Consistent assignment of the vibrations of symmetric and asymmetric *ortho*-disubstituted benzenes

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Abstract

The form of molecular vibrations, and changes in these, give valuable insights into geometric and electronic structure upon electronic excitation or ionization, and within families of molecules. Here, we give a description of the phenyl-ring-localized vibrational modes of the ground (S_0) electronic states of a wide range of *ortho*-disubstituted benzene molecules including both symmetrically- and asymmetrically-substituted cases. We conclude that the use of the commonly-used Wilson or Varsányi mode labels, which are based on the vibrational motions of benzene itself, is misleading and ambiguous. In addition, we also find the use of the M_i labels for monosubstituted benzenes [A. M. Gardner and T. G. Wright. J. Chem. Phys. 135 (2011) 114305], or the recently-suggested labels for *para*-disubstituted benzenes [A. Andrejeva, A. M. Gardner, W. D. Tuttle, and T. G. Wright, J. Molec. Spectrosc. **321**, 28 (2016)] are not appropriate. Instead, we label the modes consistently based upon the Mulliken (Herzberg) method for the modes of *ortho*-difluorobenzene (*p*DFB) under C_s symmetry, since we wish the labelling scheme to cover both symmetrically- and asymmetrically-substituted molecules. By studying the vibrational wavenumbers from the same force field while varying the mass of the substituent, we are able to identify the corresponding modes across a wide range of molecules and hence provide consistent assignments. We assign the vibrations of the following sets of molecules: the symmetric *o*-dihalobenzenes, *o*-xylene and catechol (*o*-dihydroxybenzene); and the asymmetric *o*-dihalobenzenes, *o*-halotoluenes, *o*-halophenols and *o*-cresol. In the symmetrically-substituted species, we find a pair of in-phase and out-of-phase carbon-substituent stretches, and this motion persists in asymmetrically-substituted molecules for heavier substituents. When at least one of the substituents is light, then we find that these evolve into localized carbon-substituent stretches.

Keywords: Vibrations; Frequencies; Ground electronic state; ortho-Disubstituted Benzenes

1. Introduction

Vibrations are one of the ways that the spectroscopist gains insight into the geometric and electronic structure of molecules. In particular, vibrational activity during an electronic transition or ionization gives information on the resultant changes in the geometry that occur, which in turn can be related to the details of the orbitals involved. Similarly, changes in vibrational wavenumbers across a family of similar species can give information on changes in electronic structure, once mass effects have been considered. In practice, spectroscopists observe a series of spectral lines, which they then have to assign in terms of the normal modes of the molecule. In a simple picture, the assignments would be in terms of symmetry-allowed fundamentals, overtones and combinations, but further complications can arise from Fermi resonance, and vibronic effects such as Herzberg-Teller coupling.

Comparing spectra between molecules can be difficult as even quite small changes in structure, such as the substitution of a single atom, can lead to significant changes in the appearance of the spectrum. This can arise from a change in symmetry, mass shifts in vibrational wavenumber, and electronic effects. Each of these can change the wavenumbers of vibrations quite significantly. Additionally, in electronic or photoelectron spectra, the electronic structure changes can also induce modifications to the vibrations; furthermore, substituent changes can alter the energy separation of electronic states, and hence the strength of Herzberg-Teller (HT) coupling – this can affect the relative intensities of HT-active vibrations. As a consequence, assigning a vibrationally-resolved spectrum with no further information can be somewhat daunting and almost always comparison to similar molecules is made and, increasingly, to quantum chemical calculations.

In the present work, we focus on substituted benzenes, and note that the comparison of vibrations between such molecules has also been obfuscated by the widespread use of two (or more properly three) main labelling schemes. First, there is comparison of the vibrations of a substituted molecule with those of benzene by using the Wilson mode labels [1]. This does not work because the vibrations of the substituted molecule can be very different to those of the parent benzene: something we have discussed in detail for single-substituted species [2]. A heroic attempt has been made by Varsányi [3] to give Wilson-like labels to an enormous range of substituted benzenes; however, as we point out in [2], different labels were used for the same vibrations when moving between (arbitrarily-defined) "heavy" and "light" substituents. Thus, we dismiss the use of these latter labels, which are labelled "Wilson" or "Varsányi" modes interchangeably throughout the literature. The second set of oft-employed labels are those of Herzberg [4] and Mulliken [5], with "Mulliken labels" now being the more-frequently used term. These are constructed by arranging the vibrations into symmetry classes, taken in a particular order that is given in the second volume [4] of Herzberg's classic texts, and then within each symmetry class, ordering the vibrations in decreasing wavenumber. It immediately becomes clear that comparing between molecules with different symmetries is problematic, as are cases where substituents are

not single atoms (and so additional vibrations enter the list); moreover, if a substituent group undergoes large amplitude internal motion, such as the internal rotation of a methyl group, then even deciding on what symmetry to use can be an issue.

We have taken a pragmatic approach to this problem, aided by the availability of quantum chemical calculations. Briefly, and as outlined in more detail in Ref. [2] for monosubstituted benzenes, we calculated the force field of benzene using a quantum chemistry code, and then artificially increased the mass of one hydrogen, recalculating the vibrational wavenumbers for each mass within this fixed force field. By plotting the wavenumbers as a function of mass, the variations could be clearly seen. Of note was that these variations had settled down at a mass of around 15 amu, and very much smaller changes in wavenumber were observed as the mass was increased further. This turns out to be highly fortuitous, since 14 amu is the mass of an NH_2 group, 15 amu that of CH_3, 17 amu that of OH and 19 amu that of F, with other common substituents being of higher mass. We applied this scheme to a wide range of monosubstituted benzenes, focusing on the ring-localized modes and assuming that substituents were point masses. What was remarkable was that only small perturbations appeared to arise from electronic (mesomeric or inductive) effects, and the variations in wavenumber mostly arose from mass changes. In a series of papers, we have applied this labelling scheme to the vibrationally-resolved electronic spectra of jet-cooled monohalobenzenes [6],[7],[8] and showed that the vibrational activity observed was similar across the series; further application was made to the electronic and high-resolution photoelectron spectra of toluene [9],[10].

It is notable that, in the same way that a single substitution changes the vibrations of benzene significantly, so too does the second substitution on moving from fluorobenzene to *p*-difluorobenzene. As a consequence, different labels are required for the *para*-disubstituted cases from those in the monosubstituted case (and different to benzene itself), in order to obtain a consistent labelling scheme [11]. This is a little inconvenient, but emphasises that caution is merited in assuming that vibrations given the same Wilson/Varsányi label in different molecules have the same motion. We have applied this approach to symmetrically- and asymmetrically-substituted *para*-disubstituted benzenes, in examining the induced vibrational activity following electronic excitation and ionization in *para*-fluorotoluene (*p*FT) [12], [13], *para*-xylene (*p*Xyl) [14], [15], and *para*-chlorofluorobenzene (*p*ClFB) [16]. With our labelling scheme, we were able to highlight the similarity in vibrational activity in those cases.

Herein, we shall examine the vibrations of *ortho*-disubstituted benzenes and will conclude that it is not possible to use the Wilson/Varsányi or Mulliken/Herzberg labelling schemes and, further, that it is also not possible to use the monosubstituted or *para*-disubstituted labels. (In an upcoming paper, we shall demonstrate the same is true for *meta*-disubstituted benzenes [17].) We shall therefore put forward a separate labelling scheme that covers symmetrically- and asymmetrically-substituted molecules based on the lowest common point group for the family, C_s symmetry here, and based on the *o*-difluorobenzene (*o*DFB) species.

2. Computational Details

All of the harmonic vibrational frequencies were obtained using B3LYP/aug-cc-pVTZ calculations via the GAUSSIAN 09 software package [18]**.** For bromine and iodine atoms, the fully relativistic effective core potentials, ECP10MDF and ECP28MDF respectively, were used with corresponding aug-cc-pVTZ-PP valence basis sets. All of the calculated harmonic vibrational wavenumbers were scaled by the usual factor of 0.97 as an approximate method of obtaining anharmonic wavenumber values. This level of calculation has been shown to be very reliable for the S_0 vibrational wavenumbers of a range of substituted benzenes [2], [11]. In the following, we shall calculate vibrational wavenumbers for the actual molecule, but also vibrational wavenumbers that are calculated using one molecule's force field, but then artificially changing the mass of one or two atoms to match those of substituents (atomic or otherwise). In this way, we can map out changes in the vibrational wavenumbers that occur solely from the mass effect and any deviations from these. In addition, we shall calculate generalized Duschinsky matrices using FC-LabII [19] to illustrate the mixed nature of the vibrations of one molecule when expressed as those of another. In each case we show results for the lowest energy conformer we found at the specified level of theory, although in the case of o-xylene the search was not exhaustive owing to convergence issues for some orientations. In any case, experience has shown that we do not expect the conformation to affect the phenyl-localized modes to any great extent for these molecules, and it is certainly the case that much higher levels of theory would be required to obtain quantitative energy differences between some of these conformers.

3. Labelling the S_0 vibrational modes of oDFB

We have covered much of the background to our methodology in refs. [2] and [11]; hence, we present the results succinctly here.

As a first step, we compare the vibrations of oDFB with those of benzene. There is an immediate problem, since a choice of axis system must be made. The C_2 axis in oDFB bisects the C-C bond that has the two fluorine atoms attached to it, and so is the z axis according to convention; in contrast, the C_6 axis in benzene is perpendicular to the molecular plane, and by convention is the z axis. Hence, in moving from benzene to an o-disubstituted benzene molecule, then the molecule moves from lying in the xy plane for benzene to the yz plane for an o-disubstituted benzene molecule. However, these axis systems are just conventions, and so for ease of comparison, we compare the vibrations of benzene and oDFB with both molecules lying in the yz plane; further, to compare motions the atoms in the molecules need to be aligned, and we align the molecules in an "obvious" relative orientation as shown in Figure 1.

Figure 1 represents the vibrations of oDFB in terms of those of benzene using a Duschinsky matrix approach, where one set of vibrations are expressed as linear combinations of another set. As noted in the caption, the shading indicates how well the vibration of one molecule represents that of the other, with black meaning the

vibrations are identical, white meaning there is essentially no resemblance, and the depth of shade of grey representing the degree of similarity. As may be seen from this figure, the modes fall nicely into C_{2v} symmetry blocks, but there is mixing between the modes: that is, the Wilson modes of benzene are not a good representation of the normal modes of oDFB, and this is true across the four C_{2v} symmetry classes. It is interesting to note that while the 6a/b, 9a/b etc. degenerate vibrations of benzene separate into a_1/b_2 or a_2/b_1 pairs, matching the corresponding a/b label in each case is not true, owing to the location of the z axis; for example, the 18b mode is of a_1 symmetry and the 18a mode is of b_2 symmetry, while the reverse separation occurs for the 9a/b vibrations.

In setting up the Duschinsky matrix, we have noted that the molecules need to be aligned with atoms in corresponding positions, but some caution is required in doing this. So, in the present case, if we rotate the benzene molecule's axis system relative to that of oDFB by 60°, but keep the same atomic motions associated with the same atoms, then we still have an alignment of the atoms, but find that there is mixing between the a_1 and b_2 modes, and also between the a_2 and b_1 modes, and so the relative orientation shown in Figure 1 is the more natural one. (The reader can visualize this by looking at the motion of the v_{9a} mode shown to the right in Figure 1 and seeing that it is a close match to that of $^oD_5$ – see below for a description of this labelling – but if the benzene molecule is rotated by 60°, there is still alignment of the atoms, but the motions no longer correspond.) In summary, our conclusion is that the association of the benzene Wilson modes with those in an o-disubstituted benzene molecule is even more problematic than in the monosubstituted [2] or $para$-disubstituted cases [11].

In Table 1 we present the data used to make up Figure 1 in a different way, with the notation explained in the footnotes. As may be seen from both Figure 1 and Table 1, the oDFB normal modes are significant mixtures of the benzene ones and in many cases it is not possible to associate a unique Wilson label with a particular oDFB normal mode.

We now compare the oDFB normal modes with those of monofluorobenzene (FBz) (the M_i modes of Ref. [2]) using a similar approach. As noted above, to construct the Duschinsky matrix, the atoms must be in the same orientations, i.e. the molecules need to be aligned; however, there is no unique way of doing this. We show what we feel is the most obvious way of comparing the modes, by aligning the C–F bond in FBz with one such bond in oDFB. The resulting Duschinsky matrix is shown in Figure 2, and the breakdowns of the oDFB modes in terms of the FBz ones are given in Table 1. As may be seen from Figure 2, there is not a good match between the FBz and oDFB modes, with the mixing being considerable, and only a small number of vibrations of oDFB are largely identifiable with a single M_i mode, with the others being significant mixtures of modes.

We now consider how the vibrations of benzene evolve into those of oDFB as we simultaneously (and artificially) change the masses of two adjacent hydrogens from 1 amu to 19 amu – this allows the mass-only effects on the vibrational wavenumbers to be examined. We have done this by aligning the axis systems of

benzene and oDFB as we did above, which separates the vibrations into C_{2v} symmetry classes. In Figure 3 we show the full-range plots for the a_1 and b_2 symmetry vibrations, while in Figure 4 we show the plots for all four C_{2v} symmetry classes, but omitting the high-wavenumber vibrations for the a_1 and b_2 symmetry classes. We first consider the evolution of the modes from benzene to oDFB, which correspond to the left-hand sides of each quadrant. There are significant changes in the wavenumbers of many of the vibrations as the mass changes, and interestingly a number of the curves look like they undergo "avoided crossings". We interpret these as the normal modes changing and becoming significant admixtures of the original normal modes, within the same symmetry class. Notably, once the artificial masses reach ~10 amu the curves become more settled, which we have taken to imply that the form of the normal modes are now largely stable and this persists to higher mass. In the case of the p-disubstituted benzenes in Ref. [11], we gave detailed commentaries on the evolution of the benzene modes as the mass increased and the interested reader can look at Ref. [11] and then apply the same ideas while looking at the left-hand side of the present Figures 3 and 4, while comparing to the breakdowns given in the present Table 1. Again, it is clear that some modes are very mass sensitive, with the motion altering significantly at low masses, causing the changing wavenumber. The changes in motion lead to the evolving modes being represented by linear combinations of the original Bz modes. The summary of this analysis is similar to that in the previous paragraph: it is not possible to use the Wilson mode labels for the vibrations of o-disubstituted benzenes – a corresponding conclusion also reached in the case of p-disubstituted benzenes [11].

We now explain why we do not simply use the ^pD_i labels that we deduced previously for the $para$-disubstituted benzenes [11]. On the right-hand sides of Figures 3 and 4, again we have taken the force field for benzene, but now change the mass of two opposite hydrogen atoms from 1 to 19 amu simultaneously, as indicated. For the purposes of this comparison, we have aligned the molecules as shown. This maintains each vibration in the same C_{2v} symmetry class as we change the masses, and so allows the correlation of pDFB vibrations on the right-hand side with oDFB vibrations on the left-hand side, via the vibrations of benzene in the centre. Note that this is not the same C_{2v} axis system employed in Ref. [11], and is used here simply to allow a more direct comparison of the $ortho$ and $para$ vibrational motions; note that this also allows the atoms and the axis systems to remain aligned. However, the numbering of the pDFB modes given on the right-hand side of the diagram does correspond to that given in Ref. [11]. Use of the same axis system also allows us to deal with the fact that with the original axis system used for pDFB [11] there are $3a_2+6b_2$ out of plane modes, while in the system used here for pDFB and oDFB there are $5a_2 + 4b_1$ such modes. In addition, although there are the same number of each of the a_1 and b_2 in-plane modes in the two axis systems, and the same vibrations belong to one of these two classes, some vibrations change their symmetries between the two axis systems. Further, when considered in its full D_{2h} point group, the pDFB vibrations have u and g symmetry. To help the reader identify the various vibrations in the diagram, we have used different colours for each of the a and b symmetry vibrations across the two a_1, b_2 and a_2, b_1 pairs of classes, as indicated; we also used dashed lines to imply u

symmetry and solid lines for g symmetry. As may be seen from Figure 4, this means that lines where the colour or line type is different can cross (as they have different D_{2h} symmetries), while if these are both the same, then the vibrations mix and an avoided crossing is observed. (Note that in Figure 1 of Ref. [11] the first point was not correctly indicated, so that the $^PD_{19}$ and $^PD_{18}$ modes can cross, for example.) So, looking at the a_1 vibrations in the top right panel, we see that the $^PD_3$ and $^PD_5$ vibrations interact and undergo an avoided crossing, while the $^PD_{11}$ and $^PD_{30}$ vibrations can cross. On the left-hand side, it is the case that no curve can cross (as they all have the same symmetry in the full point group of the molecule), and so, for example, we see a clear avoided crossing between the $^oD_{18}$ and $^oD_{21}$ vibrations. Further consideration of these curves, together with the breakdowns provided in Table 1, give insight into the interactions/mixings that are occurring between different vibrations; it is particularly interesting that there are some contributions from the highest a_1 modes into the lowest ones. Similar comments also apply to the other classes.

It is clear that large mass-dependent changes are occurring early on as we move away from benzene in the centre of the figure. It is true again, however, that the changes largely settle down, from about 15 amu onwards. Evidently, if we start on the far right-hand side of the diagrams in Figures 3 and 4 and trace a mode from pDFB through benzene to oDFB, we will have encountered various avoided crossings and, therefore, mixings of the modes. If we compare the motions on the far left- and far right-hand sides via a Duschinsky matrix approach, as shown in Figure 5, we can see that there are very few modes that have the same motions for both oDFB and pDFB. For these reasons, we have had to accept that the labelling scheme for the *ortho*-disubstituted benzenes will need to be different to that of the *para*-disubstituted molecules. Indeed, the significant changes in the modes implied by Figure 5 provides a general word of caution in trying to compare vibrations between different isomers of substituted benzenes. Note that in certain special cases, for example replacing the *ortho* hydrogen in fluorobenzene by a deuterium atom, there will still be significant mixing of modes and so more caution would need to be exerted; we discussed this point in depth in the case of the monosubstituted species [2], looking at monodeuterated benzene.

Having concluded that we need to employ a new labelling scheme for *ortho*-disubstituted benzenes, we now look at whether employing the modes of oDFB as the basis for this is sound. In Figure 6, mass-correlation diagrams are presented that employ the force-field of oDFB whilst simultaneously changing the masses of both fluorine atoms artificially to that of each of the naturally-occurring isotopes of the halogens with the highest abundance. It may be seen there that, although there is a trend for the wavenumber to lower with increasing mass as expected, there is little indication of significant mixing between the modes and this is confirmed by Duschinsky matrices (not shown). Additionally, in Figure 7, we show a mass-correlation diagram again using the force field of oDFB and changing the mass of only the *ortho* fluorine from mass 19 to mass 127, and again little mixing is seen, which is again confirmed by Duschinsky matrices (not shown). As a consequence, and in line with similar conclusions outlined in our earlier papers [2, 11], we take the normal modes of oDFB as the basis for the labels of *ortho* disubstituted molecules, with the label numbers

being given by the standard Mulliken scheme [5]. However, because we wish the labels to be applicable across both symmetrically- and asymmetrically-substituted molecules, we construct these labels in the C_s point group, and denote them ^oD_i, with the presuperscript to be included only when required to avoid ambiguity considering different isomers, and i running from 1 (for the highest wavenumber a' vibration) to 30 (for the lowest a'' vibration). Note that our labels are restricted to the phenyl-ring localized modes, and so any substituents are effectively treated as point masses when determining the ^oD_i labels, with substituent-localized vibrations being treated separately, as required. This means that even in cases where the substituents lower the overall point group symmetry to C_1, the proposed scheme is still valid.

In summary, we propose the use of ^oD_i labels for the normal modes of the phenyl-ring-localized vibrations of *ortho*-disubstituted benzenes. The normal mode diagrams are indicated in Figure 8 and it is relatively straightforward to assign a label to a vibration with a particular wavenumber, based either on expected mass trends, or by calculating and visualizing the motion with widely-available quantum chemical software. As examples of this, in Figure 9 we show the calculated motions of five *o*DFB, *o*ClFB and *o*DCB a' modes. The $^oD_{11}$ and $^oD_{13}$ modes look very similar across the series, with just small variations in motion in line with keeping the centre of mass fixed with the changing halogen masses. The $^oD_{10}$, $^oD_{12}$ and $^oD_{14}$ modes have some similarities, but can be identified by noting the following. $^oD_{10}$ is either a symmetric, in-phase, stretch of the two substituents, or is the higher of the localized C-X and C-Y stretches, where X and Y are substituents. $^oD_{12}$ is either an asymmetric, out-of-phase, stretch of the two substituents, or is the lower of the localized C-X and C-Y stretches, where X and Y are substituents. $^oD_{14}$ is identifiable as having out-of-phase bending of the pairs of C–H bonds on opposite sides of the ring.

4. Assigning the vibrations

We shall now consider four families of *ortho*-disubstituted benzenes, assign ^oD_i labels and discuss previous assignments where appropriate, these are: symmetric disubstituted benzenes involving halogens, OH or CH_3; and the asymmetric dihalobenzenes, halotoluenes, halophenols and cresol. We have found it straightforward to identify the ^oD_i label from the calculated motion in all of these cases, as discussed below.

4.1 Symmetric disubstituted benzenes

A summary of the available experimental and the present calculated vibrational wavenumbers are presented in Table 2. The thirty vibrational wavenumbers of the ground electronic state ($\tilde{X}^1A_1$) of the C_{2v} molecule, *o*DFB have been summarized by Varsányi [3], with Wilson-like labels given to these; the readily-available values were cited as being taken from two papers by Green and coworkers [20],[21] and one by Steele [22], with cited work in Green [20] also including Raman studies from Refs. [23], [24] and [25]. Most of those values are from infrared or Raman studies of the liquid, although the infrared ones for *p*DIB are from studies of a solution. We report a summary of the values in Table 2, favouring the infrared values over the Raman

values where both have been given. In a few cases, to give vibrations with similar motions the same ^oD_i label, a couple of switches in wavenumber ordering from that in oDFB was required – in these cases we have also reordered the experimental vibrational wavenumbers to match. The values for oDFB were slightly modified by Swinn and Kable [26] in their laser-induced fluorescence/dispersed fluorescence study of jet-cooled gaseous molecules, who also gave Mulliken labels together with Varsányi ones; interestingly, from band positions and assignments given in that work [26], slightly different S_0 values can be derived, which we would expect to be more comparable with the calculated values. As a consequence, where available, these values have been preferred in Table 2. In keeping with the construction of the ^oD_i labels, we have separated the vibrations into a' and a'' symmetry, but have also indicated both the C_{2v} Mulliken numbering (as used in Ref. [26], for example), as well as the C_{2v} symmetry, in Table 2. In the following, the dihalogens are abbreviated in an obvious way, as we have done for oDFB, and oXyl = $ortho$-xylene (xylene = dimethylbenzene). The corresponding vibrational wavenumbers for oDClB, oDBrB, oDIB and oXyl are all from Green [20]. For catechol (also known as pyrocatechol, o-dihydrobenzene or benzene-1,2-diol), there have been a number of studies [23, 27, 28, 29, 30, 31] and we have favoured the gas-phase values of Wilson [29] and then the more-recent values on the liquid [31] over the earlier values summarized in [27], where available. We have deduced the assignments from the given symmetry and comments given in these papers, with a few discussion points given below. (Note that the conformers used for catechol and oXyl are given in a footnote to Table 2.)

In Table 2, we give our calculated wavenumbers, and it may be seen that there is generally very good agreement with the experimental values across the board, with there being only a small number of missing experimental values. In most cases, it is straightforward to track the vibrational modes across this family of molecules, particularly as many of the original experimental assignments were able to deduce the C_{2v} symmetry class of a vibration from a band profile and/or comparing infrared and Raman activity. There are several points to highlight. For the heavier dihalobenzenes we find that we need to switch the ordering of the D_{10} and D_{13} vibrational wavenumbers, and also the D_{12} and D_{14} vibrations. For pDIB we also see that the calculated value of 308 cm^{-1} for D_{19} is not in good agreement with the experimental value of 206 cm^{-1}. In fact, the latter value was noted in the text has having an uncertain assignment, and it is not clear why it was associated with the given fundamental. Given the coincidence of the calculated values for D_{19} and D_{18}, it is possible that the experimental values for these were overlapped. It is possible that the two values noted in Ref. [20] of 200 cm^{-1} and 206 cm^{-1} could actually be assigned to the D_{21} first overtone and the D_{20} respectively, and we currently hypothesise this. We thus conclude that the assignment of the 206 cm^{-1} band in pDIB to D_{19} is erroneous and reassign this to D_{20}; we then hypothesise that the D_{18} and D_{19} bands are coincident. Figure 6 shows a comparison of the experimental values to the ones calculated from the oDFB force-field and using artificial isotopes.

For catechol, there have been a number of infrared and Raman studies on the liquid, and one also on the vapour. We have preferred the values from the vapour studies [29], and then those from the recent work of

Koh et al. [31]. We note that the value for D_9 from the vapour study would be 1364 cm^{-1}, but a fundamental in that work of 1324 cm^{-1} (assigned to an OH-localized vibration therein) was preferred by Koh et al. [31] and this value appears to be in better agreement with the calculated value herein. We note that assignments of three phenyl-ring localized vibrations at 1275 cm^{-1}, 1195 cm^{-1} and 1035 cm^{-1} in Ref. [29] seem to be erroneous based on the present calculated values. Indeed, some assignments have been modified slightly in Ref. [28] and again in Ref. [31] with some uncertainty implied as to which vibrations are OH-localized and which are phenyl-ring localized. Lastly, the value of 501 cm^{-1} reported for one of the in-plane vibrations in Ref. [27] also seems to be erroneous based on later studies and our calculated values.

It is interesting to note that the D_{10} and D_{12} vibrations may be well described as in-phase and out-of-phase C-X stretches, where X is a substituent, a similar situation was observed in the *para*-disubstituted species and in Ref. [11] we noted that these modes evolved into largely localized C-X and C-Y stretches in the asymmetric species, where X and Y are different substituents.

4.2 Asymmetric dihalobenzenes

A summary of the available experimental and the present calculated vibrational wavenumbers are presented in Table 3. The experimental values for the asymmetric *o*-dihalobenzenes have been taken from Ref. [20] which are mostly infrared spectroscopic data for the liquid, but with some Raman values taken from Refs. [24], [32] and [33] (also summarized in Ref. [20]). To obtain consistency, we have given vibrations with similar motions the same D_i label, which sometimes leads to the vibrations being in a different wavenumber order to those in *o*DFB − in these cases we have also reordered the experimental vibrational wavenumbers to match. As may be seen, there are only a small number of missing experimental values, and in general there is good agreement across the whole series. With the given assignments, it is again possible to track the same vibration across the series of molecules. We find that the order of vibration D_{10}–D_{15} has changed from that in *o*DFB and so these are not in wavenumber order; however, the motions of modes given the same D_i number are a good match across the series, meaning the assignment is sound. We note that the experimental value of the D_{18} band for *o*ClIB of 366 cm^{-1} [20] is in poor agreement with the calculated value of 425 cm^{-1}; in fact the 366 cm^{-1} value could be associated with the 20^1+21^1 combination band, and so we think this value for D_{18} in Ref. [20] is incorrect.

As noted in the previous sub-section, from our work on the *para*-disubstituted species, we would expect the D_{10} and D_{12} vibrations to evolve into localized C–X and C–Y stretches and in a number of cases, this seems to be the case and so we label these vibrations with this character in Table 3. In such cases, and in a similar way to what we did in Ref. [11], we have given the label D_{10} consistently to the highest wavenumber C-X stretch and the label D_{12} to the lowest wavenumber C–Y stretch. We note that there are some other vibrations with various small amounts of C–X and C–Y stretch character, and so this localization of motion is not complete, but it is a good approximation in some cases, and we find that the D_{10} vibrational wavenumbers of

the *ortho*-disubstituted benzenes are generally similar to the D_5 vibrational wavenumbers for the corresponding *para* ones [11]. When the lightest substituent is Cl or heavier, this localization does not occur – we think this is related to the distorted motion – and so in such cases we retain the symmetric and asymmetric labelling in Table 3.

4.3 o-halotoluenes

A summary of the available experimental and the present calculated vibrational wavenumbers for the phenyl-ring-localized vibration of the four commonly-occurring *o*-halotoluenes are presented in Table 4. (The conformers employed are shown in a footnote to this table.) Again, these values come from the work of Green [20] and are mostly infrared spectroscopic values obtained on the liquid, with a few being from Raman studies [25]. Again, we have given vibrations with similar motions the same D_i label, which sometimes leads to the vibrations being in a different wavenumber order to those in *o*DFB – in these cases we have also reordered the experimental vibrational wavenumbers to match. Again, there are several missing experimental values, but there is good agreement across the whole series and so the given assignments allow the same vibration to be tracked across the series of molecules. The reader will recall that the ^oD_i labels only cover the phenyl-ring localized motions, and so do not include the vibrations largely localized to the methyl group, which form a separate set. Experience from our previous work [2, 11] and herein show that coupling between the methyl-localized and ring-localized sets of vibrations seems to be small, but will clearly be present and so may need to be taken account of in higher precision measurements. However, for the infrared and Raman studies referred to here, and our application to vibrationally-resolved electronic excitation (and dispersed fluorescence) spectra mentioned in the above text, the localized sets appear to be sufficient.

Here we find a localization of the C–X and C–CH$_3$ stretch motions across the series, and in a similar manner to the convention we adopted in Ref. [11], we use D_{10} always to label the carbon–halogen stretch and then D_{12} to label the C–CH$_3$ stretch (labelled C–Me) in Table 4.

4.3 o-halophenols and o-cresol

 A summary of the available experimental and the present calculated vibrational wavenumbers for the phenyl-ring localized vibrations of the *o*-halophenols and o-cresol are presented in Table 5. (The conformers employed are shown in a footnote to this table.) These are taken from Green [34] and are mainly infrared spectroscopic studies of liquids, but with some values taken from a Raman study [25], but cited in Ref. [34]. We have given vibrations with similar motions the same D_i label, which sometimes leads to the vibrations being in a different wavenumber order to those in *o*DFB – in these cases we have also reordered the experimental vibrational wavenumbers to match. Once again, the agreement between the calculated and experimental values is generally very good and trends in the vibrations can be followed across the series. Again, we note that vibrations localized to the hydroxyl groups, or methyl group in the case of *o*-cresol, are

not part of the ^oD_i vibrational set. It is interesting to note that there is no conclusive evidence for perturbation of any of the out-of-plane phenyl-ring localized vibrations, even when the substituents are moving in opposite directions relative to the ring (see mode diagrams in Figure 8 and values in Table 5). This is a little surprising as it may be expected that there would be some hydrogen-bonding-type interaction between the hydroxyl group and the halogen. Further evidence for the absence of any significant interaction comes from the similarity of the *o*-cresol vibrational wavenumbers and those of *o*FPhOH where the masses are quite similar.

We find localization of the C–OH and C–X stretch motions in most cases, and in a similar manner to the convention we adopted in Ref. [11], we use D_{10} to label the C–OH stretch and D_{12} to label the carbon-halogen, or carbon-methyl (labelled C–Me) stretch in Table 5. The exception is for *o*FPhOH, where this localization does not occur cleanly, and so we retain the symmetric/asymmetric labels for D_{10} and D_{12} in this case.

5. Conclusions

In the present work, we have shown that it is possible to label the phenyl ring-localized vibrations of a range of *ortho*-disubstituted benzenes consistently, such that vibrations with the same atomic motion have the same label. In doing this we have seen that the ordering of the vibrations changes between species – this means that application of the usual Mulliken (Herzberg) labelling scheme for each species would give different labels to the same vibrations. We have shown how the *ortho* motions are related to those of the other species, and shown that these are often heavily mixed versions of each other. This leads to the conclusion that the vibrational motions of the *ortho*-disubstituted benzenes are significantly different to those of benzene, monosubstituted benzenes or *para*-disubstituted species. This means both that different labelling schemes are required and, further, that some caution is required when drawing conclusions on vibration-specific trends across different isomers. It is worth noting that the centre-of-mass in benzene, monosubstituted benzenes and *para*-disubstituted benzenes stays on the *z*-axis (at least for the most part) whether the substitution is symmetric or not, while for asymmetric *ortho*-disubstituted species, the centre of mass migrates towards the heavier substituent, causing significant distortions of the motions of the other atoms, to compensate. Despite this, it was still possible to trace the motions as a function of mass for a fixed force field, but also to be able to identify to which of the ^oD_i motions (given in Figure 8) a calculated vibration corresponded.

As in the *para*-disubstituted benzenes [11], in a number of cases we were able to discern the localization of the in-phase and out-of-phase motions of the carbon-substituent bond stretching motions from the symmetrically- to the asymmetrically-substituted species. We have thus labelled these vibrations consistently, in a similar way to that used in Ref. [11].

We anticipate that the use of this labelling scheme for *ortho*-disubstituted benzenes will reveal trends in vibration-specific behaviour between species more clearly, as we have found when examining the

vibrationally-resolved electronic and photoelectron spectra of both monosubstituted and *para*-disubstituted benzenes.

Acknowledgements

Figure Captions

<u>Figure 1</u>: Generalized Duschinsky matrix showing how the vibrational modes of oDFB can be expressed in terms of the benzene ones – clearly significant mixing of the benzene modes occurs – see text for further discussion. Black shading indicates a normalized coefficient value of 1.00, while white indicates a value of 0.00, with grey shading indicating intermediate values, see text for details.

<u>Figure 2</u>: Generalized Duschinsky matrix showing how the vibrational modes of oDFB can be expressed in terms of the FBz ones – clearly significant mixing of the fluorobenzene modes occurs – see text for further discussion. Black shading indicates a normalized coefficient value of 1.00, while white indicates a value of 0.00, with grey shading indicating intermediate values, see text for details. Note that although the vibrations can each be labelled with a C_{2v} symmetry class, these would be different for FBz and oDFB, as the C_2 axis and atoms cannot be simultaneously aligned in the two molecules.

<u>Figure 3</u>: Mass-correlated vibrational wavenumbers showing how the vibrations of benzene (centre) evolve into those of pDFB (right) and oDFB (left) for the a_1 and b_2 vibrations, according to the indicated axis system. The force field of benzene is employed and the masses of the indicated hydrogen atoms are artificially varied from 1 to 19 amu in each case: ^{19}H in the figure indicates that the mass of the indicated hydrogen atom has been artificially changed to 19 amu. The oDFB labels have been included on the left, while on the right hand side the numbers refer to the ^pD_i modes as in Ref. [11]. An expanded region of both of these plots is shown as part of Figure 4, which also gives the Wilson modes in the centre. Note that we have used the same colour scheme and line type as employed in Figure 4.

<u>Figure 4</u>: Mass-correlated vibrational wavenumbers showing how the vibrations of benzene (centre) evolve into those of pDFB (right) and oDFB (left) for the vibrations separated into the four C_{2v} symmetry classes, according to the indicated axis system. The force field of benzene is employed and the masses of the indicated hydrogen atoms are artificially varied from 1 to 19 amu in each case: ^{19}H in the figure indicates that the mass of the indicated hydrogen atom has been artificially changed to 19 amu. The oDFB labels have been included on the left, on the right hand side the numbers refer to the ^pD_i modes from Ref. [11], while the Wilson modes are given in the centre. To aid the reader further, we have also indicated the appropriately colour-coded D_{2h} symmetry classes on the right-hand side of each panel. To allow comparison with Ref. [11], the pink/red lines indicate a_1 or a_2 symmetry vibrations, and blue/green lines indicate b_1 or b_2 vibrations, respectively – in each case now referring to the axis system used in that work. Further, vibrations on the right-hand side belong to the D_{2h} point group and so have g/u symmetry – this is indicated by solid/dashed lines respectively. See text for further discussion.

<u>Figure 5</u>: Generalized Duschinsky matrix showing how the vibrational modes of oDFB can be expressed in terms of the pDFB ones, with the molecules aligned as indicated – clearly significant mixing of the modes occurs – see text for further discussion. Black shading indicates a normalized coefficient value of 1.00, while white indicates a value of 0.00, with grey shading indicating intermediate values, see text for details. The alignment given allows separation of the modes for both molecules into C_{2v} symmetry blocks, but we have also indicated the C_s symmetry partition that is appropriate for asymmetrically-substituted *ortho*-disubstituted benzenes, and as used for the construction of the ^oD_i labels.

Figure 6: Mass-correlated vibrational wavenumbers showing how the vibrations of oDFB (left-hand side) evolve as a function of mass in symmetric dihalo species; the highest wavenumber vibrations have been omitted (refer to Table 2). The vibrations have been separated into the two C_s symmetry classes, and in each class we have indicated the a or b character with colour, as indicated. The force field of oDFB is employed and the masses of both fluorine atoms are artificially varied from 19 to 127 amu simultaneously in each case, to match the mass of the most abundant, naturally-occurring isotope of the halogens. The numbering of the ^oD_i labels is included on the left. Note that crossings between vibrations of different symmetry is allowed.

Figure 7: Mass-correlated vibrational wavenumbers showing how the vibrations of oDFB (left-hand side) evolve as a function of mass in asymmetric dihalo species; the highest wavenumber vibrations have been omitted (refer to Table 3). The vibrations have been separated into the two C_s symmetry classes. The force field of oDFB is employed and the mass of the $ortho$ fluorine atom is artificially varied from 19 to 127 amu in each case, to match the mass of the most abundant, naturally-occurring isotope of the halogens. The numbering of the ^oD_i labels is included on the left. (Note that the theoretical lines do not cross for D_{10} and D_{11}, as required; however, the experimental data indicate that there is a switch in the ordering of these two vibrations between pDFB and the cases where one fluorine atom is replaced by a heavier halogen – this effect is very small, and must be a result of subtle changes in the force field. The actual assignments of the vibrations, however, are based on the atomic motion.)

Figure 8: Calculated vibrational modes for oDFB (B3LYP/aug-cc-pVTZ), labelled using the ^oD_i notation in the present work. See text for details.

Figure 9: A selection of calculated vibrational modes for oDFB, oClFB and oDClB (B3LYP/aug-cc-pVTZ), labelled using the ^oD_i notation in the present work. (Green circle represents F and a red circle represent Cl; C and H are both open circles.) Note that the D_{10} and D_{12} modes are largely the in-phase and out-of-phase C-F (or C-Cl) stretches for oDFB (oDClB), while in oClFB these modes have evolved in being largely-localized C-F and C-Cl stretches, respectively. See text for details and discussion.

Table 1. Labelling schemes for the S_0 vibrations of oDFB

Mode[a]	Mulliken C_{2v} [b]	oDFB - Varsányi[c]	Mixed (Bz)[c,d]	Mixed (FBz)[e]
			a'	
${}^oD_1 (a_1)$	1	2	**2**,20b(7a)	**M_1**,$M_2(M_{21})$
${}^oD_2 (b_2)$	21	7b	**20a**(13,7b)	M_{21}, M_2, M_{22}
${}^oD_3 (a_1)$	2	20b	**7a**,20b	**M_{22}**, M_2
${}^oD_4 (b_2)$	22	20a	**13**,7b	**M_3**(M_{22})
${}^oD_5 (a_1)$	3	8a	**9a**	**M_{23}**, M_4
${}^oD_6 (b_2)$	23	8b	**9b**	**M_4**, M_{23}
${}^oD_7 (a_1)$	4	19b	**18b**	**M_5**, M_{24}
${}^oD_8 (b_2)$	24	19a	**18a**(3)	**M_{24}**, M_5
${}^oD_9 (a_1)$	5	14	**15**	**M_{26}**, M_{25}
${}^oD_{10} (a_1)$	6	7a	1(20b,18b,19b,2,8a,7a)	**M_6**(M_9, M_{21}, M_{28})
${}^oD_{11} (b_2)$	25	3	**3**,19a(8b)	$M_{25}, M_{26}(M_7, M_{28})$
${}^oD_{12} (b_2)$	26	13	12,8b(7b,13,6b)	$M_6(M_9, M_7, M_{21})$
${}^oD_{13} (a_1)$	7	9a	**14**,8a	**M_{27}**(M_7)
${}^oD_{14} (b_2)$	27	18a	8b,19a,12	$M_7, M_{28}(M_8, M_9, M_{27})$
${}^oD_{15} (a_1)$	8	18b	**19b**,1(14)	**M_8**, $M_{28}(M_9)$
${}^oD_{16} (b_2)$	28	12	12,6b(7b,13)	$M_{10}, M_9(M_{29}, M_{21})$
${}^oD_{17} (a_1)$	9	1	1,6a(20b,19b,2,7a)	$M_{10}(M_{29}, M_9, M_{21})$
${}^oD_{18} (a_1)$	10	6a	**6a**(20b)	**M_{29}**, M_{11}
${}^oD_{19} (b_2)$	29	6b	6b(19a,8b,3,18a)	$M_{11}, M_{30}(M_{29}, M_8, M_7)$
${}^oD_{20} (b_2)$	30	9b	6b(19a,7b,13,3)	M_{11}, M_{30}
${}^oD_{21} (a_1)$	11	15	8a,14(19b,6a)	$M_{30}(M_7, M_{28}, M_8, M_{25})$
			a''	
${}^oD_{22} (a_2)$	12	5	**5**,17a	**M_{15}**(M_{12})
${}^oD_{23} (b_1)$	17	17b	**17b**(10a)	**M_{12}**, $M_{16}(M_{15})$
${}^oD_{24} (a_2)$	13	17a	**10b**(17a,5)	$M_{16}, M_{13}(M_{12})$
${}^oD_{25} (b_1)$	18	11	10a,11	**M_{17}**(M_{13}, M_{18})
${}^oD_{26} (a_2)$	14	4	**4**,10b(17a)	**M_{18}**, $M_{17}(M_{13})$
${}^oD_{27} (a_2)$	15	16a	**16a**,4(10b,17a)	$M_{19}(M_{18}, M_{14}, M_{13})$
${}^oD_{28} (b_1)$	19	16b	**16b**(11,10a)	**M_{14}**, M_{19}
${}^oD_{29} (b_1)$	20	10a	16b,11(10a)	**M_{20}**(M_{14}, M_{19})
${}^oD_{30} (a_2)$	16	10b	16a(17a,5,10b,4)	$M_{20}(M_{14}, M_{13}, M_{16})$

[a] This work – see text. Labels based on Mulliken numbering in C_s symmetry.

[b] Mulliken numbering in C_{2v} symmetry.

[c] It should be noted that we have highlighted in Ref. [2] that several Wilson modes have been misnumbered in various texts over the years, with the following switches often being required: 8a ↔ 9a, 8b ↔ 9b, 18a ↔ 19a, 18b ↔ 19b and 3 ↔ 14; where they have occurred, these misnumberings have been corrected in the present work. For example, such misnumberings are present in the work of Varsányi [3] and these have been carried forward into other work, such as Ref. [26].

[d] These express the S_0 oDFB ${}^oD_i$ modes in terms of those of the benzene Wilson modes using a generalized Duschinsky approach involving artificial isotopologues – see text and Ref. [11]. Values outside parentheses have mixing coefficients > 0.2 and are termed major contributions, with bolded values being dominant contributions (mixing coefficients > 0.5). Those inside parentheses are minor contributions, and have values between 0.05 and 0.2.

If there is more than one contribution of each type, these are given in numerical order. Vibrations with a mixing coefficient < 0.05 are ignored.

[e] These express the S_0 oDFB ^oD_i modes in terms of those of fluorobenzene, numbered as M_i modes (see ref. [2]), using a generalized Duschinsky approach involving artificial isotopologues – see text and Ref. [11]. Values outside parentheses have mixing coefficients > 0.2 and are termed major contributions, with bolded values being dominant contributions (mixing coefficients > 0.5). Those inside parentheses are minor contributions, and have values between 0.05 and 0.2. If there is more than one contribution of each type, these are given in numerical order. Vibrations with a mixing coefficient < 0.05 are ignored.

Table 2: Vibrational wavenumbers for o-$C_6H_4X_2$ (X = F, Cl, Br, I, CH_3 and OH)

Mode		oXyl		Catechol		oDFB		oDClB		oDBrB		oDIB	
D_i	C_{2v}	Expt[a]	Calc[b]	Expt[c]	Calc[b]	Expt[a,d]	Calc[b]	Expt[a]	Calc[b]	Expt[a]	Calc[b]	Expt[a]	Calc[b]
						a'							
$^oD_1$ (a_1)	1	3080	3092	3081[e,g]	3104	3081	3110	3072	3111	3067	3110	3065	3108
$^oD_2$ (b_2)	21	3080	3077	3060[h]	3095	3081	3104	3072	3108	3067	3106	3065	3104
$^oD_3$ (a_1)	2	3064	3063	3051[h]	3082	3045	3096	-	3096	-	3095	3052	3092
$^oD_4$ (b_2)	22	3048	3059	3051[h]	3059	3060	3085	-	3083	-	3083	3052	3079
$^oD_5$ (a_1)	3	-	1568	1616[h]	1603	1625[d]	1596	1576	1559	1567	1554	1556	1547
$^oD_6$ (b_2)	23	-	1596	1607[h]	1596	1619[d]	1591	1576	1565	1567	1557	1556	1550
$^oD_7$ (a_1)	4	1494	1480	1504[h]	1498	1507[d]	1495	1458	1446	1449	1437	1439	1429
$^oD_8$ (b_2)	24	1468	1459	1479[h]	1463	1472	1448	1438	1422	1431	1417	1425	1409
$^oD_9$ (a_1)	5	1292	1285	1324[g]	1320	1299[d]	1292	1276	1267	1268[e]	1261	1260[m]	1249
$^oD_{10}$ (a_1)	6	1222	1205 (sym)	1263[e,g]	1259 (sym)	1279[d]	1254 (sym)	1130[k]	1105 (sym)	1106[k]	1084 (sym)	1086[k]	1070 (sym)
$^oD_{11}$ (b_2)	25	1290	1281	1251[h]	1229	1253	1252	1252	1241	1255	1241	1255	1243
$^oD_{12}$ (b_2)	26	1185	1169 (asym)	1151[i,j]	1133 (asym)	1206	1182 (asym)	1038[l]	1015 (asym)	1012[l]	995 (asym)	990[l]	980 (asym)
$^oD_{13}$ (a_1)	7	1155	1149	1151[h]	1142	1153[d]	1141	1155[k]	1149	1159[k]	1150	1160[k]	1153
$^oD_{14}$ (b_2)	27	1121	1111	1092[h]	1076	1101	1090	1130[l]	1115	1107[l]	1109	1100[l]	1104
$^oD_{15}$ (a_1)	8	1052	1042	1030[g]	1021	1027[d]	1017	1040[e]	1026	1035	1023	1029	1016
$^oD_{16}$ (b_2)	28	826	813	859[h]	839	856	838	740	726	700	690	672	669
$^oD_{17}$ (a_1)	9	733[e]	724	768[h]	757	766[d]	752	660	652	640	635	631	626
$^oD_{18}$ (a_1)	10	581	574	564[g]	574	568[d]	565	480	464	375	364	317	308
$^oD_{19}$ (b_2)	29	505	495	542[g]	542	546	536	427	415	358[e]	348	317[n]	308
$^oD_{20}$ (b_2)	30	406	399	-	435	438[d]	430	336	327	251	244	206[n]	201
$^oD_{21}$ (a_1)	11	255	291	320[g]	299	286[d]	279	202	193	129	123	98	92
						a''							
$^oD_{22}$ (a_2)	12	[970][f]	976	963[g]	954	970	966	975	972	[975][f]	975	[970][f]	977
$^oD_{23}$ (b_1)	17	930	932	916[h]	912	929[d]	930	940	943	940	944	939	946
$^oD_{24}$ (a_2)	13	860	861	851[g]	836	850[d]	847	850	854	854	854	855	857
$^oD_{25}$ (b_1)	18	741	739	741[h]	734	749	748	748	747	745	745	745	743
$^oD_{26}$ (a_2)	14	702[e]	713	721[g]	724	705[d]	703	695[e]	689	[695][f]	680	[695][f]	687
$^oD_{27}$ (a_2)	15	[505][f]	511	582[g]	559	556[d]	549	504[e]	509	494	496	478	482
$^oD_{28}$ (b_1)	19	435	438	456[g]	451	452[d]	452	435	438	431	431	420	425
$^oD_{29}$ (b_1)	20	325	251	299[j]	289	275	284	239	228	217[e]	206	200	187
$^oD_{30}$ (a_2)	16	180	171	198[g]	185	186[d]	183	152	132	136[e]	112	124	100

[a] Infrared spectroscopy of the liquid unless otherwise indicated, from Ref. [20].

[b] B3LYP/aug-cc-pVTZ values scaled by 0.97 – this work (see text). For consistency with the following tables, we have noted the symmetric and asymmetric stretch nature of D_{10} and D_{12} explicitly. The conformer used for oXyl was *trans* eclipsed-eclipsed, where one CH bond from each methyl is in the plane of the phenyl ring, and these are oriented away from each other. The conformer used for catechol was the expected lowest energy one, consistent with other work, with the OH groups parallel and hydrogen bonded.

[c] Experimental values taken from Refs. [27] and [31], favouring the latter, more-recent work.

[d] A number of experimental values were derived by us from assignments and band positions given in the jet-cooled dispersed fluorescence study [26].

[e] Raman studies of liquid [25].

[f] Estimated value from Ref. [20].

[g] Infrared and Raman values summarized in a surface-enhanced Raman spectroscopy study by Koh et al. [31].

[h] Value for vapour [29].

[i] We favour the given value based on the calculated value and its motion, although the assignment was not given in Ref. [27].

[j] From a summary of values used in thermochemical study by Kudchadker et al. [27].

[k] Wavenumber ordering has been switched from that in Ref. [20].

[l] Wavenumber ordering has been switched from Ref. [20].

[m] Raman studies of liquid [24]
[n] Reassigned from Ref. [20] – see text.

Table 3: Vibrational wavenumbers for *o*-C$_6$H$_4$XY: asymmetric *ortho*-dihalobenzenes

Mode	*o*ClFB		*o*BrFB		*o*FIB		*o*BrClB		*o*ClIB		oBrIB	
	Expt[a]	Calc[b]	Expt[a]	Calc[b]	Expt[a]	Calc[b]	Expt[a]	Calc[b]	Expt[a]	Calc[b]	Expt[a]	Calc[b]
a′												
D_1	3082[c]	3110	3078	3109	3074	3108	3086	3110	3088	3109	3078	3109
D_2	3062	3105	3065	3105	3051	3104	3067	3106	3062	3105	3059	3105
D_3	-	3096	-	3095	-	3094	-	3095	-	3094	-	3094
D_4	-	3085	-	3084	-	3083	-	3082	-	3081	-	3081
D_5	1597	1579	1592	1575	1582	1571	1572	1556	1566	1553	1562	1550
D_6	1588	1575	1580	1572	1572	1568	1565	1562	1566	1557	1562	1554
D_7	1481	1470	1480	1465	1472	1459	1458	1442	1447	1437	1441	1433
D_8	1450	1436	1448	1433	1442	1429	1435	1419	1425	1415	1424	1412
D_9	1288	1283	1287	1281	1280	1278	1269[d]	1264	1267	1259	1260[d]	1255
D_{10}	1240[e]	1221 (C-F)	1235[e]	1219 (C-F)	1233[e]	1215 (C-F)	1115[e]	1094 (sym)	1103[e]	1085 (sym)	1094[e]	1076 (sym)
D_{11}	1266[e]	1250	1263[e]	1249	1261[e]	1247	1252[e]	1241	1256[e]	1241	1253[e]	1241
D_{12}	1068[e]	1048 (C-Cl)	1050[e]	1034 (C-Br)	1042[e]	1010 (C-I)	1023[e]	1004 (asym)	1013[e]	995 (asym)	1003[e]	988 (asym)
D_{13}	1158[e]	1145	1158[e]	1145	1160[e]	1145	1160[e]	1150	1158[e]	1150	1160[e]	1151
D_{14}	1126[e]	1110	1117[e]	1105	1113[e]	1101	1124[e]	1114	1116[e]	1111	1105[e]	1107
D_{15}	1031	1020	1026	1017	1022	1029	1036[e]	1025	1035[e]	1024	1031[e]	1020
D_{16}	826	813	820	810	819	808	719	710	717	703	686	680
D_{17}	681	669	650	647	640	637	646	640	636	633	633	639
D_{18}	553	541	544	533	540	529	444	434	-[f]	425	354	342
D_{19}	496	483	472	460	462	451	387	375	243	358	222	328
D_{20}	375	366	297	289	253	246	282	274	224	237	209	219
D_{21}	229	221	189	181	165	159	164	157	146	139	113	107
a″												
D_{22}	974	972	970	973	980	973	980	977	976	978	975	978
D_{23}	934	935	938	937	942	938	940	944	941	945	941	944
D_{24}	850	848	851	848	851	848	854	853	855	855	854[g]	852
D_{26}	749	749	751	750	751	750	746	747	745	746	744	744
D_{25}	698	701	694	697	694	690	689	686	689	682	[685][h]	677
D_{27}	535	534	530	530	527	525	501	503	495	497	484	489
D_{28}	443	442	439	439	437	435	433	435	430	430	426	427
D_{29}	268	260	261	253	253	247	230	218	213	209	209	196
D_{30}	168	152	155	137	143	125	140	122	132	112	127	105

[a] Infrared spectroscopy of the liquid unless otherwise indicated, from Ref. [20].

[b] B3LYP/aug-cc-pVTZ values scaled by 0.97 – this work (see text). We have noted the symmetric and asymmetric stretch, or the localized nature, of D_{10} and D_{12} explicitly.

[c] Raman studies of liquid [33].

[d] Raman studies of liquid [24].

[e] Note that some or all of the vibrations D_{10}–D_{15} are not in the same wavenumber order as in *o*DFB, but vibrations with similar motions have been given the same D_i label. The experimental wavenumbers have been ordered to match the calculated ordering.

[f] A value of 366 cm^{-1} was given for this vibration in Ref. [20], but this appears to be an incorrect assignment – see text.

[g] Value mistyped in Ref. [20]; this value is consistent with the values for the other species and a Raman value cited in that work.

[h] Estimated value from Ref. [20].

Table 4: Vibrational wavenumbers for *o*-halotoluenes[a]

Mode	*o*FT		*o*ClT		*o*BrT		*o*IT	
	Expt[a]	Calc[b]	Expt[a]	Calc[b]	Expt[a]	Calc[b]	Expt[a]	Calc[b]
a'								
D_1	3067	3105	3067	3107	3060	3106	3060	3103
D_2	3045	3082	3057	3081	-	3081	-	3080
D_3	-	3095	-	3095	-	3094	-	3093
D_4	-	3069	-	3069	-	3068	-	3067
D_5	1621	1574	1592	1560	1592	1556	1590	1553
D_6	1589	1603	1572	1585	1565	1582	1562	1576
D_7	1490	1482	1473	1465	1467	1462	1462	1459
D_8	1467	1429	1458	1419	1456	1417	1453	1415
D_9	1299	1293	1282	1277	1274	1273	1274	1268
D_{10}	1233[c]	1216 (sym)	1054[c] (C-Cl)	1028 (C-Cl)	1031[c] (C-Br)	1009 (C-Br)	1016[c] (C-I)	997 (C-I)
D_{11}	1267[c]	1268	1253[c]	1266	1252[c]	1266	[1250][c,e]	1265
D_{12}	1187	1169 (asym)	1207[c] (C-Me)	1192 (C-Me)	1208[c] (C-Me)	1193 (C-Me)	1206[c] (C-Me)	1192 (C-Me)
D_{13}	1147	1143	1158[c]	1148	1158[c]	1149	1157[c]	1150
D_{14}	1112	1100	1129[c]	1120	1120[c]	1117	1117[c]	1114
D_{15}	1037	1028	1042	1037	1045[c]	1037	1046[c]	1038
D_{16}	840	823	805	790	798	786	795	784
D_{17}	747[d]	737	678	669	656	650	643	642
D_{18}	576	568	553	541	543	533	538	529
D_{19}	525	516	445	432	411[d]	400	405	391
D_{20}	426	422	366	359	297	286	250	244
D_{21}	272	268	246	239	215[d]	201	193	182
a''								
D_{22}	[970][e]	973	970	978	970	978	970	978
D_{23}	935	934	935	939	935	938	936	939
D_{24}	855[f]	850	854	854	855	852	855	853
D_{25}	754	752	747	746	744	743	743	741
D_{26}	704	707	701	704	694	701	693	699
D_{27}	536	538	508	513	501	505	494	498
D_{28}	441	442	436	437	433	434	430	430
D_{29}	288	262	246	237	238	229	231	223
D_{30}	186	174	164	151	157	131	148	124

[a] Infrared spectroscopy of the liquid unless otherwise indicated, from Ref. [20].

[b] B3LYP/aug-cc-pVTZ values scaled by 0.97 – this work (see text). The conformer in each case has the methyl group eclipsed (one C–H bond in the plane of the phenyl ring) and pointing away from the halogen atom. We have noted the symmetric and asymmetric stretch, or the localized nature, of D_{10} and D_{12} explicitly (where C–Me denotes a carbon-methyl bond).

[c] Note that some or all of the vibrations D_{10}–D_{15} are not in the same wavenumber order as in *o*DFB, but vibrations with similar motions have been given the same D_i label. The experimental wavenumbers have been ordered to match the calculated ordering.

[d] Raman studies of liquid [25].

[e] Estimated value from Ref. [20].

[f] A value of 955 cm^{-1} is given in Table 4 of Ref. [20], but this appears to be a typographical error based on the quoted Raman value therein, and has been corrected here.

Table 5: Vibrational wavenumbers for *o*-halophenols and *o*-cresol [a]

Mode	*o*-cresol		*o*FPhOH		*o*ClPhOH		*o*BrPhOH		*o*IPhOH	
	Expt[a]	Calc[b]	Expt[a]	Calc[b]	Expt[a]	Calc[b]	Expt[a]	Calc[b]	Expt[a]	Calc[b]
a′										
D_1	3060[c]	3096	3062[c]	3108	3085[c]	3109	3076[c]	3108	3071[c]	3106
D_2	3049[c,d]	3081	[c]	3100	3060[d]	3101	3035[c]	3100	3043[c]	3099
D_3	3028[c]	3065	[c]	3093	[c]	3094	[c]	3093	3026[c]	3091
D_4	--[c]	3053	[c]	3081	[c]	3081	[c]	3080	[c]	3079
D_5	1587[e]	1583	1616	1602	1584	1575	1586	1570	1584	1565
D_6	1608[e]	1599	1599	1592	1595	1584	1599	1581	1591	1576
D_7	1492	1492	1513	1489	1480	1468	1476	1464	1472	1459
D_8	1462	1429	1461	1459	1461	1449	1449	1446	1445	1442
D_9	1324	1317	1349	1342	1337	1330	1334	1327	1333	1324
D_{10}	1255[e] (C-OH)	1239 (C-OH)	1262[e] (sym)	1249 (sym)	1252[e] (C-OH)	1239 (C-OH)	1249[e] (C-OH)	1238 (C-OH)	1246[e] (C-OH)	1235 (C-OH)
D_{11}	1300[e]	1292	1292[e]	1286	1294[e]	1285	1292[e]	1285	1293[e]	1283
D_{12}	1207 (C-Me)	1197 (C-Me)	1218 (asym)	1201 (asym)	1057[e] (C-Cl)	1015 (C-Cl)	1040[e] (C-Br)	1003 (C-Br)	1039[e] (C-I)	994 (C-I)
D_{13}	1149	1144	1152	1141	1154[e]	1144	1153[e]	1144	1154[e]	1145
D_{14}	1102	1089	1092	1078	1124[e]	1108	1114[e]	1103	1108[e]	1099
D_{15}	1043	1036	1023	1015	1028	1032	1022	1028	1021	1029
D_{16}	842	828	857	837	835	821	829	818	827	817
D_{17}	748	738	763	753	677	665	654	646	641	638
D_{18}	586	575	570	568	557	548	547	540	547	537
D_{19}	529	516	551	540	492	480	470	459	465	454
D_{20}	429	425	440	431	375	364	295	284	250	243
D_{21}	265	282	295	287	253	244	211	203	189	181
a″										
D_{22}	[967][f]	965	970	962	974	969	969	967	966	968
D_{23}	928	923	922	925	930	932	930	932	932	933
D_{24}	844	837	844	845	846	846	844	844	845	844
D_{25}	749	747	746	743	747	745	746	744	747	744
D_{26}	711[c]	711	712[c]	711	705	706	700	700	699	695
D_{27}	542	544	570	553	538	538	533	534	531	530
D_{28}	442	441	448	447	440	431	435	429	434	432
D_{29}	315	258	330	283	263	256	256	248	250	242
D_{30}	191	171	198	187	174	155	159	140	143	126

[a] Infrared spectroscopy of the liquid unless otherwise indicated, from Ref. [34].

[b] B3LYP/aug-cc-pVTZ values scaled by 0.97 – this work (see text). The conformer used for the halophenols was "cis" with the OH in the phenyl plane and pointing towards the halogen. The conformer used for *o*-cresol was eclipsed, with one C–H group of the methyl in the plane of the phenyl ring, and *trans* with this C–H pointing away from the OH group, which is also in the plane of the phenyl ring and pointing away from the methyl group. We have noted the symmetric and asymmetric stretch, or the localized nature, of D_{10} and D_{12} explicitly.

[c] Ordering of these vibrations was uncertain in Ref. [34].

[d] Raman studies of liquid [25].

[e] Note that for *o*-cresol, the D_5 and D_6 vibrations are not in the same wavenumber order as in *o*DFB, but vibrations with similar motions have been given the same D_i label; this is also the case for D_{10} and D_{11} for *o*-cresol and

oFPhOH, and for D_{10}–D_{14} for oClPhOH, oBrPhOH and oIPhOH. The experimental wavenumbers have been ordered to match the calculated ordering.
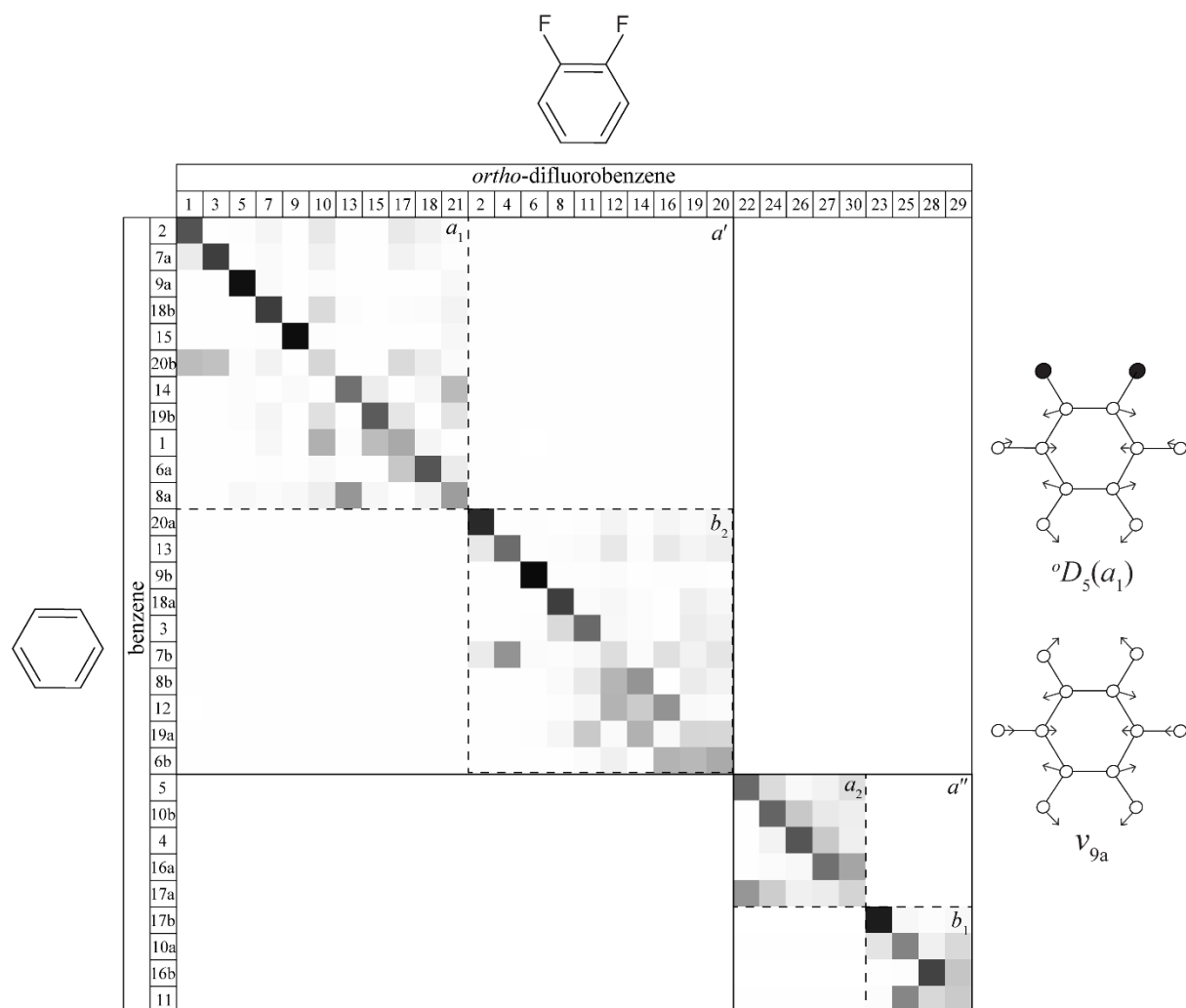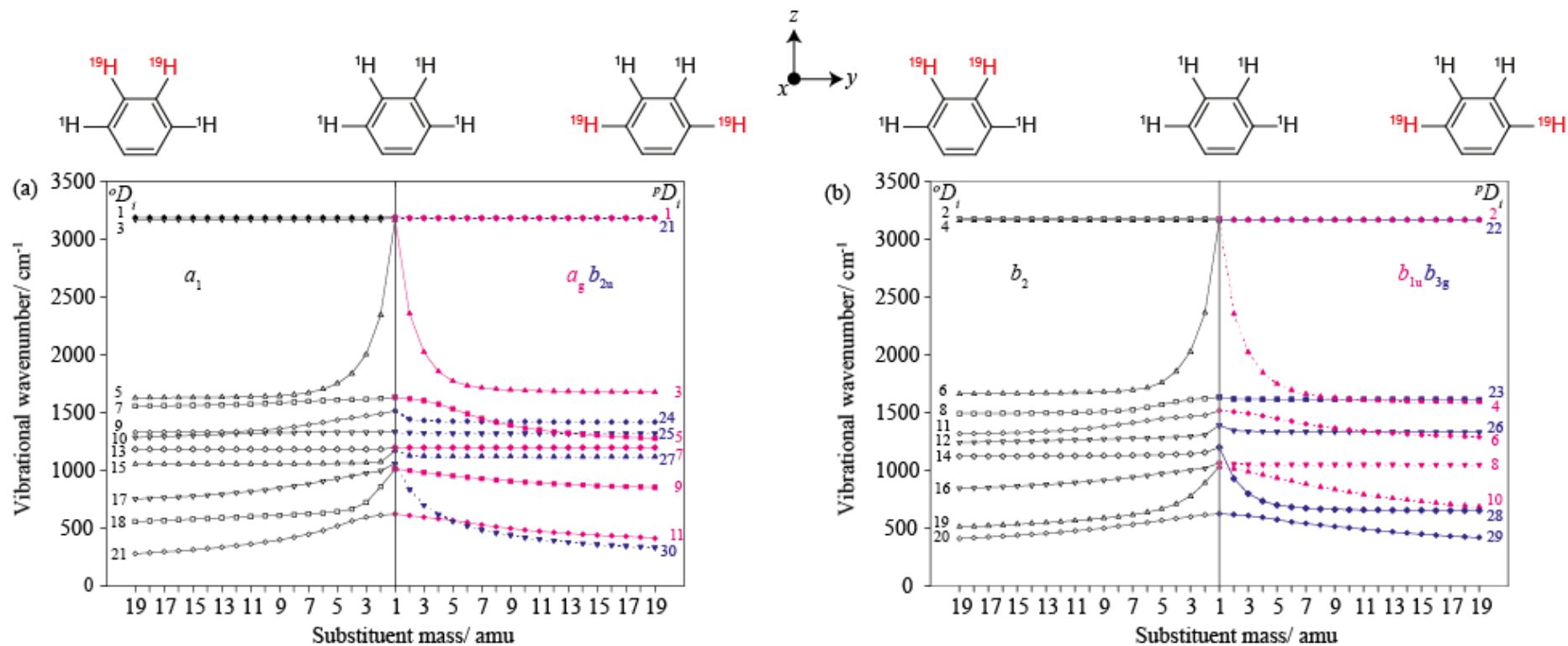
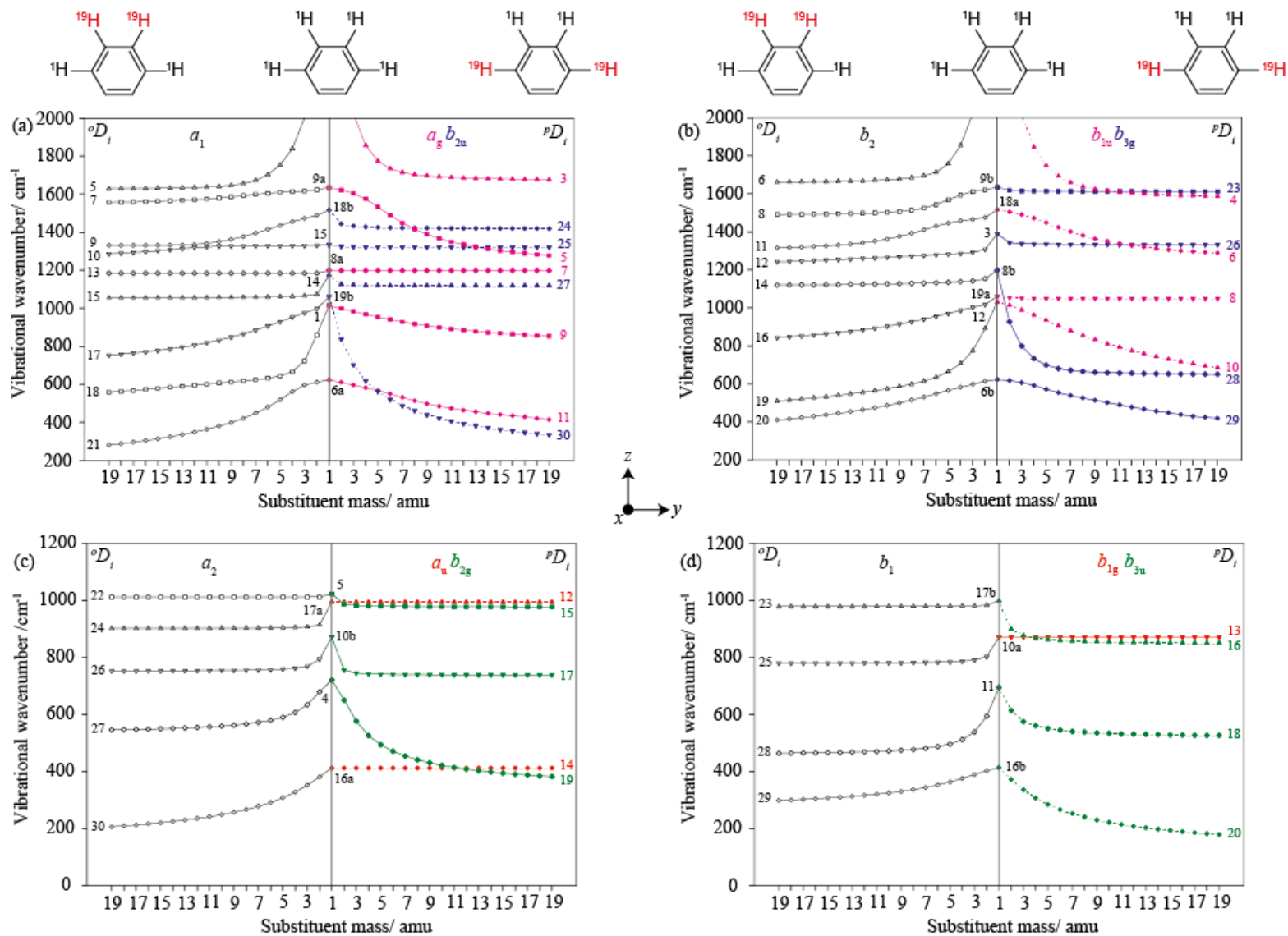^{f} Estimated value from Ref. [34].

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5
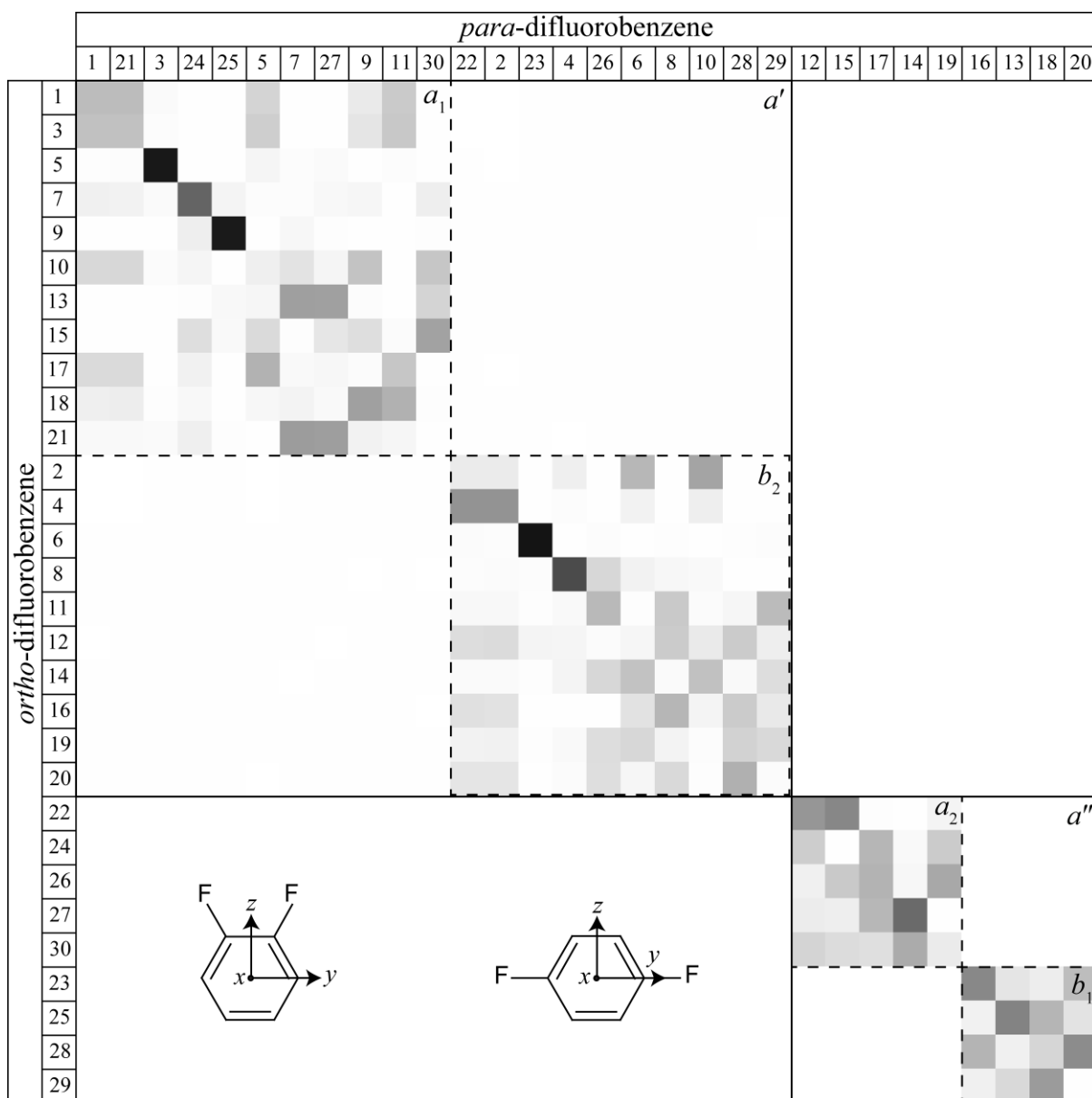
Figure 6

Figure 7

Figure 8

$^oD_1(a')$ $^oD_2(a')$ $^oD_3(a')$ $^oD_4(a')$ $^oD_5(a')$

$^oD_6(a')$ $^oD_7(a')$ $^oD_8(a')$ $^oD_9(a')$ $^oD_{10}(a')$

$^oD_{11}(a')$ $^oD_{12}(a')$ $^oD_{13}(a')$ $^oD_{14}(a')$ $^oD_{15}(a')$

$^oD_{16}(a')$ $^oD_{17}(a')$ $^oD_{18}(a')$ $^oD_{19}(a')$ $^oD_{20}(a')$

$^oD_{21}(a')$ $^oD_{22}(a'')$ $^oD_{23}(a'')$ $^oD_{24}(a'')$ $^oD_{25}(a'')$

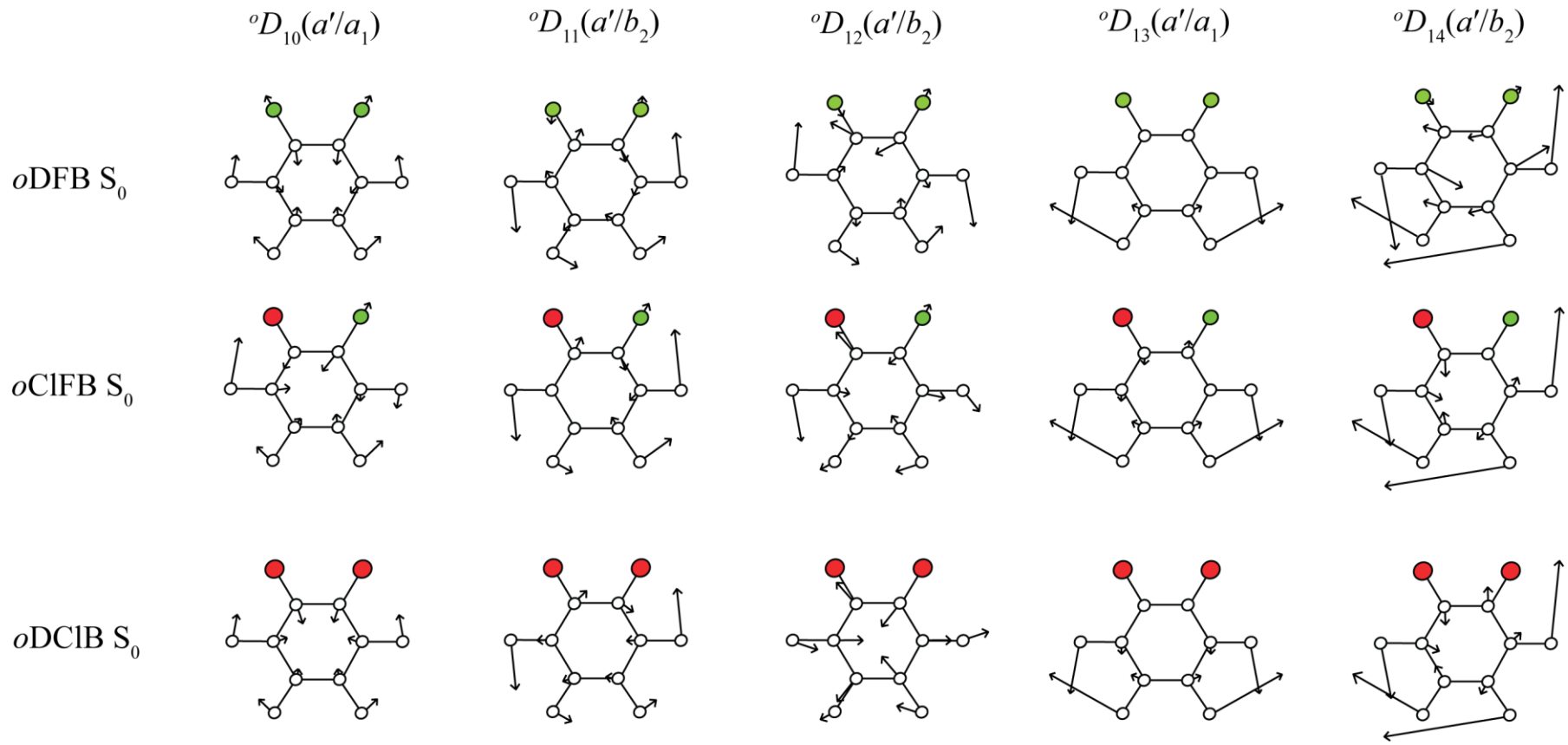$^oD_{26}(a'')$ $^oD_{27}(a'')$ $^oD_{28}(a'')$ $^oD_{29}(a'')$ $^oD_{30}(a'')$
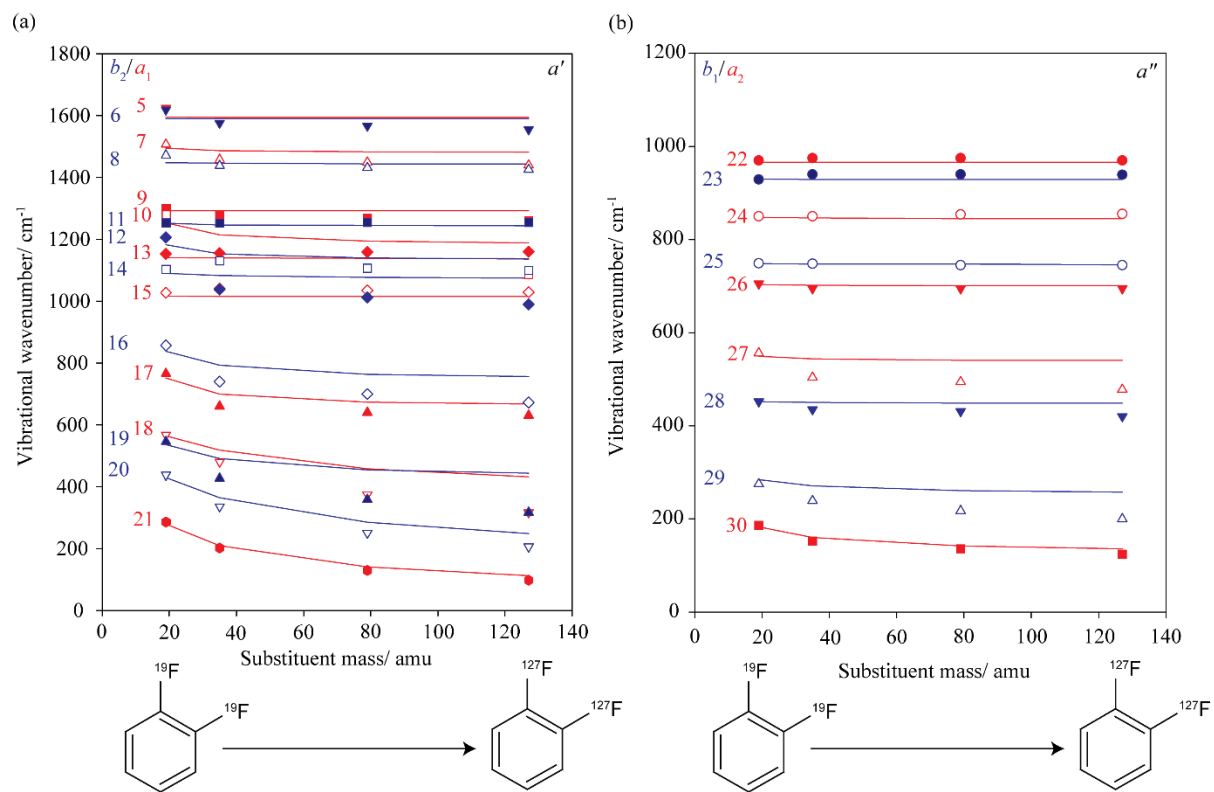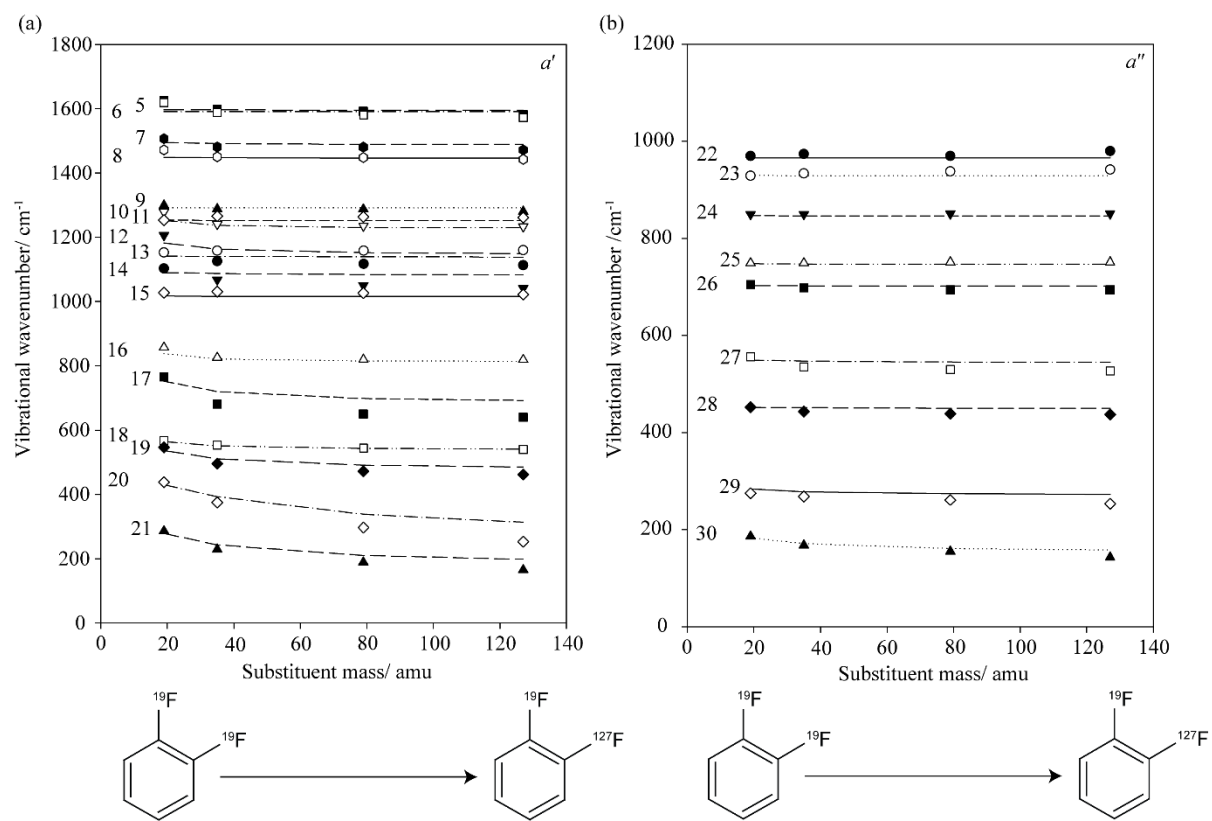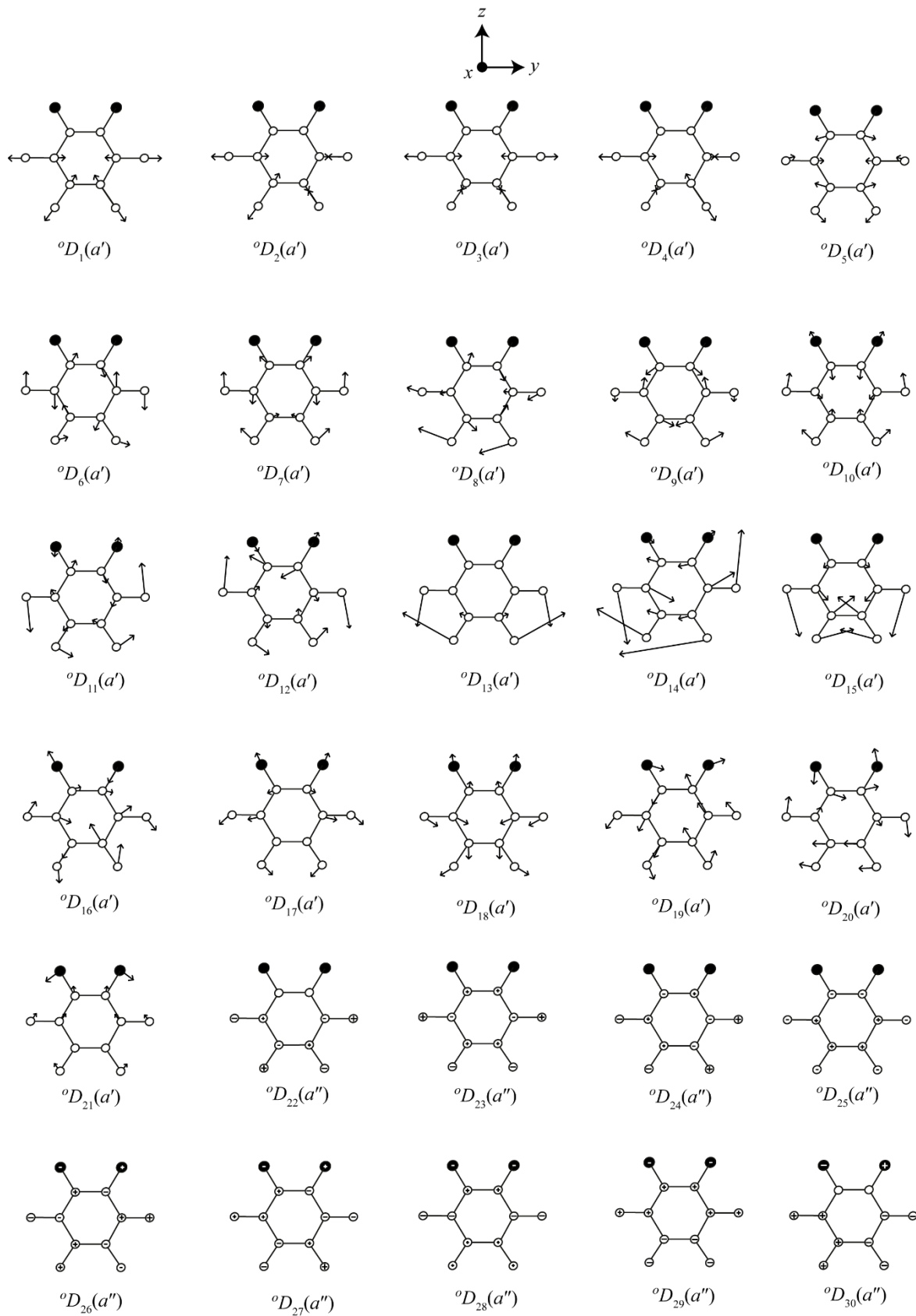
Figure 9

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