic* frequency calculations at MP2/3-21G gave information about centrifugal distortion. A summary of the results is listed in Table 1; the calculated rotational constants helped guide the initial fit of experimental spectroscopic constants.

For the normal isotopomer, a total of 49 R-branch *a*-type transitions were assigned as shown in Table 2, determining the rotational constants and two centrifugal distortion constants – D_J and D_{JK} employing the Watson-S reduced Hamiltonian [18]. Other quartic distortion constants were fixed to the values from *ab initio* results for the normal isotopic species. The constants are in good agreement

with those of the *ab initio* structure (Table 1). It is not surprising that uncertainties of the *A* rotational constants are larger than those for the *B* and *C* rotational constants, since only *a*-type transitions that are mainly dependent on those two constants have been detected. Ray's asymmetry parameter [24], calculated by $\kappa = (2B-A-C)/(A-C)$, is -0.94148 very close to -1 suggesting a near prolate asymmetric rotor. As for six singly ^{13}C substituent species, 10-15 transitions for each species were found in natural abundance to fit the rotational constants given in Table 1. Due to the symmetry, the population of $^{13}\text{C}_2$ and $^{13}\text{C}_3$ are doubled and showed stronger transitions resulting in more observed transitions for these isotopic species. The centrifugal distortion constants were fixed to those of the normal 4FPA. All isotopic species excluding the $^{13}\text{C}_1$ isotopologue have been well-fitted with small uncertainties less than 4 kHz . All observed transitions for minor isotopomers are listed in Table 3.

Second moments (P_{aa} , P_{bb} , and P_{cc}) of each isotopic species in Table 1 reflect the position of each substituted atom along each of the principal axes. These are useful parameters to confirm whether spectroscopic fits for isotopic species have been done correctly. The four carbon atoms located on the *a*-axis – C1, C4, C7, and C8 (as shown in Fig.1) produce smaller P_{bb} values than the atoms lying outside the *ac* plane. The longer the distance from the axis, the bigger the corresponding second moment becomes. As a result in the $^{13}\text{C}_8$ substituent species, when the atom lies farthest from the *b*-axis, we see the largest P_{aa} value; the smallest P_{aa} value occurs for the $^{13}\text{C}_2$ species where the substituted carbon is next to the *b*-axis. Finally, the P_{cc} value close to zero for all species suggests that this molecule has a planar structure. Further discussion on the molecular structure appears in Section 3.2.

3.2. Structure

To discover the gas-phase structure of 4-fluorophenylacetylene, three approaches have been applied in this study – (i) calculating theoretical values employing Møller–Plesset (MP2) perturbation methods, (ii) analyzing singly substituted isotopic species and deriving Kraitichman coordinates, and (iii) fitting atomic principal axis coordinates to experimental planar moments. As shown in Fig.1, an equilibrium structure optimized at MP2/6-311++G(2d,2p) level indicates that this molecule has a planar structure with C_{2v} symmetry. Thus, it has been supposed that there are six unique carbon atoms in 4FPA for heavy atom substitution.

Table 4 shows the principal axis coordinates of the six atoms obtained by Kraitichman's equations [25] and *ab initio* calculation. The signs of the substitution coordinates, which are determined as absolute values, stayed the same as that of *ab initio* coordinates when bond variables were estimated.

The *a*-coordinates of the experimental structure are in good agreement with those of the calculated structure within $0.001\text{-}0.01\text{ \AA}$. The *b*-coordinates of carbon atoms lying off the *a*-axis – C2 and C3 – show less than $0.001\text{ \AA}$ differences between the Kraitichman and *ab initio* values, while *b*-coordinates of atoms on the *a*-axis result in complex values, with larger uncertainties. The *b*-coordinates of C1, C4, C7 and C8 were replaced by zero with Costain uncertainties [26-27] to evaluate reasonable structural parameters for the Kraitichman structure. Structural parameters for 4FPA from *ab initio* calculation (r_e), substitution analysis (r_s), and least squares fit (r_0) are listed in Table 5.

The r_0 structure has been determined by fitting the atomic coordinates of our *ab initio* structure to experimental planar moments, determined from experimental rotational constants of the normal and minor isotopic species. Since P_{cc} for all isotopomers is close to zero, only P_{aa} and P_{bb} have been used in the fit. Note that just the structural variables given in Table 5 were adjusted. Compared to the

equilibrium state structure (r_e), the bond distances and bond angles are almost the same, agreeing to within 0.005 Å and 0.5° except for $r(\text{C7,C8})$. These results also suggest that the selected basis set in this calculation is suitable for this molecule. The substitution structure (r_s) is also in good agreement with the inertial fit (r_0) and a summary of structural parameters for comparison is shown in Figure 2.

3.3. Dipole moments

Applied electric fields cause splitting of rotational transitions (referred to as the Stark effect). These shifted transitions for the parent isotopologue of 4FPA were measured by the Balle-Flygare resonant cavity FTMW [13], applying external electric fields up to 330 V cm⁻¹. The assignment of patterns was based on Stark coefficients derived from second order perturbation theory and the predicted dipole moment from *ab initio* calculation. Figure 3 shows an example of observed Stark shifts for the $3_{03}-2_{02}$ transition. The slopes of linear regression in the graph gives the mean experimental Stark coefficients ($\Delta\nu/E^2$).

All observed frequencies for each different applied electric field were least-squares fitted to μ_a by QSTARK [22] keeping the rotational constants and centrifugal distortion constants of the normal 4FPA fixed at values in Table 1. A list of the frequencies is shown in Table 6 and the resulting standard deviation of the difference between observed and calculated transition frequency values of 2.8 kHz is within the expected precision of measurement. By comparing observed Stark coefficients to calculated values from second order perturbation theory, the experimental dipole moment components of 4FPA were determined to be $\mu_a = \mu_{\text{total}} = 0.8930$ (11) and 0.8935(9) D depending on the methods of least squares fitting (Table 6, 7) while μ_b and μ_c components were fixed to zero due to symmetry. The discrepancies in the Stark coefficients are within 0.02-0.6 MHz V⁻² cm², and the dipole components from DIPOLE are consistent with those values from QSTARK. In addition, the *ab initio* structure optimized at the level of MP2/6-311++G(2d,2p) gives a theoretical dipole moment component of $\mu_a = \mu_{\text{total}} = 0.9533$ Debye ($\mu_b = \mu_c = 0$) which are in good agreement with the experimental ones.

4. Discussion

In this paper, rotational transitions in the 6-18GHz microwave region for the normal and six ¹³C isotopic species of 4FPA have been studied. The spectra were measured by a chirped-pulse or a resonant cavity FTMW spectrometer, and fitted to derive spectroscopic parameters such as rotational constants, centrifugal distortion constants, and planar moments (Table 1). The parameters for the major and minor isotopic species made determination of a gas phase molecular structure possible (Table 2). In addition, experimental dipole moment components were obtained by observing Stark shifts of specific transitions (Table 7).

4-fluorophenylacetylene is a substituted benzene which has two substituents, the acetylenic group and a fluorine atom, on opposite sides of the ring (*para*). The ring distortion in each *mono*-substituted benzene, such as fluorobenzene [2-3] and phenylacetylene (ethynylbenzene) [5-8] which has just an acetylenic group, has previously been reported by microwave study and electron diffraction analysis. A summary of their structure is listed in Table 8. Note that a rearrangement of atomic numbering in fluoro-substituted compounds makes it more efficient to compare their structures with that of 4FPA. With a fluorine bonded to the C4 atom in fluorobenzene such as in 4FPA, the C3C4C5 bond angle

increased by 3.4° compared to that of benzene, whereas the angle C6C1C2 adjacent to the acetylenic group in phenylacetylene varies by less than 1° . The results in phenylacetylene have been inconsistent, as discussed in ref [6]; the C6C1C2 angles derived from microwave spectroscopy are greater than 120° [5, 6], while those from electron diffraction method are smaller [7, 8] (Table 8). In our optimization, the angle of its r_e structure proved to be 119.3° , smaller than 120° , at the MP2/6-311++G(2d,2p) level of Gaussian 03 [19]. Toluene is also compared with others, which proved to have the smaller bond angle ($119.26(40)^\circ$ [28] or 118.7° [29]) at the substituent carbon (C1) than benzene.

The *para*-di-homosubstituted benzene derivatives – such as 1,4-difluorobenzene [30], 1,4-diethynylbenzene [31], and 1,4-xylene [32] – have no dipole moment by symmetry, so they can be studied only by electron diffraction techniques (Table 8). The ring geometry of 1,4-difluorobenzene is very similar to that of fluorobenzene; especially, the C3C4C5 angle adjacent to a fluorine of fluorobenzene is $123.4(2)^\circ$ and that of 1,4-difluorobenzene is $123.53(4)^\circ$. 1,4-diethynylbenzene also has an analogous structure to the structures of phenylacetylene determined by the electron diffraction method, showing a little smaller angle than 120° at the C6C1C2 angle. Meanwhile, the substituted angle in 1,4-xylene appears slightly smaller than the C6C1C2 angle for toluene. It is supposed that the effect of the methyl group could reach the opposite side and it could reduce the opposite angle, since the C3C4C5 angle – on the opposite side of the methyl group substituted carbon (C1) in toluene – was also smaller than 120° . Thus, the smaller angle at C1 and C4 atoms in 1,4-xylene as $117.1(3)^\circ$ than the C6C1C2 angle in toluene could be explained by the effect of two methyl groups, reducing the opposite angle each other.

Both *para*-heterosubstituted benzene derivatives, 4-fluorophenylacetylene and 4-fluorotoluene [33], show decreased angles at C6C1C2 and C3C4C5 compared to their mono-substituted compounds (Table 8). The C6C1C2 angle of 4FPA (or 4-fluorotoluene) is slightly smaller than that of phenylacetylene (or toluene), and the C3C4C5 angle ($\sim 122.4^\circ$) of both compounds is smaller than that of fluorobenzene by about 1° . For 4-fluorotoluene, the influence of the methyl group mentioned above, which seems to reduce the opposite endocyclic angle of the carbon substituted by the methyl group, could account for the decrease of the C3C4C5 angle. Unlike the methyl group in toluene, the acetylenic group in phenylacetylene has not decreased the opposite angle significantly. The smaller C3C4C5 angle in 4FPA than fluorobenzene's, though the difference is only one degree, is particularly interesting since the fluorinated angle in 3FPA is comparable to that of fluorobenzene, 123.5° [1].

The angle opening in substituted benzene compounds has been reported almost for the past half-century. One of the interpretations for the ring geometric changes is hybridization effects [34]. It is known that orbitals of a central atom attached to multiple groups could hybridize. Bent's rule [35], originally stated by Walsh, explains that orbitals directed towards electropositive substituents have more s-character, thus other orbitals directed toward relatively electronegative substituents have more p-character. With benzene being substituted by an electronegative substituent such as fluorine, the hybrid orbital bonded to the substituent has more p-character whereas the other two orbitals bonded to carbons in the ring have more s-character (less p-character). Their s electrons concentrate in nucleus of a center carbon atom more tightly than p electrons, thus the C–C bond lengths decreases and the endocyclic angle between two C–C bonds increases as the s-character of bonding orbitals towards carbons in the ring increases.

In addition, Domenicano [34] suggested that conjugation between substituents and the ring also has an effect on ring geometry. A certain π bonding in a C–X bond – between a carbon and a

substituent – tends to shorten the bond distance in the C–X bond. It also could be explained by an increase in the s-character of the hybrid orbital of the carbon bonded to the substituent and an increase in the p-character of the other two orbitals of the carbon directed toward adjacent carbons in the ring. This influence is the reverse of the hybridization effect expected in fluorinated benzene; the p-character of the carbon orbitals towards carbons in the ring decreases and the bond angle between C–C bonds increases, according to the hybridization effect. As a result, conjugation would increase C–C bond lengths of the ring and close up the angle between two C–C bonds regardless of whether the substituent is a π -donor or π -acceptor.

The NBO (Natural Bond Orbitals) analysis using Gaussian 03 [19] enables us to quantify the s- and p-character of hybrid orbitals in r_e structures. The results of 4FPA have been compared with those of phenylacetylene and fluorobenzene optimized at MP2/6-311++G(2d,2p) level in Figure 4. Compared to phenylacetylene (Fig. 4(c)), in 4FPA (Fig. 4(a)), the C3C4C5 angle increases and the C3–C4 and C4–C5 bond lengths decreases corresponding to the trend of experimental structures in Table 8. The p-character of the C4 orbital directed towards F increases by 6.3% and the s-character of the other orbitals towards C3 or C5 increases by 2.2%. These changes are in agreement with the hybridization effect of fluorine. The C6C1C2 angle of 4FPA decreases by 0.2° and the s-character of the C1 orbital directed towards C≡C increases by 0.4%. These changes are consistent with the trend of the conjugation effect, albeit the changes are very small.

In addition, the ratio between the s- and p-character of orbitals at C1 of 4FPA (Fig. 4(a)) is slightly changed from that of fluorobenzene (Fig. 4(b)). The p-character of the C1 orbital directed towards the C≡C decreases by 2.9% and the s-character of the C1 orbitals towards carbons in the ring decrease by 1.5%. The C6C1C2 angle of 4FPA also decreases by 0.5° and the C6–C1 and C1–C2 distances increase in agreement with the experimental results in Table 8. The C3C4C5 angle of 4FPA, compared to fluorobenzene, decreases by 0.2° and the s-character of the C4 orbital directed towards F increases by 0.2%. The slight changes, unfortunately, are not enough to explain the reason why the C3C4C5 angle of 4FPA is smaller than that of fluorobenzene by 1° in the experimental results, since the C3C4C5 angle of fluorobenzene in our optimization unexpectedly proved to be 122.5° less than the experimental structures [2, 3]. However, conjugation shown in resonance structures of 4FPA (Figure 5) would have an impact on the smaller C6C1C2 and C3C4C5 angles compared to that of phenylacetylene and fluorobenzene, since these slight but comparable trends in variation are consistent with the conjugation effect mentioned above.

The mono-substituted and the *para*-heterosubstituted benzene usually have only one dipole moment component by their symmetry. Table 9 shows the dipole moment component of 4FPA and related species. 4FPA has two substituents on the opposite side, fluorine and the acetylenic group. Both mono-substituted compound, fluorobenzene [4] and phenylacetylene [5], have the same direction of dipole moment such as benzene ring to F in fluorobenzene and ring to C≡C in phenylacetylene. Opposite directions of the two substituents, –F and –C≡C–H, in 4FPA lead to an intermediate value of dipole moment between fluorobenzene and phenylacetylene. Subtracting the dipole moment of phenylacetylene (0.656(5) D) from that of fluorobenzene (1.66(3) D) gives a comparable value (1.00(3) D) to the experimental dipole moment of 4FPA (0.8935(9) D).

In the same way, directions of dipole moment in fluorobenzene [4] and toluene [36] are opposite, ring to F in fluorobenzene and CH₃ to ring in toluene, and two substituents contribute to a same direction of dipole moment in 4-fluorotoluene. Thus, the sum of two values (2.04(3) D) is consistent with the experimental dipole moment of 4-fluorotoluene [36-37]. Furthermore, in the case of 3FPA,

when the included angle between C–C≡C–H and C–F is supposed to be 120°, the result of vector summation is 1.45 D and it is in agreement with the experimental dipole moment, 1.361(1) [1].

5. Conclusion

By measuring its microwave spectrum, the molecular characters of 4-fluorophenylacetylene (4FPA) has been studied including spectroscopic parameters, experimental and calculated structures, and dipole moment components. The experimental rotational constants and centrifugal distortion constants were comparable to the theoretical results given by *ab initio* calculation. Though some coordinates of carbons on the *a*-axis involve large uncertainties, the substitution structure (r_s) was consistent with the least-squares fitting structure (r_0), and both are in good agreement with the equilibrium structure (r_e) optimized at MP2/6-311++G(2d,2p) of Gaussian03. Dipole moments determined by Stark effect measurements were also close to those of the *ab initio* structure.

Ring geometry of 4FPA has been compared to that of mono-substituted, *para*-di-homosubstituted, and *para*-heterosubstituted benzene having fluorine, an acetylenic group, or a methyl group as their substituents. The endocyclic angle at the carbon substituted by fluorine increased and the angle at the carbon adjacent to the acetylenic and methyl group decreased, compared to benzene. Effects of substituents on ring geometry have been discussed in terms of hybridization and conjugation effects from an NBO analysis. Dipole moment variations in *para*-heterosubstituted benzene were also compared with the value of mono-substituted benzene. As the first microwave study on 4FPA, structural information and dipole moment component studied here are expected to help understand its reactivity, interactions and other characters more.

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Figure 1. The atom numbering for carbon-13 atoms of 4-fluorophenylacetylene with its three principal axes: *a*, *b*, and *c*.

Table 1. Spectroscopic constants of 4-fluorophenylacetylene (4FPA) and its six ^{13}C isotopologues. See Fig.1 for atom numbering.

	<i>Ab initio</i> ^a	normal	$^{13}\text{C}_1$	$^{13}\text{C}_2$	$^{13}\text{C}_3$	$^{13}\text{C}_4$	$^{13}\text{C}_7$	$^{13}\text{C}_8$
A (MHz)	5670.326	5652.812(22)	5652.95(20)	5562.112(39)	5561.775(80)	5653.04(13)	5652.28(15)	5652.83(13)
B (MHz)	962.620	966.92885(11)	964.74291(56)	966.66563(12)	965.09559(18)	961.85226(36)	955.28942(40)	941.87301(34)
C (MHz)	822.917	825.67680(11)	824.08760(45)	823.52309(10)	822.36861(15)	821.97889(29)	817.17440(32)	807.33617(28)
D_J (kHz) ^b	0.01199	0.01377(60)	[0.01377]	[0.01377]	[0.01377]	[0.01377]	[0.01377]	[0.01377]
D_{JK} (kHz) ^b	0.4336	0.2468(61)	[0.2468]	[0.2468]	[0.2468]	[0.2468]	[0.2468]	[0.2468]
D_K (kHz)	0.6629	[0.6629]	[0.6629]	[0.6629]	[0.6629]	[0.6629]	[0.6629]	[0.6629]
d_1 (Hz)	2.386	[2.386]	[2.386]	[2.386]	[2.386]	[2.386]	[2.386]	[2.386]
d_2 (Hz)	0.989	[0.989]	[0.989]	[0.989]	[0.989]	[0.989]	[0.989]	[0.989]
P_{aa} ($\text{u}\text{\AA}^2$) ^c	525.0	522.6698(3)	523.8532(12)	522.8124(7)	523.6656(11)	525.4277(12)	529.0339(12)	536.5744(13)
P_{bb} ($\text{u}\text{\AA}^2$) ^c	89.13	89.4088(3)	89.4057(12)	90.8669(7)	90.8752(11)	89.4045(12)	89.4131(12)	89.4090(13)
P_{cc} ($\text{u}\text{\AA}^2$) ^c	0	-0.0056(3)	-0.0048(12)	-0.0059(7)	-0.0087(11)	-0.0050(12)	-0.0015(12)	-0.0063(13)
κ	-0.9424	-0.94148	-0.94174	-0.93958	-0.93977	-0.94209	-0.94287	-0.94447
N^d	-	49	10	15	14	10	10	10
Δv_{rms} (kHz) ^e	-	2.1	4.6	1.6	2.2	3.0	3.3	2.8

^a MP2/6-311++G(2d,2p) level, with distortion constants determined using an *anharmonic* frequency calculation at the MP2/3-21G level.

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

^c 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} .

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

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

Table 2. Observed microwave frequencies (in MHz) of the normal isotopic species of 4-fluorophenylacetylene.

$^{12}\text{C}_8\text{H}_5\text{F}$	J'	K_{-J}'	K_{+J}'	J''	K_{-J}''	K_{+J}''	Obs. freq.	Obs.-calc.
	3	1	3	2	1	2	5163.9914	-0.0003
	3	0	3	2	0	2	5365.2434	-0.0005
	3	2	2	2	2	1	5377.8109	0.0012
	3	2	1	2	2	0	5390.3818	0.0007
	3	1	2	2	1	1	5587.7033	-0.0002
	4	1	4	3	1	3	6881.7531	0.0011
	4	0	4	3	0	3	7139.0580	0.0001
	4	2	3	3	2	2	7167.9631	-0.0016
	4	3	2	3	3	1	7176.5579	-0.0051
	4	3	1	3	3	0	7176.8255	-0.0001
	4	2	2	3	2	1	7199.3251	0.0002
	4	1	3	3	1	2	7446.4955	-0.0008
	5	1	5	4	1	4	8596.5814	0.0003
	5	0	5	4	0	4	8900.5803	0.0014
	5	2	4	4	2	3	8956.0193	-0.0031
	5	4	2	4	4	1	8969.9741	0.0025
	5	4	1	4	4	0	8969.9741	-0.0016
	5	3	3	4	3	2	8973.3578	-0.0007
	5	3	2	4	3	1	8974.2755	-0.0017
	5	2	3	4	2	2	9018.4621	0.0022
	5	1	4	4	1	3	9301.9189	-0.0014
	6	1	6	5	1	5	10307.9040	0.0001
	6	0	6	5	0	5	10647.2168	0.0010
	6	2	5	5	2	4	10741.4653	0.0041
	6	5	1	5	5	0	10763.4163	0.0026
	6	5	2	5	5	1	10763.4163	0.0027
	6	3	4	5	3	3	10771.6900	-0.0010
	6	3	3	5	3	2	10774.1370	-0.0008
	6	2	4	5	2	3	10849.8491	0.0014
	6	1	5	5	1	4	11152.9653	0.0001
	7	1	7	6	1	6	12015.2480	0.0038
	7	0	7	6	0	6	12376.9778	0.0009
	7	2	6	6	2	5	12523.7652	0.0009
	7	3	5	6	3	4	12571.6419	-0.0005
	7	3	4	6	3	3	12577.1372	0.0006
	7	2	5	6	2	4	12694.9432	-0.0017
	7	1	6	6	1	5	12998.5117	0.0041
	8	1	8	7	1	7	13718.2336	-0.0043
	8	0	8	7	0	7	14088.7655	-0.0021
	8	2	7	7	2	6	14302.4249	0.0031
	8	3	6	7	3	5	14373.1780	-0.0049
	8	3	5	7	3	4	14384.1378	0.0006
	8	2	6	7	2	5	14554.2988	-0.0020
	8	1	7	7	1	6	14837.2858	-0.0032
	9	1	9	8	1	8	15416.6396	-0.0009
	9	0	9	8	0	8	15782.6433	0.0007
	9	2	8	8	2	7	16076.9375	0.0019
	9	2	7	8	2	6	16427.3015	0.0025
	9	1	8	8	1	7	16667.8989	-0.0004

Table 3. Observed transition frequencies (in MHz) of carbon-13 isotopic species of 4-fluorophenylacetylene (See Fig. 1 for atom numbering).

$^{13}\text{C}_1$	J'	K_{-l}'	K_{+l}'	J''	K_{-l}''	K_{+l}''	Obs. freq.	Obs.-calc.
	3	0	3	2	0	2	5354.0333	0.0037
	4	0	4	3	0	3	7124.2307	-0.0034
	5	1	5	4	1	4	8579.3090	-0.0040
	5	0	5	4	0	4	8882.2608	0.0091
	5	1	4	4	1	3	9281.6808	-0.0001
	6	1	6	5	1	5	10287.2551	0.0052
	6	0	6	5	0	5	10625.5136	0.0040
	6	1	5	5	1	4	11128.7610	-0.0028
	7	1	7	6	1	6	11991.2324	-0.0040
	7	0	7	6	0	6	12352.0190	-0.0048
$^{13}\text{C}_2$	J'	K_{-l}'	K_{+l}'	J''	K_{-l}''	K_{+l}''	Obs. freq.	Obs.-calc.
	3	0	3	2	0	2	5357.4057	-0.0019
	4	1	4	3	1	3	6868.0219	0.0015
	4	0	4	3	0	3	7127.9334	-0.0010
	4	1	3	3	1	2	7440.3055	0.0001
	5	1	5	4	1	4	8579.1628	-0.0022
	5	0	5	4	0	4	8885.6124	-0.0024
	5	1	4	4	1	3	9293.8817	-0.0006
	6	1	6	5	1	5	10286.6569	0.0029
	6	0	6	5	0	5	10627.7746	0.0005
	6	1	5	5	1	4	11142.8609	0.0004
	7	1	7	6	1	6	11990.0005	0.0014
	7	0	7	6	0	6	12352.3984	-0.0014
	7	1	6	6	1	5	12986.0539	0.0013
	8	1	8	7	1	7	13688.8302	-0.0017
	8	0	8	7	0	7	14058.4653	0.0013
$^{13}\text{C}_3$	J'	K_{-l}'	K_{+l}'	J''	K_{-l}''	K_{+l}''	Obs. freq.	Obs.-calc.
	3	0	3	2	0	2	5349.3122	-0.0009
	4	1	4	3	1	3	6857.9899	-0.0019
	4	0	4	3	0	3	7117.2303	-0.0027
	4	1	3	3	1	2	7428.6161	-0.0011
	5	1	5	4	1	4	8566.6622	-0.0013
	5	0	5	4	0	4	8872.3859	0.0039
	5	1	4	4	1	3	9279.3121	0.0000
	6	1	6	5	1	5	10271.7016	0.0014
	6	0	6	5	0	5	10612.0931	-0.0044
	6	1	5	5	1	4	11125.4383	0.0008
	7	1	7	6	1	6	11972.6138	-0.0018
	7	0	7	6	0	6	12334.3730	0.0010
	7	1	6	6	1	5	12965.8150	0.0008
	8	1	8	7	1	7	13669.0453	0.0031
$^{13}\text{C}_4$	J'	K_{-l}'	K_{+l}'	J''	K_{-l}''	K_{+l}''	Obs. freq.	Obs.-calc.
	3	0	3	2	0	2	5339.1783	0.0021
	4	0	4	3	0	3	7104.6004	0.0036
	5	1	5	4	1	4	8556.4195	-0.0022
	5	0	5	4	0	4	8857.9678	-0.0010
	5	1	4	4	1	3	9254.8940	-0.0019
	6	1	6	5	1	5	10259.8749	0.0063
	6	0	6	5	0	5	10596.7432	0.0002
	6	1	5	5	1	4	11096.7335	0.0002
	7	1	7	6	1	6	11959.4019	-0.0049
	7	0	7	6	0	6	12318.9459	-0.0001
$^{13}\text{C}_7$	J'	K_{-l}'	K_{+l}'	J''	K_{-l}''	K_{+l}''	Obs. freq.	Obs.-calc.
	3	0	3	2	0	2	5305.3954	0.0014
	4	0	4	3	0	3	7059.9242	0.0007
	5	1	5	4	1	4	8504.3121	-0.0021
	5	0	5	4	0	4	8802.7125	0.0021
	5	1	4	4	1	3	9194.0294	-0.0021
	6	1	6	5	1	5	10197.5303	-0.0046

	6	0	6	5	0	5	10531.2639	0.0058
	6	1	5	5	1	4	11023.9425	0.0001
	7	1	7	6	1	6	11886.9435	0.0041
	7	0	7	6	0	6	12243.6135	-0.0047
¹³ C ₈	<i>J'</i>	<i>K_{-i}'</i>	<i>K_{+i}'</i>	<i>J''</i>	<i>K_{-i}''</i>	<i>K_{+i}''</i>	Obs. freq.	Obs.-calc.
	3	0	3	2	0	2	5236.2738	0.0018
	4	0	4	3	0	3	6968.5059	0.0026
	5	1	5	4	1	4	8397.6535	-0.0024
	5	0	5	4	0	4	8689.6081	0.0013
	5	1	4	4	1	3	9069.5457	-0.0054
	6	1	6	5	1	5	10069.9396	0.0017
	6	0	6	5	0	5	10397.1905	-0.0039
	6	1	5	5	1	4	10875.0633	0.0039
	7	1	7	6	1	6	11738.5901	-0.0003
	7	0	7	6	0	6	12089.3720	0.0013

Table 4. Kraitchman coordinates of 4-fluorophenylacetylene and a comparison with the principal axis *ab initio* coordinates.

	Kraitchman		<i>Ab initio</i> ^a	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
C1	1.09095(12)	0.048i(26)	1.1007	0.0000
C2	0.37755(26)	1.21063(67)	0.3908	-1.2111
C3	0.99720(10)	1.21410(93)	-1.0015	-1.2152
C4	1.66504(8)	0.061i(21)	-1.6713	0.0000
C7	2.52980(5)	0.093(14)	2.5312	0.0000
C8	3.73809(4)	0.020i(69)	3.7489	0.0000

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

Table 5. Summary of equilibrium (r_e)^a, substitution (r_s)^b, and ground state (r_0)^c structural parameters for 4-fluorophenylacetylene. See Fig 2 for atom numbering.

parameters	r_e	r_s	r_0
r(C1,C2) (Å)	1.404	1.405(35)	1.402(2)
r(C2,C3) (Å)	1.392	1.375(4)	1.393(4)
r(C3,C4) (Å)	1.388	1.386(28)	1.388(1)
r(C1,C7) (Å)	1.431	1.439(2)	1.436(2)
r(C7,C8) (Å)	1.218	1.208(1)	1.209(1)
r(C4,F) (Å)	1.352		1.348(1)
∠(C6,C1,C2) (°)	119.3	119.0(2)	119.8(2)
∠(C1,C2,C3) (°)	120.5	120.7(9)	120.3(2)
∠(C2,C3,C4) (°)	118.7	118.7(7)	118.5(1)
∠(C3,C4,C5) (°)	122.3	122.4(1)	122.7(1)
∠(C2,C1,C7) (°)	120.4	120.5(26)	120.1(1)
σ(× 10 ³)			4.2

^a *ab initio* structure was optimized at the MP2 level using the basis set of 6-311++G(2d,2p).

^b The *b* coordinates of C1, C4, C7 and C8 were replaced by zero with the Costain errors because of their uncertain values.

^c This fit depends on only P_{aa} and P_{bb} including those parameters: : r(C1,C2), r(C2,C3), r(C1,C4), r(C1,C7), r(C7,C8), r(C4,F), ∠(C1,C2,C3), ∠(C6,C1,C2).

Figure 2. Comparison of (a) *ab initio* (MP2/6-311++G(2d,2p)), (b) microwave r_s structure, and (c) microwave r_0 structure for 4-fluorophenylacetylene.

Table 6. Stark effect transition frequencies (in MHz) for the 4-fluorophenylacetylene taken from the last iteration of QSTARK.

J'	K_{-l}'	K_{+l}'	J''	K_{-l}''	K_{+l}''	$ M $	E^2	Obs. freq.	Obs.-calc.
3	0	3	2	0	2	0	0	5365.2433	-0.0005 ^a
3	0	3	2	0	2	0	27181.95	5365.1673	0.0013
3	0	3	2	0	2	0	39092.76	5365.1329	0.0010
3	0	3	2	0	2	0	52991.63	5365.0906	-0.0015
3	0	3	2	0	2	0	69212.82	5365.0416	-0.0040
3	0	3	2	0	2	0	0	5365.2433	-0.0005 ^a
3	0	3	2	0	2	1	52991.63	5365.2011	-0.0001
3	0	3	2	0	2	1	69212.82	5365.1880	-0.0002
3	0	3	2	0	2	1	87228.55	5365.1728	-0.0009
3	0	3	2	0	2	1	107988.87	5365.1564	-0.0007
3	0	3	2	0	2	2	0	5365.2433	-0.0005 ^a
3	0	3	2	0	2	2	17523.11	5365.3379	0.0000
3	0	3	2	0	2	2	27181.95	5365.3916	0.0018
3	0	3	2	0	2	2	39092.76	5365.4536	-0.0001
3	0	3	2	0	2	2	52991.63	5365.5242	-0.0041
3	0	3	2	0	2	2	69212.82	5365.6103	-0.0051
3	1	2	2	1	1	0	0	5587.7041	0.0029 ^a
3	1	2	2	1	1	0	69212.82	5587.6493	0.0016
3	1	2	2	1	1	0	87228.55	5587.6357	0.0019
3	1	2	2	1	1	0	107988.87	5587.6197	0.0019
3	1	2	2	1	1	0	0	5587.7041	0.0029 ^a
3	1	2	2	1	1	1	10274.6	5587.5951	0.0077
3	1	2	2	1	1	1	17523.11	5587.5100	0.0030
3	1	2	2	1	1	1	27181.95	5587.4020	0.0019
3	1	2	2	1	1	1	39092.76	5587.2651	-0.0032
3	1	3	2	1	2	0	0	5163.9922	0.0032 ^a
3	1	3	2	1	2	0	69212.82	5163.9327	0.0016
3	1	3	2	1	2	0	87228.55	5163.9168	0.0008
3	1	3	2	1	2	0	107988.87	5163.9008	0.0021
3	1	3	2	1	2	0	0	5163.9922	0.0032 ^a
3	1	3	2	1	2	1	10274.6	5164.1111	-0.0025
3	1	3	2	1	2	1	17523.11	5164.2039	0.0024
3	1	3	2	1	2	1	27181.95	5164.3225	0.0039
3	1	3	2	1	2	1	39092.76	5164.4668	0.0039
$\sigma(\times 10^3)$							2.8		
$\mu_a = \mu_{\text{total}}$ (Debye)							0.8930(11)		

^a The zero-field transitions were not included in the fitting.

Figure 3. Observed Stark shifts for the 3_{03} - 2_{02} transitions of the normal isotopic species of 4FPA. The slopes of linear regression give the average Stark coefficient ($\Delta\nu/E^2$) for each M value.

Table 7. Observed and calculated Stark coefficients^a and derived dipole moment components for the 4-fluorophenylacetylene compared to *ab initio* results.

	$ M $	$10^5 \times (\Delta\nu/E^2)$ obs.	$10^5 \times (\Delta\nu/E^2)$ calc.
$3_{03} \leftarrow 2_{02}$	0	-0.2882	-0.2867
$3_{03} \leftarrow 2_{02}$	1	-0.0804	-0.0806
$3_{03} \leftarrow 2_{02}$	2	0.5328	0.5375
$3_{12} \leftarrow 2_{11}$	0	-0.0784	-0.0775
$3_{12} \leftarrow 2_{11}$	1	-1.1156	-1.1100
$3_{13} \leftarrow 2_{12}$	0	-0.0855	-0.0839
$3_{13} \leftarrow 2_{12}$	1	1.2114	1.2150
$\mu_a = \mu_{\text{total}}$ (Debye)		0.8935(9)	0.9533 ^b

^a Stark coefficients are in units of $\text{MHz V}^{-2} \text{cm}^2$.

^b Calculated using Gaussian03 at MP2/6-311++G (2d,2p) level.

Table 8. Comparison of structural parameters^a for gas phase mono- and para-substituted benzene.

molecules	methods	$r(C1,C2)$	$r(C2,C3)$	$r(C3,C4)$	$\angle(C6C1,C2)$ $-C\equiv CH/-CH_3$	$\angle(C1,C2,C3)$	$\angle(C2,C3,C4)$	$\angle(C3,C4,C5)-F$	Ref.
fluorobenzene ^b	MW	1.397(1)	1.395(1)	1.383(3)	119.8	120.5	117.9	123.4 ^e	[2]
	ED	1.401(3)	1.399(3)	1.387(3)	120.2(4)	120.2(3)	118.0(2)	123.4(2) ^e	[3]
phenylacetylene	MW ^c	1.388(4)	1.396(5)	1.398(1)	120.8(4) ^e	119.8(4)	119.9(2)	119.9(2)	[5]
(ethynylbenzene)	MW ^d	1.3928(8)	1.3953(6)	1.3956(4)	120.70(8) ^e	119.53(5)	120.22(2)	119.81(2)	[6]
	ED	1.407(3)	1.397(3)	1.400(3)	119.8(4) ^e	120.0(4)	120.1(5)	120.1(7)	[7]
	ED	1.4072(2)	1.3932(2)	1.3972(2)	119.23(17) ^e	120.20(13)	120.24(4)		[8]
toluene	MW	1.395(3)	1.396(3)	1.395(1)	119.26(40) ^e	120.49(29)	120.19(55)	119.38(12)	[27]
	ED	1.408(5)	1.396(4)		118.7 ^e	120.4(4)	120.6(3)	119.4(6)	[28]
1,4-difluorobenzene ^b	ED	1.3867(7)	1.3987(7)		123.53(3)			123.53(3) ^e	[29]
1,4-diethynylbenzene	ED	1.4061(4)	1.3901(4)		119.4(2) ^e			119.4(2)	[30]
1,4-xylene	ED	1.405(3)	1.392(3)		117.1(3) ^e			117.1(3)	[31]
4-fluorophenylacetylene	MW	1.405(35)	1.375(4)	1.386(28)	119.0(2) ^e	120.7(9)	118.7(7)	122.4(1) ^e	This work
4-fluorotoluene ^b	MW	1.398(1)	1.389(1)	1.384(1)	118.3(1) ^e	121.3(1)	118.4(1)	122.2(1) ^e	[32]

^a The unit of bond length is angstrom (Å) and that of bond angle is degrees (°).^b The carbon atom numbering is re-assigned in order to locate C4 adjacent to fluorine like that of 4FPA.^c This is a partial substitution structure, because the coordinates of atoms C1, C2, H2, H3, and H4 are not substitution coordinates.^d The bond parameters are listed as $r_m^{(2)}$ mod(IRLS) in Table 12, ref. [6] : IRLS iteratively reweighted least-squares fit with biweight weighting function.^e The bold characters represent parameters related to carbons attached to substituents.

Figure 4. Summary of the natural bond orbital (NBO) analysis for (a) 4-fluorophenylacetylene, (b) fluorobenzene, and (c) phenylacetylene (ethynylbenzene) optimized at the MP2 level using the basis set 6-311++G(2d,2p) in Gaussian03. Note that the keyword POP=NBO was used for the analysis.

Figure 5. Possible resonance structures for 4FPA with fluorine donating its lone pair towards the π orbitals of the aromatic ring. One additional resonance contributor with the negative charge located on C5 instead of C3 is also possible.

Table 9. Comparison of dipole moment components for gaseous mono- and para-substituted benzene.

molecules	dipole moment	Ref.
fluorobenzene	1.66(3)	[4]
phenylacetylene	0.656(5)	[5]
toluene	0.375(10)	[35]
4-fluorophenylacetylene	0.8935(9)	This work
4-fluorotoluene	2.00(10)	[35]
	1.96(2)	[36]