# Measuring rotational constant of a molecule without dipole moment and confirming low frequency vibrations using microwave spectroscopy: $^{13}CC_5H_6$/ $C_6H_5D$•••Ar complex

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## Abstract

This manuscript reports the rotational spectrum of the $^{13}CC_5H_6$•••Ar and $C_6H_5D$•••Ar isotopologues. These two complexes are asymmetric tops and the experimental $A$ rotational constants are a direct measure of the $C$ rotational constant of the $^{13}CC_5H_6$ and $C_6H_5D$, respectively. For $C_6H_5D$, our measurement is in reasonable agreement with the previous direct determination and for $^{13}CC_5H_6$, there has been no prior experimental measurement of the rotational constant to the best of our knowledge. These experiments demonstrate the idea of an electrophore, we proposed earlier. *Ab initio* MP2 and DFT calculations have been carried out to determine the centrifugal distortion constants for the parent $C_6H_6$•••Ar complex and the two isotopologues. We show that comparison of these distortion constants with the experimental values can help in choosing the appropriate theoretical methods for predicting the low frequency vibrations accurately. DFT method is found to give results closer to the experiments compared to MP2 method for the centrifugal distortion constants and low frequency vibrations. Idea of an electrophore can be extended to complexes as well including the parallel-displaced benzene dimer which is of enormous interest but as of now there is no experimental evidence for the same.

## 1. Introduction

Microwave spectroscopy has been valuable in the determination of accurate structures of small molecules with appreciable dipole moments [1,2] .As there were not many of these molecules, interest in microwave spectroscopy was vanishing in the 1970s. Then came the introduction of the pulsed

nozzle Fourier transform microwave (PNFTMW) spectrometer by Balle and Flygare [3]. This technique had high sensitivity and resolution and it opened up several avenues. Several groups built this spectrometer all over the world expanding the horizons of microwave spectroscopy research and in an earlier review we had summarized the advances and applications of the Balle-Flygare spectrometer [4]. While the sensitivity and resolution of this

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technique enabled numerous investigations that would not have been possible earlier, there remained a major disadvantage: narrow bandwidth. Within two years after this review was published Pate has given the next fillip to the field introducing chirped pulse Fourier transform microwave (CPFTMW) spectrometer [5,6]. This enabled the collection of 'microwave spectrum' rather than the observation of one line at a time and searching laboriously for all the lines. One could start seeing a broad band spectrum in papers, rather than many tables listing numerous transition frequencies. There still remains one problem that cannot be solved by microwave spectroscopy: Experimentally measuring the rotational constants of a molecule that has no dipole moment, benzene for example or can it be?

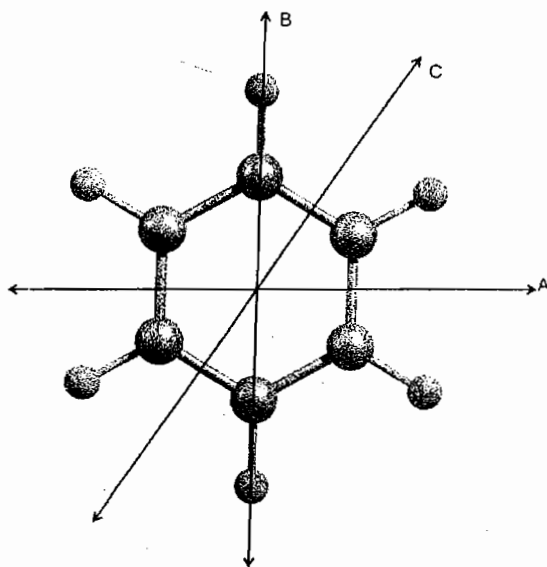We had proposed the concept of an electrophore as an atom or molecule, which could combine with

another molecule having no dipole moment thereby forming a complex with a dipole moment [4]. Let us look at the structure of $C_6H_6$ (see Fig. 1). It is an oblate top with the *A* and *B* axes in the plane and the *C* axis perpendicular to the plane. As it has no dipole moment, these constants can not be determined by microwave spectroscopy. If benzene were to form a complex with an atom which approaches along its *C* axis (Fig. 2), the resulting complex would also be a symmetric top. However, the complex will have a dipole moment due to polarization. The *C* axis of benzene would become the *A* axis for the complex. However, this does not help in measuring the rotational constants of $C_6H_6$ as the experiment can only determine the *B* rotational constant for the complex. It will depend on the intermolecular distance and the masses of $C_6H_6$ and the atom. Moreover, this does not give any structural details about benzene, as one often assumes the monomer structure to be unaffected when interpreting the



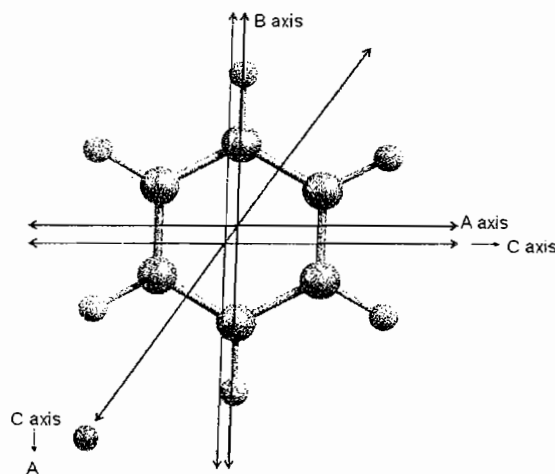Fig. 1. Structure of benzene with the principle inertial axes shown.



Fig. 2. An atom approaching along *C* axis of benzene and forming a complex. Inertial axes change following this as shown in the figure. Darker lines are for the complex.

Table 1

Observed transitions for Ar—$C_6H_5D$ complex

| $J'$ $K_{-1}'$ $K_{+1}'$ | | | $J$ $K_{-1}$ $K_{+1}$ | | | Frequency (MHz) | Residue (KHz) |
|---|---|---|---|---|---|---|---|
| 2 | 0 | 2 | 1 | 0 | 1 | 4676.3410 | -1.3 |
| 3 | 1 | 3 | 2 | 1 | 2 | 6989.3680 | -10.9 |
| 3 | 0 | 3 | 2 | 0 | 2 | 7013.9980 | 0.0 |
| 3 | 1 | 2 | 2 | 1 | 1 | 7039.2970 | 10.4 |
| 4 | 1 | 4 | 3 | 1 | 3 | 9318.6640 | -3.6 |
| 4 | 0 | 4 | 3 | 0 | 3 | 9351.0300 | -5.2 |
| 4 | 2 | 3 | 3 | 2 | 2 | 9351.6800 | 4.8 |
| 4 | 2 | 2 | 3 | 2 | 1 | 9352.9750 | -4.5 |
| 4 | 1 | 3 | 3 | 1 | 2 | 9385.2150 | 6.9 |
| 5 | 0 | 5 | 4 | 0 | 4 | 11687.2550 | 6.3 |
| 5 | 1 | 5 | 4 | 1 | 4 | 11647.5100 | -15.8 |
| 5 | 2 | 3 | 4 | 2 | 2 | 11691.4660 | -4.2 |
| 5 | 3 | 3 | 4 | 3 | 2 | 11688.7210 | 5.9 |
| 5 | 1 | 4 | 4 | 1 | 3 | 11730.6980 | 5.1 |
| 6 | 0 | 6 | 5 | 0 | 5 | 14022.4480 | 13.3 |
| 6 | 1 | 6 | 5 | 1 | 5 | 13975.8460 | -2.4 |
| 6 | 2 | 5 | 5 | 2 | 4 | 14025.5710 | 8.5 |
| 6 | 2 | 4 | 5 | 2 | 3 | 14030.1070 | -14.8 |
| 6 | 1 | 5 | 5 | 1 | 4 | 14075.6250 | -4.2 |
| 7 | 1 | 7 | 6 | 1 | 6 | 16303.5500 | 18.6 |
| 7 | 0 | 7 | 6 | 0 | 6 | 16356.3740 | -19 |
| 7 | 2 | 6 | 6 | 2 | 5 | 16361.6900 | 12.8 |
| 7 | 3 | 4 | 6 | 3 | 3 | 16362.5783 | -8.7 |
| 7 | 2 | 5 | 6 | 2 | 4 | 16368.9677 | 6.3 |
| 7 | 1 | 6 | 6 | 1 | 5 | 16419.8937 | -9.8 |
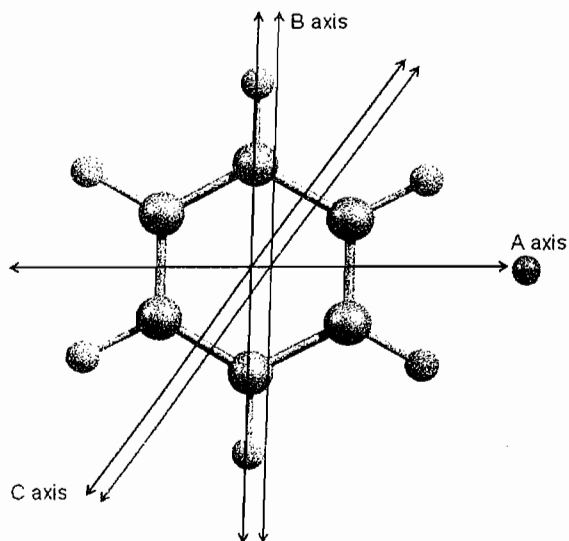


Fig. 3. An atom approaching along the *A* axis of benzene and forming a complex. The inertial axes remain unaffected but the center of mass changes. Darker lines are for the complex.

experiment will give all three rotational constants. More importantly, the *A* axis for the complex is the same as the *A* or *B* axes for $C_6H_6$ and the rotational constants for the complex and $C_6H_6$ along these axes would be the same as the atom approaching in this axis would not contribute to the moments of inertia about this axis (See Fig. 3). This would give a microwave spectrum from which the *A* rotational constant of $C_6H_6$ can be determined.

Is there a way to get the *C* rotational constant of $C_6H_6$ from an experimentally determined microwave spectrum? There appears to be no way. If $C_6H_6$ is made asymmetric, for example, by substituting an isotope, it would be possible. If a complex is formed with $C_6H_5D$ or $^{13}CC_5H_6$ with an atom approaching it along the $C_6$ axis of $C_6H_6$, the complex would be an asymmetric top and the *A* rotational constant for the complex would be the *C* rotational constant

complex rotational constants. If a complex of $C_6H_6$ can be formed with an atom approaching it along the *A* or *B* axis (both being equivalent for $C_6H_6$), the complex would become an asymmetric top and

Table 2

Observed transitions for Ar—$^{13}CC_5H_6$ complex

| $J'$ | $K_{-1}'$ | $K_{+1}'$ | $J$ | $K_{-1}$ | $K_{+1}$ | Frequency (MHz) | Residue (KHz) |
|---|---|---|---|---|---|---|---|
| 3 | 1 | 3 | 2 | 1 | 2 | 7039.9600 | -8.5 |
| 3 | 0 | 3 | 2 | 0 | 2 | 7048.0170 | 1.4 |
| 3 | 1 | 2 | 2 | 1 | 1 | 7055.9620 | 11.4 |
| 4 | 1 | 4 | 3 | 1 | 3 | 9386.2520 | 2.8 |
| 4 | 3 | 2 | 3 | 3 | 1 | 9395.8950 | 9.2 |
| 4 | 0 | 4 | 3 | 0 | 3 | 9396.9410 | 7.4 |
| 4 | 2 | 3 | 3 | 2 | 2 | 9396.5000 | -18.6 |
| 4 | 2 | 2 | 3 | 2 | 1 | 9396.6350 | -13.7 |
| 4 | 1 | 3 | 3 | 1 | 2 | 9407.5520 | -6.7 |
| 5 | 1 | 5 | 4 | 1 | 4 | 11732.2200 | 11.7 |
| 5 | 3 | 3 | 4 | 3 | 2 | 11744.3000 | 15.5 |
| 5 | 2 | 4 | 4 | 2 | 3 | 11745.0400 | -10.8 |
| 5 | 0 | 5 | 4 | 0 | 4 | 11745.4900 | -1.1 |
| 5 | 2 | 3 | 4 | 2 | 2 | 11745.3000 | -11.1 |
| 5 | 1 | 4 | 4 | 1 | 3 | 11758.8500 | 5.2 |
| 6 | 1 | 6 | 5 | 1 | 5 | 14077.7650 | -0.3 |
| 6 | 5 | 2 | 5 | 5 | 1 | 14089.0200 | -1.1 |
| 6 | 2 | 5 | 5 | 2 | 4 | 14093.1750 | -9.7 |
| 6 | 0 | 6 | 5 | 0 | 5 | 14093.6100 | 12 |
| 6 | 2 | 4 | 5 | 2 | 3 | 14093.6500 | 9.7 |
| 6 | 1 | 5 | 5 | 1 | 4 | 14109.7300 | 1.5 |
| 7 | 0 | 7 | 6 | 0 | 6 | 16441.1565 | -7.7 |

for the $C_6H_5D$ or $^{13}CC_5H_6$ isotopologue. This is evident from the work of Gutowsky, Emilsson and Arunan who investigated the microwave spectrum of $C_6H_6\cdots H_2O$ complex. They noted that the

$C_6H_5D\cdots H_2O$ and $C_6H_5D\cdots D_2O$ were asymmetric tops and had identical $A$ rotational constants (2765.5 MHz) within experimental uncertainty [7]. A rigid structure for the complex would have resulted in $A$ rotational constants that differ by 10 MHz between the isotopologues having $H_2O$ and $D_2O$. Free internal rotation in the complex ensured that $H_2O/D_2O$ did not contribute to the moments of inertia along the $A$ principle axis for the complex [2,8]. However, this was different from the experimentally determined $C$ rotational constant of $C_6H_5D$, 2749.676(6) MHz [9]. Bauder could record the rotational spectrum of $C_6H_5D$ as it has a small dipole moment due to the difference in C-H and C-D vibrations. However, pure rotational spectrum of $^{13}CC_5H_6$ has not been recorded yet. A reasonable estimate of $C$ rotational constant for $^{13}CC_5H_6$ was not provided in Ref. [7] due to the assignment problems in the $^{13}CC_5H_6\cdots H_2O$ spectrum. This was corrected by Ram Prasad, Krishnan and Arunan later and they have reported a value of 2832(3) MHz for the same[8]. Moreover, the same authors have reported that the combined fit of $m = 0$ and $1$ ($m$ is the internal rotor angular momentum) lead to an $A$ value of 2787(1) MHz, which is significantly smaller. It was felt that such determinations on $C_6H_6\cdots Ar$ would give a more realistic estimate for the monomer rotational constants. Bauder's group has in fact studied this complex [10]. However, both $^{13}CC_5H_6$ and $C_6H_5D$ isotopologues were not investigated. In this manuscript, the rotational spectrum of these two isotopologues are reported and compared with the parent isotopologue. Results from these complexes are unlikely to give any new information about the complex. However, our main motivation was the direct determination of $C$ rotational constant of asymmetric benzene isotopologues.
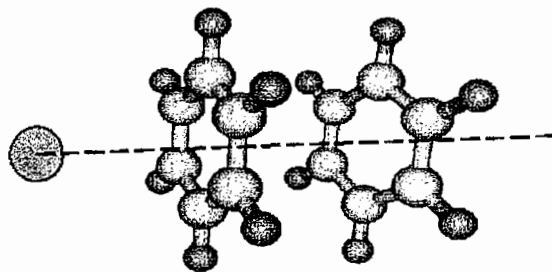
Fig. 4. Structure of $Ar \cdots C_6H_6 \cdots C_6H_6$. Argon atom can induce a dipole moment by forming a complex with parallel displaced benzene dimer. Microwave spectrum can give structural information about the benzene dimer.

The centrifugal distortion constants of $C_6H_6 \cdots Rg$ (Rg = Ar/Kr) have been analyzed in detail to extract the intermolecular potential and also some information about intermolecular vibrations [11]. There have been several such attempts to use the centrifugal distortion constants to extract information about intermolecular potentials and vibrations [11-15]. These depended on models and programmes developed in-house. Recently, such vibrational-rotational calculations have been incorporated in several packages, such as Gaussian 09 [16], which makes it easy for every-one. Such electronic structure theory calculations have become standards for calculating short amplitude high frequency vibrations. Scaling factors are well established for these modes which improve the accuracy of theoretical predictions [17-19]. However, such scaling factors do not work for large amplitude low frequency vibrations. Moreover, experimental data on these modes are scarce. Development of terahertz spectroscopy does offer some hope in this direction [20]. The question we address here is the following: Can we use the centrifugal distortion constants to determine which of the methods and basis sets work better

for predicting the low frequency vibrations? The $C_6H_6 \cdots Ar$ data is used here for this exploratory study as well.

## 2. Experimental and theoretical methods

The pulsed nozzle Fourier transform microwave spectrometer used in this work has been described in detail in earlier publications [4,21]. In this spectrometer, a pulsed nozzle is used to cool down a gaseous mixture diluted in Ar/He by supersonic expansion. This enables the formation of weakly bound complexes that would not be stable at ambient conditions. The microwave spectra of such complexes are recorded using the Fabry-Perot cavity Fourier transform spectrometer. Due to the high Q of cavity, the spectral bandwidth is typically about 1 MHz only. The operational frequency range of the spectrometer is between 3 and 22 GHz. Hence, each of the transitions listed in the Table 1, was recorded separately. Recently, a new microwave signal generator (HP N5183, 100 kHz – 31.8 GHz) has replaced the one that was used earlier (HP 83630L, 10 MHz – 26.5 GHz) [21] Also, the original software based on Labwindows[22] has been developed using Labview interface [23]. This was necessitated following the loss of hardware and software in an unexpected natural calamity. Spectral transitions for $C_6H_5D \cdots Ar$ and $^{13}CC_5H_6 \cdots Ar$ were predicted based on the known structure of $C_6H_6 \cdots Ar$ and readily observed. Benzene and $C_6H_5D$ (99.9 % D) were procured from Aldrich and $^{13}CC_5H_6$ was observed in natural abundance. Argon (99.999%) was obtained from Bhuruka Gases Ltd and it was flown through silica gel and charcoal traps to remove any residual $H_2O$/hydrocarbons. All the theoretical calculations were performed using the commercial Gaussian09 suite of programs.

Table 3

Rotational and Centrifugal Distortion Constants for the Ar•••$C_6H_6$ isotopologues

| Complex/Constant | $Ar—C_6H_5D$ | $Ar—{}^{13}CC_5H_6$ | $Ar—C_6H_6$ | $Ar—C_6D_6$ |
|---|---|---|---|---|
| $A$(MHz) | 2760.3(17) | 2810(22) | —- | |
| $B$(MHz) | 1177.46150(91) | 1177.3994(12) | 1181.25953(14) | 1112.4412(6) |
| $C$(MHz) | 1160.82539(91) | 1172.0720(12) | —- | |
| $D_J$(KHz) | 3.1566(83) | 3.212(14) | 3.2577( 17) | 2.673(6) |
| $D_{JK}$(KHz) | 17.589(93) | ·· 16.59(25) | 17.8011(76) | 14.53(4) |
| $H_{JK}$(KHz) | —- | -0.0040(36) | | |
| $\sigma^a$ (KHz) | 10.72 | 11.08 | 1.84 | 10.4 |
| $N$ | 25 | 22 | | |
| Reference | This work | This work | [10] | [10] |

a- mean residual deviation.

## 3. Results and discussion

### 3.1 Observed transitions and determined rotational constants

The observed transitions for both isotopologues $C_6H_5D$•••Ar and $^{13}CC_5H_6$•••Ar are given in Tables 1 and 2. These transitions could be fitted to a Watson S-reduction Hamiltonian and the rotational and centrifugal distortion constants are given in Table 3. Not surprisingly, the distortion constants are very close to those determined for the parent isotopologue, $C_6H_6$•••Ar. The RMS deviations for both these asymmetric complexes were close to 10 kHz compared to less than 2 kHz for the parent symmetric top. More importantly, the $A$ rotational constants for the $C_6H_5D$•••Ar and $^{13}CC_5H_6$•••Ar complexes were determined to be 2760.3(17) and 2810(22) MHz, respectively. For the $C_6H_5D$•••Ar complex, this value can be compared to the $C$ rotational constant for the $C_6H_5D$. As mentioned earlier, the direct measurement reported by Bauder [9] yields 2749.674(6) MHz, which differs by about 10 MHz.

For the $C_6H_5D$•••$H_2O/D_2O$ complexes, the $A$ rotational constant was determined to be 2765.5(3) MHz [7]. For $^{13}CC_5H_6$, there has been no previous experimental measurement of $A$ rotational constant and based on comparisons with the $C_6H_5D$, our measurement of 2810(22) MHz should be reasonably good. This may be compared with the value of 2832(3) MHz determined from $^{13}CC_5H_6$•••$H_2O$ complex spectrum The uncertainty in $^{13}CC_5H_6$ constant is significantly more than that for the $C_6H_5D$ which is possibly due to the lower signal to noise. These numbers could be improved if more transitions from higher J/K are measured. However, the calculated rotational constant for the $^{13}CC_5H_6$ isotopologue, based on the experimental structure[24] of $C_6H_6$ is 2812.884 MHz, which is very close to the $C$ rotational constant determined for the $^{13}CC_5H_6$•••Ar complex. Clearly Ar as an electrophore has resulted in a more accurate determination of the $C$ rotational constants for $C_6H_5D$ and $^{13}CC_5H_6$. Still, these constants are somewhat different from the respective monomer values and the possible reasons are discussed next.

Table 4

Rotational, centrifugal distortion constants, and low frequency vibrations of $C_6H_6 \cdots Ar$ isotopologues $Ar \cdots C_6H_6$

| Theory /basis set | A(MHz) | B(MHz) | C(MHz) | $D_J$ | $D_{JK}$ | Low frequency modes($cm^{-1}$) |
|---|---|---|---|---|---|---|
| B3LYP/6-311++G(2d,2p) | 2865.55 | 1110.88 | 1110.65 | 2.9 | 16.03 | 31.3, 36.4, 42.4 |
| B3LYP/6-311++(3df,2p) | 2867.28 | 1111 | 1110.77 | 3.34 | 12.38 | 33.5, 38.1, 40.3 |
| MP2/6-311+G(2d,2p) | 2848.24 | 1235.42 | 1235.42 | 2.66 | 13.76 | 39.9, 39.9, 49.7 |
| Experimental[10] | —— | 1181.25953(14) | —— | 3.2577(17) | 17.8011(76) | 33.1, 33.1, 39.6 |
| $Ar \cdots C_6H_5D$ | | | | | | |
| B3LYP/6-311++G(2d,2p) | 2770.48 | 1106.77 | 1092.11 | 2.8 | 15.53 | 31.3, 36.4, 42.4 |
| B3LYP/6-311++(3df,2p) | 2772.08 | 1106.89 | 1110.77 | 3.23 | 12.04 | 33.5, 36.8, 40.3 |
| MP2/6-311+G(2d,2p) | 2753.81 | 1231.12 | 1213.14 | 2.57 | 13.32 | 38.8, 39.9, 49.7 |
| Experimental | 2760(2) | 1177.4615(9) | 1160.8254(9) | 3.157(8) | 17.59(9) | |
| $Ar \cdots 1,3,5-C_6H_3D_3$[11] | | | | | | |
| B3LYP/6-311++G(2d,2p) | 2594.12 | 1077.93 | 1077.68 | 2.64 | 14.84 | 30.0, 34.7, 42.0 |
| B3LYP/6-311++(3df,2p) | 2595.49 | 1078.03 | 1077.8 | 3.03 | 11.59 | 32.1, 36.3, 39.7 |
| MP2/6-311+G(2d,2p) | 2579.02 | 1196.36 | 1136.36 | 2.4 | 12.41 | 38.3, 38.3, 49.4 |
| Experimental | —— | 1145.58441(77) | —— | 2.9384(94) | 16.038(67) | 31.9, 31.9, 39.3 |
| $Ar \cdots C_6D_6$[11] | | | | | | |
| B3LYP/6-311++G(2d,2p) | 2369.67 | 1047.37 | 1047.11 | 2.41 | 13.78 | 28.8, 33.1, 41.7 |
| B3LYP/6-311++(3df,2p) | 2370.77 | 1047.47 | 1047.21 | 2.78 | 10.86 | 30.8, 34.6, 39.2 |
| MP2/6-311+G(2d,2p) | 2356.29 | 1160.22 | 1160.22 | 2.17 | 11.25 | 37.0, 37.0, 49.1 |
| Experimental | —— | 1112.4412(6) | —— | 2.673(6) | 14.53(4) | 30.9, 30.9, 39.1 |
| $Ar \cdots {}^{13}CC_5H_6$ | | | | | | |
| B3LYP/6-311++G(2d,2p) | 2835.28 | 1106.47 | 1102.13 | 2.87 | 15.87 | 31.2, 36.1, 42.4 |
| B3LYP/6-311++ (3df,2p) | 2836.99 | 1106.59 | 1102.25 | 3.3 | 12.19 | 33.2, 38.0, 40.3 |
| MP2/6-311+G (2d,2p) | 2817.65 | 1232.4 | 1226.64 | 2.6 | 13.49 | 39.7, 40.0, 49.9 |
| Experimental | 2822(32) | 1177.400(2) | 1172.073(2) | 3.23(2) | 16.79(5) | |

The principle coordinates for the complex are only slightly different from that of the monomer and hence, this difference can not be attributed to that. The center of mass of $C_6H_6$ gets shifted closer to the D in $C_6H_5D$, but only by 0.003 Å. As the electronic structure of the monomer does not alter much, the location of Ar atom in these two complexes would not change. Though the *A* axis for the $C_6H_5D \cdots Ar$ complex would be slightly tilted from the *C* axis of $C_6H_5D$, this change also can not account for the change of 10 MHz. Assuming these two axes as parallel shifted by 0.003 Å, parallel axis theorem shows that the change in the rotational constant will be of the order 0.1 MHz. Thus, this change must have its origin in the large amplitude vibrations, particularly the degenerate bending modes. For $C_6H_6 \cdots Ar$, there has been an estimate of these vibrational frequencies based on the analysis of centrifugal distortion constants. Here, we use the standard Gaussian 09 software to calculate the vibration-rotational interaction constants and these results are discussed in the next section.

*3.2 Ab initio calculations of distortion constants and large amplitude vibrations*

The $C_6H_6 \cdots Ar$ complex was fully optimized at both MP2 and DFT level calculations with various triple zeta basis sets. At the DFT level calculations, the full optimization resulted in lower symmetry. Normal mode frequency calculations indicated that the optimized structures were true minima. These calculations were extended to determine the anharmonic vibration-rotation coupling via perturbation theory as implemented in Gaussian09. These resulted in zero-point vibrationally averaged rotational constants and centrifugal distortion constants that can be directly compared to the experimental results.

We focus our discussion here on these constants and the frequencies of the three large amplitude vibrations for the complex. Our main emphasis here is to see which levels of calculations do better for the large amplitude vibrations. All these data are presented in Table 4.

The data are presented for $C_6H_6 \cdots Ar$, $C_6H_5D \cdots Ar$, $1,3,5$-$C_6H_3D_3 \cdots Ar$, $C_6D_6 \cdots Ar$ and $^{13}CC_5H_6 \cdots Ar$. These complexes were chosen as experimental results are available for all. As mentioned above, the DFT calculations with B3LYP functional and 6-311++G(2d,2p) and 6-311++G(3df,2p) basis sets resulted in a slightly asymmetric geometry and the rotational constants *B* and *C* differ by 0.2 MHz. This has also led to the removal of the degeneracy in the bending modes and these frequencies differ by a few $cm^{-1}$. MP2/ 6-311+(2d,2p) level calculations led to the experimentally found symmetric structure with a doubly degenerate bending mode. However, both these level of calculations led to rotational constants differing by − 70 MHz for DFT and + 44 MHz for MP2 for $C_6H_6 \cdots Ar$. The three large amplitude vibrational modes were predicted at 33.1 $cm^{-1}$ (doubly degenerate intermolecular bending) and 39.6 $cm^{-1}$ (intermolecular stretching) based on the analysis of centrifugal distortion constants for $C_6H_6 \cdots Ar$ [11] MP2 calculations overestimate these vibrational frequencies by 6 $cm^{-1}$ for the degenerate bending and 10 $cm^{-1}$ for the stretching modes. Not surprisingly, the centrifugal distortion constants calculated at this level are $D_j$ = 2.57 kHz and $D_{jk}$ = 13.76 kHz compared to the experimental values of 3.258(1) kHz and 17.801(8) kHz. The DFT(B3LYP) calculations do a better job here. With 6-311++(3df,2p) basis set, the $D_j$ is calculated to be 3.34 kHz which is very close to the experimental value. Not surprisingly,

the intermolecular stretching mode which contributes significantly to $D_j$ is calculated to be 40.3 cm$^{-1}$ at this level in close agreement with the earlier determination. The B3LYP/6-311++G(2d,2p) level calculations give the best agreement for $D_{JK}$, 16.03 kHz. Hence, the frequency of degenerate bending modes, 33.9 cm$^{-1}$ (averaged), at this level agrees very well with the earlier determination of 33.1 cm$^{-1}$. Our attempt here is not to evaluate these methods rigorously. Rather, in a pragmatic way, it can be seen that the methods that reproduce experimental $D_j$ give an accurate estimate of intermolecular stretching frequency and the methods that reproduce $D_{jk}$ can predict the intermolecular bending modes accurately. As centrifugal distortion constants are available for a larger number of complexes than for which large amplitude vibrational frequencies are known, it is suggested that *ab initio* predictions of these frequencies can be corroborated by comparison of experimental centrifugal distortion constants. It must be mentioned that the description of these modes as stretching and bending are reasonable approximations only.

As evident from all the data presented in Table 3, all levels of calculations can reproduce the effect of isotopic substitution on centrifugal distortion constants of these complexes. For example, the experimental $D_j$ decreases in the order $C_6H_6 > {}^{13}CC_5H_6$ $> C_6H_5D > C_6H_3D_3 > C_6D_6$ and all levels of theory predict the difference nearly quantitatively.

### 3.3 Is the concept of electrophore useful?

One natural question that arises is that why should any one go through the trouble of determining the rotational constants of a molecule that does not have a dipole moment through microwave spectroscopy. Rotationally resolved vibrational [25] and electronic spectroscopy [26] can often help. However, none of the other techniques can match microwave spectroscopy in resolution and the structures determined by microwave spectroscopy are accurate. The determination of Si=C double bond length by microwave spectroscopy resolved a long standing controversy [27]. Preliminary work on $C_6H_6\cdots C_2H_4$ complex indicates that the $A$ rotational constant for the complex is very close to the $A$ rotational constant of $C_6H_6$ [28]. Hence, for benzene both rotational constants can now be determined by microwave spectroscopy. We present one example of a complex, which appears to be of enormous interest with no experimental data available as on date: parallel displaced benzene dimer [29].

The benzene dimer has attracted enormous interest. There have been numerous publications on this dimer. Theoretical calculations have shown that both T-shaped and parallel-displaced structures are possible [29].Obtaining the microwave spectrum of this dimer was a big challenge and in 1993 Arunan and Gutowsky reported some important microwave transitions which provided positive confirmation of the T-shaped geometry [30]. Several more transitions of this important dimer remain unassigned. The spectrum is not yet completely solved and detailed molecular symmetry group analysis was presented recently [31]. For the parallel-displaced structure as of now there is no experimental data though theoretical calculations show it to be a minimum. The interaction in this structure could be characterized as $\pi$-$\pi$ interactions as opposed to the T-shaped structure which has a C-H$\cdots\pi$ interaction. The -$\pi$ interaction is very important in biological chemistry and the structure of DNA is influenced by this

and hydrogen bonding [3]. However, in biological systems, the aromatic rings contain a heteroatom and such interactions have been seen both experimentally [33] and theoretically [34]. Does the π stacked structure exist only for heteroaromatics and not for simple benzene, as there is no experimental evidence? Absence of evidence is not evidence for absence. If parallel-displaced benzene dimer exists, it should be able to form a complex with Argon as shown in Fig. 4. Now this structure will have a dipole moment. While, the complex rotational constants may or may not be related to the benzene dimer rotational constants, the distance between the two benzene planes can be accurately determined. However, the rotational constants for this trimer are predicted to be of the order of 100's of MHz only. The recent technological advances [35,36] indicate that a spectrometer that can work below 1 GHz should become available. If microwave evidence for a parallel-displaced benzene dimer could be obtained, it will be worth all the efforts in building such a spectrometer. The concept of electrophore would have become important. Whether it will become as important as the concept of a chromophore in electronic spectroscopy is not clear now.

## 3. Conclusion

In this manuscript, the rotational spectrum of $C_6H_5D\cdots Ar$ and $^{13}CC_5H_6\cdots Ar$ isotopologues have been presented. It has been shown that the experimental $A$ rotational constants for these complexes are very close to the $C$ rotational constants of the benzene isotopologue and these have been determined using microwave spectroscopy for the molecules without dipole moment. The argon atom assumes the role of an electrophore giving a dipole moment

to benzene. Anharmonic vibration-rotation interaction calculations have been performed on $C_6H_6\cdots Ar$ complex to show that experimental centrifugal distortion constants can be used for validating the predictions of large amplitude/low frequency vibrational modes. Scaling factors do not work for these modes and this approach could be used to test various models. Finally, the concept of electrophore could become impoitant if it can lead to structural information of important complexes, for example parallel-displaced benzene dimer.

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