Microwave spectra and structure of Ar-1,3-difluorobenzene

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ABSTRACT: The microwave spectrum of the dimer Ar-1,3-difluorobenzene from 2-18 GHz is reported. The spectrum has been observed using a chirped pulse Fourier transform microwave (CP-FTMW) spectrometer that has recently been expanded to include the 2-6 GHz region of the electromagnetic spectrum. Details of this upgraded spectrometer are reported. 87 transitions were observed for the parent dimer spectrum, which was adequately fit to a semirigid rotational Hamiltonian consisting of *A*, *B*, and *C,* as well as four quartic centrifugal distortion constants. Observations of ^{13}C species in natural abundance were aided by utilizing smaller chirp ranges of 7-9 GHz and 9-11 GHz regions for 1.9 million and 3.73 million averages, respectively. Assignment of ^{13}C isotopologues allowed for determination of Kraitchman coordinates of the carbon atoms as well as inertial fits of the complex. The quantum chemical structure predicts an Ar to monomer center of mass distance of 3.48 Å compared to 3.564(1) Å determined from experimental structural analysis. This new study indicates that in fluorinated benzene-Ar dimers, when the fluorines are separated by more carbon atoms, the Ar-ring center distance is decreased.

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1. INTRODUCTION

The position of the rare gas atom in complexes of argon with substituted aromatic rings provides an experimental route to probing the electron distribution in the aromatic molecule. Previous studies combined theoretical and spectroscopic approaches to exhaustively analyze the balance of forces in halobenzene-rare gas dimers.[1-7] It was found that for argon complexes with fluorobenzenes, there is a ~0.01 – 0.03 Å decrease in the perpendicular distance from argon to the ring plane for each fluorine substituent added.[1-7] There are small (0.005 – 0.010 Å) differences between 1,4- and 1,2-difluorobenzene,[1,4,5] and 1,2,3- and 1,2,4-trifluorobenzene-Ar distances,[1,6,7] and the position of halogen substituents in di- and trifluorobenzenes clearly plays a role in determining the Ar atom position within the dimer. The observed distance is longer in the 1,4-difluorobenzene complex than the 1,2-difluorobenzene complex, but in the trifluorobenzene species, the longer distance is observed for 1,2,3-trifluorobenzene, indicating the direction of the effect may differ depending on the total number of substituents. Furthermore, the 1,4-difluorobenzene-Ar study utilized fluorescence spectroscopy,[5] while all other studies have used microwave spectroscopy, making it difficult to know to what extent the structural details can be reliably compared. In order to fully analyze the trends in intermolecular structural parameters, we now present a structural analysis of 1,3-difluorobenzene-Ar using chirped-pulse Fourier-transform microwave (CP-FTMW) spectroscopy, which will complete the series of difluorobenzene-Ar complexes. This will provide direct insight into variation of electron distribution within the difluorobenzenes as the fluorine atom positions are varied. Comparison of 1,2-and 1,3-difluorobenzene complexes with 1,2,3- and 1,2,4-trifluorobenzene-Ar will also be interesting, as it should provide some insight on the influence of the third fluorine atom on the interaction strength and electron distributions within the aromatic species.

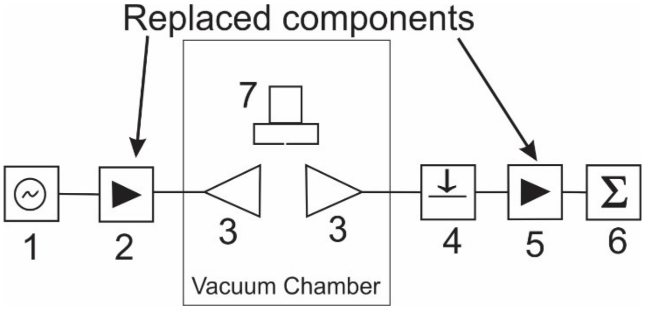

Figure 1. Diagram of the major components involved in the 2-6 GHz CP-FTMW experiment at Missouri S&T. Components 2 and 5 have been replaced from reference 7 to achieve the 2-6 GHz bandwidth. The components are: 1. Tektronix® AWG70001A 20 GHz/50 GS/s Arbitrary Waveform Generator; 2. Fairview Microwave® 50 W, TTL Controlled Power Amplifier, Model SPA-060-50-SMA, 2-6 GHz; 3. Q-par® QWH-SL-2-18-S-HG-R 2-18 GHz High Gain, Broadband Horn Antennae; 4. Advanced Technical Materials® S1517D 0.5-18 GHz, 75 W Pin Diode SPST Switch; 5. Miteq® AFS44-00101000-20-10P-44 Low Noise Amplifier, 1-10 GHz; 6. Tektronix® DPO72304DX 23 GHz/100 GS/s Digital Phosphor Oscilloscope; 7. Parker® Series 9 Solenoid Valve.

2. EXPERIMENTAL METHODS

2.1. Spectrometer Details. Experiments were carried out using a chirped pulse Fourier transform microwave (CP-FTMW) spectrometer located at Missouri S&T. Currently the spectrometer is functional from 2-18 GHz. While the 6-18 GHz CP-FTMW design has been previously detailed in the literature,[8] recent upgrades have been made which enable the CP-FTMW to collect spectra in 2-6 GHz region of the electromagnetic spectrum. These upgrades will be detailed here and are illustrated in Figure 1.

As configured, the CP-FTMW instrument at Missouri S&T contains six components to generate and receive the microwave signal. A 20 GHz, 50 GS/s arbitrary waveform generator, a TTL controlled power amplifier, a set of broadcast and receiving horn antennae, a high-power survival TTL controlled switch, a low noise amplifier, and a 100 GS/s, 23 GHz oscilloscope. All components within this setup except for the power amplifier and low noise amplifier are operable in the 2-18 GHz region. Therefore, a 50 W, TTL controlled power amplifier, model SPA-060-50-SMA was purchased from Fairview Microwave® and a low noise amplifier, model AFS44-00101000-20-10P-44, was purchased from L3 Narda Miteq®. Both of these extend the range to 2-6 GHz, but involve a stoppage of the CP-FTMW experiment to manually remove and replace the low noise and power amplifiers. Therefore, experiments can only be performed (at maximum) in separate 2-6 GHz and 6-18 GHz runs. However, experiments for 6-18 GHz are usually performed in smaller ranges. The 2-6 GHz experiment has sufficient power and range to typically be covered in the single experiment. Multiple 20 μs free induction decays (FIDs) per gas pulse are collected as mentioned in previous literature, allowing for up to 100 million FIDs to be averaged in one single experiment.[8,9] FIDs from multiple experiments are coadded on a separate computer and are Fourier transformed using Kisiel's FFTS program available on the PROSPE website.[10] Due to signal intensity and linewidth considerations, the Bartlett and Hanning Fourier transform windows have been used for these experiments. Both of these windowing types produce full width, half maximum (FWHM) linewidths of 80 kHz and have an attributed uncertainty of 10 kHz in the line centers. In some transitions, FWHM was approximately double the 80 kHz so, in those cases, 30 kHz uncertainty was attributed.

2.2. Sampling and Dimer Creation. ≥99% samples of 1,3-difluorobenzene were purchased from Sigma Aldrich® and used without further purification. Ar-1,3-difluorobenzene dimer was generated by bubbling 10 psig of Ar through 5 mL samples of 1,3-difluorobenzene in a glass, U-shaped tube. This tube is located approximately 30 cm upstream from a Parker-Hannifin®, Series 9 pulsed supersonic nozzle with a 0.8 mm orifice. When pulsed, the samples are rotationally cooled, creating some dimers. Using Ar only as the carrier provided adequate signal-to-noise (S:N) on transitions so further study with other carrier gases was not pursued.

2.3. Spectra Collection Details. For the Ar-1,3-difluorobenzene parent species, experiments were first separated into 2-6, 6-12, and 12-18 GHz runs. For these experiments 5 Hz gas pulses were utilized with 5 FIDs being collected per gas pulse. Sample spectra for the 2-6 GHz range are given in Figure 2. As the S:N ratio for the 6-18 GHz experiment tends to be a little better than the 2-6 GHz experiment, 1 million FIDs were averaged for each the 6-12 and 12-18 GHz experiments while 1.38 million were averaged for the 2-6 GHz region. After assignment of the parent species (detailed in the *Results and Discussion* section) it was noticed that, although some ^{13}C isotopologues may be observable, there were simply not enough of these transitions for any confident assignment. Given this, the chirp range was narrowed for 2 experiments in the 7-9 and 9-11 GHz range. The 9-11 GHz range was performed first and 3.73 million FIDs were collected to ensure that ^{13}C transitions would be observed with sufficient intensity for assignment. After it was certain that reducing the chirp width to 2 GHz produced a significant number of ^{13}C transitions with adequate S:N for assignment, the 7-9 GHz range was reduced to 1.9 million averages. Example spectra showing ^{13}C species in the 9-11 GHz range are presented in Figure 3.

3. COMPUTATIONAL METHODS

Ab initio calculations for the dimer were performed using Gaussian 09 Revision C.01.[11] Geometry optimizations were performed using a MP2/6-311++G(2d,2p) level of theory and basis set which we have found to provide reasonable predictions of structure and dipole moment components for weakly bound complexes in which dispersion interactions are significant. The resulting structure is shown in Figure 4 and presented in Table 1. The complexation of Ar to 1,3-difluorobenzene switches the inertial axis frame significantly from the monomer where the dipole moment has shifted from the *b*-axis to predominantly the *c*-axis.

Multiple configurations in which the argon atom started at different positions above the difluorobenzene plane were used as initial structures for optimizations; however, all calculations converged to the structure presented in this paper. This structure has the argon atom almost directly over the center of the 1,3-difluorobenzene ring, which means it is between the center of mass of 1,3-difluorobenzene-which lies in the triangle constructed from atoms C_1, C_2, and C_3-and the C_5 atom. Measuring this distance within the structure gives an Ar-C_2 distance of 3.69 Å compared to 3.78 Å for Ar-C_5. The predicted distance from Ar to the center of mass of difluorobenzene is 3.47 Å. In the present study, optimizations were intended purely as a tool to facilitate spectroscopic assignment, so no effort was made to more thoroughly investigate the potential energy surface of the Ar-1,3-difluorobenzene complex.

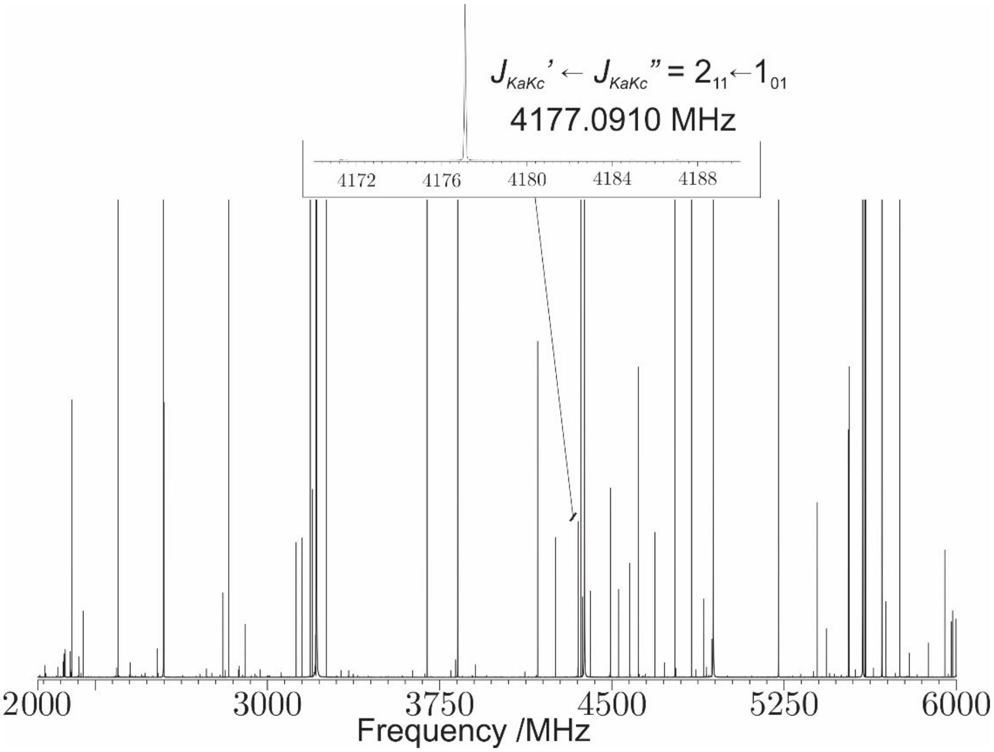

Figure 2. Sample spectra for the 2-6 GHz CP-FTMW experiment highlighting a selected Ar-1,3-difluorobenzene parent transition.

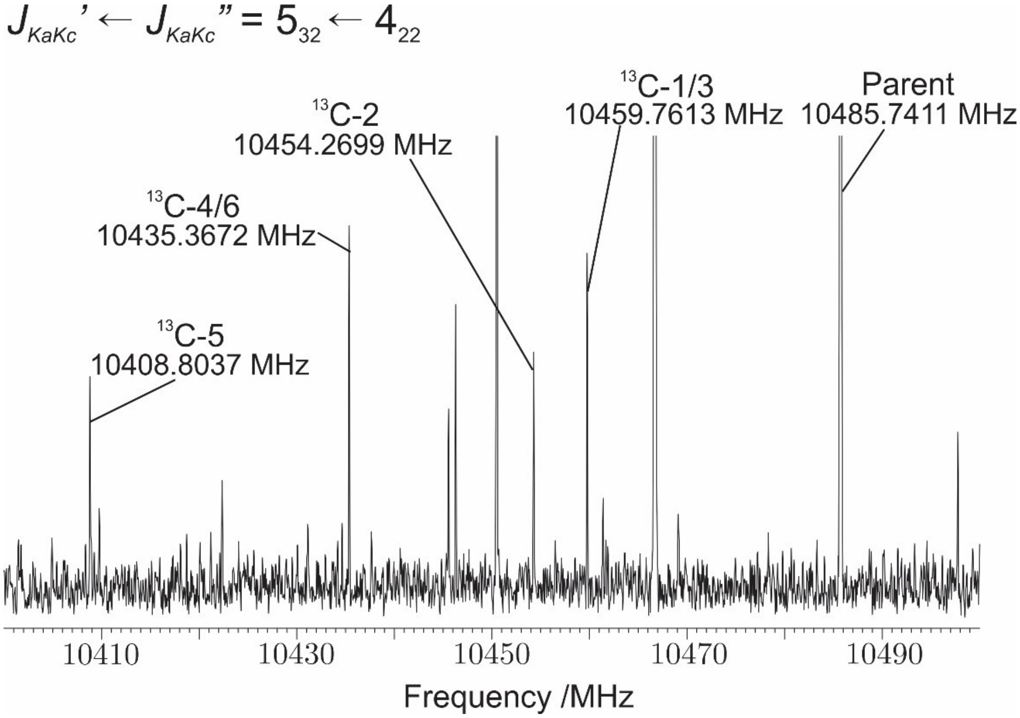

Figure 3. Selected ^{13}C transitions from experiments performed in the 9-11 GHz region of the electromagnetic spectrum. The decreased bandwidth increased S:N enough for confident transition assignments in natural abundance.

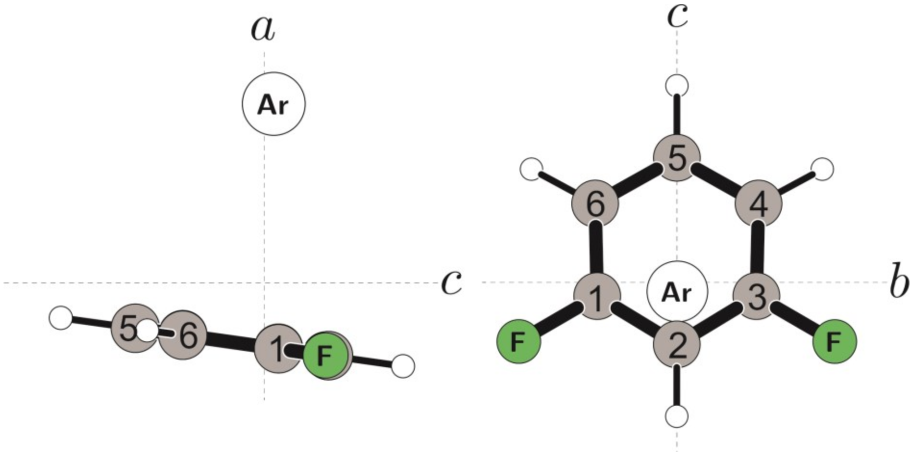

Figure 4. ***Ab initio*** **structure of the Ar-1,3-difluorobenzene complex in the** ***ac*** **and** ***bc*** **planes. The complex was calculated at the MP2/6-311++G(2d,2p) level of theory. The grey atoms are the carbon atoms of the complex. The Ar atom sits almost directly above the center of the benzene ring. The carbons have been labelled to distinguish between isotopologue references in the text.**

4. RESULTS AND DISCUSSION

4.1. Rotational Spectra Assignment. In accordance with the calculated dipole moments, the observed spectrum was predominantly *c*-type, with weaker *a*-type transitions also being observed for the parent. All transitions assigned were *R*-branch. In total, 169 transitions were measured for the dimer with 84 belonging to the parent and the remaining belonging to the various singly substituted ^{13}C isotopologues.

TABLE 1. Ar-1,3-Difluorobenzene Calculated Spectroscopic and Structural Parameters[a]

Parameter	Value
A / MHz	1198.8
B / MHz	1027.1
C / MHz	781.4
μ_a / D	0.20
μ_b / D	0.00
μ_c / D	1.55
$R_{\mathrm{cm}}{}^{b}$ / Å	3.474
$\theta_{\mathrm{Ar\text{-}com\text{-}C}}{}^{b}$ / °	95.1

[a] See text for calculation details.

[b] R_{cm} and $\theta_{\mathrm{Ar\text{-}com\text{-}C}}$ refer to the distance from Ar to the center of mass of 1,3-difluorobenzene and the angle between Ar, the center of mass of 1,3-difluorobenzene, and C_2, respectively.

Transition assignments were made using Pickett's SPFIT/SPCAT program suite[12] with Kisiel's AABS package used as a front end.[13] The resulting fits of these assignments can be found in Table 2 along with each isotopologue's second moment analysis. Quantum number assignments and input files for the fits can be found in the Supporting Information. The spectra were fit utilizing a Watson A-reduced Hamiltonian in the I^r representation.[14] The relatively small centrifugal distortion constants are an indication that the complex is not too floppy, and there were no indications of doubling or other signs of large amplitude motion within the spectrum.

As shown in Figure 2, the dimer parent transitions were strong, with some transitions being greater than 1000:1 S:N. This provided confidence that the ^{13}C species could be observed in natural abundance. However, initial fits of these species were not very fruitful as there were simply not enough transitions to produce confident fits. As mentioned earlier, this led to a second experiment utilizing high numbers of averages on narrower chirp ranges to enhance the ^{13}C isotopologue S:N values. This was very successful. Signals on the parent dimer in these species were greater than 5000:1 with multiple transitions of the isotopologue species being greater than 50:1. This is shown in Figure 3.

The process of finding and correctly assigning ^{13}C isotopologues utilized isotopic substitution of the calculated structure and scaling the rotational constants generated by the ratio of the parent experimental rotational constants to the calculated rotational constants. This worked very well as most of the ^{13}C transitions assigned were within 10 MHz of the prediction.

Assignments of ^{13}C isotopologues were aided in some instances by a plane of symmetry for the molecule, producing equivalent carbons, as shown in Figure 3, where carbons labelled 4 and 6 as well as the carbons labelled 1

Table 2. Spectroscopic Parameters and Second Moments of all Ar-1,3-Difluorobenzene Species Observed

Parameter	Parent	^{13}C(1,3)	^{13}C(2)	^{13}C(4,6)	^{13}C(5)
A / MHz	1208.3653(5)[a]	1204.330(1)	1205.950(7)	1200.317(1)	1198.697(2)
B / MHz	989.6193(3)	987.805(1)	985.927(6)	985.962(1)	982.338(2)
C / MHz	759.3074(4)	756.709(6)	758.06(2)	756.995(7)	758.83(1)
Δ_J / kHz	1.909(4)	1.95(1)	2.9(1)	1.96(1)	2.40(3)
Δ_{JK} / kHz	7.37(1)	6.98(7)	6.4(4)	7.24(8)	8.2(1)
Δ_K / kHz	-9.14(1)	-8.73(7)	-9.2(3)	-9.10(8)	-10.1(1)
δ_K / kHz	5.22(1)	5.17(6)	4.5(3)	5.11(6)	5.2(1)
N[b]	84	31	11	29	14
σ[c] / kHz	13.0	9.4	12.4	10.4	8.9
P_{aa}[d] / uÅ^2	379.0128(2)	379.924(3)	380.098(9)	379.574(3)	379.428(4)
P_{bb}[d] / uÅ^2	286.5662(2)	287.941(3)	286.576(9)	288.038(3)	286.570(4)
P_{cc}[d] / uÅ^2	131.6675(2)	131.694(3)	132.495(9)	133.000(3)	135.037(4)

[a] Numbers in parentheses represent 1σ uncertainty (67% confidence level) in the last significant digit. [b] Number of transitions in fit. [c] Microwave RMS defined as $\sqrt{\sum(obs-calc)^2/N}$. [d] Second planar moment values give the mass distribution along each principal axis; they are defined as $P_{ii} = 0.5(I_j + I_k - I_i)$ where I_j, I_k, and I_i are the moments of inertia about each molecular axis in question.

and 3 are equivalent by symmetry. Due to this symmetry, the S:N on these transitions were enhanced by about a factor of 2. This is shown in Figure 3 and reinforced by the number of transitions assigned in Table 2 where approximately double the number of transitions could be assigned for these isotopologues compared to the isotopologues not being symmetrically equivalent.

4.2. Structure Determination. Three approaches were taken to determining the structure of the complex. The first was determination of an r_0 average structure of the dimer by performing a least-squares fit of observed moments of inertia to the intermolecular structural parameters. In addition, two forms of substitution structure were determined. Since single isotopic substitution data was obtained for all of the carbon atoms of the aromatic ring, principal axis coordinates of these atoms could be determined by using Kraitchman's equations.[15,16] The final structural calculation also utilized a Kraitchman-type analysis, but determined an "extreme" Kraitchman structure by treating the Ar atom as a substitution of an atom (with original mass of zero) within the difluorobenzene monomer structure. This provides a direct determination of the principal axis coordinates of the rare gas atom within the dimer.

The least-squares fit was performed using Kisiel's STRFIT code,[17] and assuming the structure of 1,3-difluorobenzene monomer is unchanged upon complexation.[18] During the fitting process, the distance from the center of the aromatic ring to the Ar atom and the C2-ring center-Ar angle (Figure 4) were allowed to vary. From these fitted values, the Ar-difluorobenzene center of mass (com) distance and C2-com-Ar angle were calculated for ease of comparison with other species. The dihedral angle allowing Ar to move out of the dimer symmetry plane was also allowed to relax, but this still resulted in a C_s symmetry structure, to well within the experimental uncertainty, so C_s symmetry was enforced for all other structure fits. Since only parameters lying within the plane of symmetry were varied, only two moments of inertia were truly independent (similar to a planar species), and pairs of moments of inertia from all the isotopologues were fitted. These results are given in Table 3, where the fit of I_a and I_b for all isotopologues results in the lowest root-mean-square $I_{\text{obs}} - I_{\text{calc}}$ value; thus, the "best" inertial fit structure has $R_{\text{Ar-ring center}}$ = 3.537(1) Å, $R_{\text{Ar-com}}$ = 3.564(1) Å, and angle θ(Ar-ring center-C$_2$) = 90.3(1)° and angle θ(Ar-com-C$_2$) = 97.1(1)° (with uncertainties increased from propagated values based on observed variation between fits of different moments of inertia). For comparison with other Ar complexes, it is also convenient to calculate $R_\perp$, the perpendicular distance from the Ar atom to the ring plane. The inertial fit gives $R_\perp$ = 3.537(1) Å. Principal axis coordinates for this structure are given in the *Supporting Information*.

Kisiel's KRA program was used to implement Kraitchman's equations,[15,16] and this gave carbon atom principal axis coordinates as shown in Table 4. Comparison with coordinates from the inertial fit shows good agreement between the two methods.

Finally, an extreme Kraitchman approach was taken, in which the parent species was 1,3-difluorobenzene monomer (ref. 19: A = 3744.268(2) MHz, B = 1760.551(2) MHz, and C = 1197.359(2) MHz), and the isotopic substitution was taken as having a mass change equivalent to the mass of an ^{40}Ar atom. This gives Ar atom coordinates (in the inertial frame of 1,3-difluorobenzene) of a = ±0.075(20) Å, b = +0.450(3) Å, and c = +3.5314(4) Å. An equivalent calculation, with the dimer taken as the parent species, provides argon atom coordinates in the principal axis system of the dimer: a = 2.6249(6) Å, b = ±0.170(9) Å and c = –0.182(8) Å, with signs determined by comparison with inertial fit coordinates. Intermolecular parameters from this simple approach to structure determination are in excellent agreement with the inertial fit of isotopic data, giving $R_{\text{Ar-ring center}}$ = 3.5315(4) Å $R_{\text{Ar-com}}$ = 3.5600(6) Å, angle θ(Ar-ring center-C2) = 90.51(5)°, angle θ(Ar-com-C2) = 97.26(5)°, and $R_\perp$ = 3.5314(4) Å.

TABLE 3. Results of inertial fits of pairs of moments of inertia for all isotopologues to two structural parameters

	$R_{\text{Ar-ring center}}$ / Å	θ(Ar-ring center-C_2) / °	RMS ($I_{\text{obs}} - I_{\text{calc}}$) / u Å^2
I_a, I_b, I_c	3.5372(3)	90.29(3)	0.071
I_a, I_b [a]	3.5370(2)	90.34(3)	0.046
I_a, I_c	3.5364(4)	90.34(3)	0.052
I_b, I_c	3.5383(5)	90.17(5)	0.061

[a] The fit of I_a and I_b has the lowest deviation and is thus considered the preferred structure. Based on observed variation in structural parameters between different intertial fits, more realistic estimated uncertainties are ±0.001 Å in distances and ±0.1° in angles.

TABLE 4. Kraitchman Coordinates[a] for Carbon Atoms in Ar-1,3-Difluorobenzene

	a / Å	*b* / Å	*c* / Å
C(3,1)[b]	-0.9488(21)[c]	±1.1799(17)	-0.165(12)
C(2)	-1.0415(46)	-0.101(47)	-0.9131(52)
C(4,6)[b]	-0.7425(29)	±1.2134(18)	1.1631(19)
C(5)	-0.6410(42)	-0.058(46)	1.8402(15)

[a]Kraitchman coordinates are absolute values and possess no negative values; where negatives are shown the value has been given a sign in accordance with the calculated equilibrium structure sign. [b]Carbons equivalent due to symmetry; sign changes are listed respectively where appropriate. [c]Numbers in parentheses represent the Costain errors[20] starting with the last significant digit.

4.3. Discussion. The rare gas atom in weakly bound complexes with aromatic species acts as a sensitive probe of the electron density in these species. Typically, the rare gas atom sits in a "pocket" of low electron density above the aromatic ring. The distance of the rare gas above the ring, $R_\perp$, and the shift of the rare gas away from the ring center and parallel to the ring plane, $R_\parallel$, are convenient measures of the changes in interaction strength and shifting electron density of the aromatic molecule. While extensive comparison of halobenzene-Ar complexes was previously presented in reference 1 (chlorobenzene-Ar), we can now add 1,3-difluorobenzene-Ar to the series of structures for comparison. In the present analysis, we will focus on comparison of $R_\perp$ values; comparisons of $R_\parallel$ are less clear, owing to the fact that the direction of the shift of the rare gas atom (towards or away from the monomer center-of-mass) is often ambiguous.

It is of particular interest to compare di- and trifluorobenzene complexes, where the effects of varying halogen position can be probed. As fluorine atoms are moved from the 1,2- to 1,3- positions, the $R_\perp$ distance decreases from 3.545 Å to 3.537 Å, while in the 1,4-difluorobenzene complex, the distance is slightly longer at 3.550 Å (although this result was determined using fluorescence spectroscopy, so may not be directly comparable).[1,4,5]

When comparing 1,2,3-trifluorobenzene with 1,2,4-trifluorobenzene, the distance is about 0.005 Å less in the latter complex, in which the three fluorine atoms are not all adjacent to each other. It appears that there is a similar trend when comparing 1,2- and 1,3-difluorobenzene: the species that has fluorine atoms on non-adjacent carbon atoms has a slightly shorter $R_\perp$ distance.[4,6,7]

It is also logical to look at the variation in $R_\perp$ as the number of fluorine atoms increases. The distance of Ar above the ring gets shorter with each added fluorine substituent, consistent with electronegative fluorine atoms drawing electron density away from the aromatic ring. There is a decrease of about 0.03 Å in going from fluorobenzene to 1,2-difluorobenzene.[2-4] Addition of a third fluorine atom appears to have a slightly smaller effect, with decreases of about 0.02 Å between 1,2-difluorobenzene and 1,2,3-trifluorobenzene-Ar and between 1,3-difluorobenzene and 1,2,4-trifluorobenzene-Ar.[4,6,7]

It would be interesting to perform a microwave spectroscopic study of 1,4-difluorobenzene-Ar and 1,3,5-trifluorobenzene-Ar to obtain directly comparable structural data for those species and further analyze the trends noted above; however, these studies are likely to be difficult because of the small, purely induced, dipoles for the 1,4-difluorobenzene and 1,3,5-trifluorobenzene complexes. Likewise, comparison with complexes containing other halogens would help elucidate the differences in electron withdrawing ability between different halogens; however, chlorobenzene-Ar is the only other halobenzene-Ar complex available for comparison, and the differences between this and fluorine-containing species are thoroughly analyzed in reference 1, where it is clear that $R_\perp$ is considerably shorter in the chlorine-containing species. This illustrates that in order to thoroughly compare experimental and theoretical expectations for trends in intermolecular interactions of halobenzenes with rare gases, considerably more experimental work is needed. These structurally simple complexes provide an abundance of information on electronic structure, and the present work fills just one of the significant gaps in experimental structural data on halobenzene-rare gas dimers.

5. CONCLUSIONS

The effects of fluorination on electron density in aromatic ring compounds have been probed via a microwave spectroscopic investigation of the 1,3-difluorobenzene-Ar dimer. CP-FTMW spectroscopy reveals that Ar sits almost directly over the center of the aromatic ring, similar to other previously studied rare gas-halobenzene species. It appears that increasing separation of fluorine atoms within the aromatic species leads to slightly shorter perpendicular distances from the argon atom to the ring, and this could be consistent with the electronegative atoms drawing more electron density away from the ring center when they are farther apart. This study was assisted by the facile assignment of the four unique ^{13}C isotopologues in natural abundance, using the CP-FTMW spectrometer at Missouri S&T, which has recently been upgraded to cover the full 2-18 GHz bandwidth.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.
Gaussian 09 output files and SPFIT/SPCAT input and output files with quantum number assignments.

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Notes

The authors declare no competing financial interest.

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