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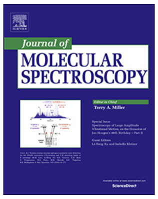

Article

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

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ABSTRACT

The assignment of vibrational structure in spectra gives valuable insights into geometric and electronic structure changes upon electronic excitation or ionization; particularly when such information is available for families of molecules. We give a description of the phenyl-ring-localized vibrational modes of the ground (S_0) electronic states of sets of *meta*-disubstituted benzene molecules including both symmetrically- and asymmetrically-substituted cases. As in our earlier work on monosubstituted benzenes (Gardner and Wright, 2011), *para*-disubstituted benzenes (Andrejeva et al., 2016), and *ortho*-disubstituted benzenes (Tuttle et al., 2018), 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. Instead, we label the phenyl-ring-localized modes consistently based upon the Mulliken (Herzberg) method for the modes of *meta*-difluorobenzene (*m*DFB) under C_s symmetry, since we wish the labelling scheme to cover both symmetrically- and asymmetrically-substituted molecules. By studying the vibrational wavenumbers obtained from the same force-field while varying the mass of the substituent, we are able to follow the evolving modes across a wide range of molecules and hence provide consistent assignments. We assign the vibrations of the following sets of molecules: the symmetric *meta*-dihalobenzenes, *meta*-xylene and resorcinol (*meta*-dihydroxybenzene); and the asymmetric *meta*-dihalobenzenes, *meta*-halotoluenes, *meta*-halophenols and *meta*-cresol. In the symmetrically-substituted species, we find two pairs of in-phase and out-of-phase carbon-substituent stretches, and this motion persists in asymmetrically-substituted molecules for heavier substituents; however, when at least one of the substituents is light, then we find that these evolve into localized carbon-substituent stretches.

1. Introduction

Vibrations are key quantities by which spectroscopists gain insight into both geometric and electronic structures of molecules. Analyzing the vibrational activity during electronic transitions or ionization allows elucidation of resultant changes in geometry and, by looking at the changes in vibrational wavenumber, information on changes in electronic structure can be inferred. For reliable comparison between like-families of molecules one desires the consistent assignment of the spectral lines, in terms of the normal modes of the molecules. Problems arise in these comparisons as even quite small changes in structure can lead to significant changes in the appearance of the spectrum. These changes may be due to a change in the symmetry point group of the molecule, shifts in vibrational wavenumber as a result of mass differences, and electronic effects.

In the present and related work, we have focused particularly on the study of substituted benzenes, where comparison between molecules has often been obfuscated through the use of three different vibrational labelling schemes: the Wilson mode labels [1]; the related Varsányi [2] scheme; and the "Mulliken" [3] (or "Herzberg") labels [4]. We have previously discussed these schemes in great detail for monosubstituted benzenes [5], and concluded these were unreliable. Our solution to these problems is highlighted in detail in Ref. [5] for the case of monosubstituted benzenes. It comprised the use of quantum chemical calculations to calculate the force field of benzene and then to increase artificially the mass of a single hydrogen atom stepwise. We found that the variations in wavenumber appeared largely to settle down when the substituent mass reached approximately 15 amu, and only small changes in wavenumber were observed for any

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vibration above this. This then allowed fluorobenzene to be chosen as a sensible basis for the labelling (a substituent of 19 amu). A notable aspect is that changes in vibrational wavenumbers were apparently not significantly dependent on electronic effects (resonance or inductive).

In a similar way, the vibrational character is expected to change for disubstitutions, which can be viewed as a disubstitution of benzene, or a further substitution of a monosubstituted benzene. In order to have consistent labelling of vibrational motions we have found that it is required to have separate labelling schemes for monosubstituted [5], *para*- [6] and *ortho*-disubstituted [7] benzenes. There is a degree of inconvenience in using multiple labelling schemes depending on the benzene isomer; however, this emphasises the point that assuming vibrations of different substituted benzenes are the same, as implied by Wilson or Varsányi labels, is misleading.

The labelling scheme for the monosubstituted benzenes has been applied in a series of papers on vibrationally-resolved electronic spectra of jet-cooled monohalobenzenes – see Refs. [8–10] – as well as in studies of toluene [11,12] using zero-kinetic-energy (ZEKE) spectroscopy and two-dimensional laser induced fluorescence [13]; similarly, we have applied the scheme for *para*-disubstituted benzenes, which can be either symmetrically or asymmetrically disubstituted, in analyzing the vibrational activity following either electronic excitation or ionization in *para*-fluorotoluene (*p*FT) [14,15], *para*-xylene (*p*Xyl) [16,17], and *para*-chlorofluorobenzene (*p*ClFB) [18]. Through the use of these schemes we have been able to show clearly the high correspondence in vibrational activity between the aforementioned molecules.

Herein, we shall complete our examination of the vibrations of the S_0 states of disubstituted benzenes by considering different *meta*-disubstituted benzenes. We shall again conclude that it is not possible to use the Wilson (or Varsányi) labels, nor the Mulliken (or Herzberg) labels consistently. Furthermore, we will conclude that it is not possible to use the monosubstituted, *para*- nor *ortho*-disubstituted schemes for *meta*-disubstituted benzenes. We put forward a new labelling scheme to be used exclusively for *meta*-disubstituted benzenes, covering both the symmetrically- and asymmetrically-disubstituted molecules. We employ a scheme based upon the lowest common point group shared by the disubstituted benzene family which, in this case, is C_s symmetry, and base it on the vibrations of *meta*-difluorobenzene (*m*DFB).

2. Computational details

All harmonic vibrational frequencies were obtained using B3LYP/aug-cc-pVTZ calculations via the GAUSSIAN 09 software package [19]. For bromine and iodine atoms, the full relativistic effective core potentials, ECP10MDF and ECP28MDF respectively, were used with corresponding aug-cc-pVTZ-PP valence basis sets. All calculated harmonic vibrational wavenumbers were scaled by a factor of 0.97 to account for anharmonicity and other deficiencies in the calculations. This level of calculation has been shown to be very reliable for the S_0 vibrational wavenumbers of a range of substituted benzenes. In the following, we shall calculate vibrational wavenumbers for the actual molecule, but also vibrational wavenumbers that are calculated using the force field of one molecule, but then artificially changing the mass of one or two atoms to match those of particular substituents (atomic or otherwise). In this way, we are able to map out changes in the vibrational wavenumbers that occur solely from the mass effect and so identify any deviations from these. In addition, we shall calculate generalized Duschinsky matrices using FC-LabII [20] to illustrate the expression of the vibrations of one molecule in terms of another. For each molecule, we show results for a specific conformer, which will be the lowest energy one that we found at the indicated level of theory.

3. Labelling the S_0 vibrational modes of *m*DFB

We have previously described our methodology in great detail in Refs. [5,6]. We will thus present our results, only including previous detail when necessary for clarity.

We begin first by comparing the vibrations of *m*DFB with those of benzene. Similar to the situation in Ref. [7], a choice must be made about the axis system to be used. For ease of comparison we require the atoms in the molecule to be aligned in a way that each atom of the first molecule must appear superimposed on an atom of the second molecule. We therefore choose to place both *m*DFB and benzene in the *yz* plane with the *z* axis passing through a C—H bond, and we select the one that is located between the C—F bonds for *m*DFB – see Fig. 1.

Fig. 1 represents a way of visualizing the vibrations of *m*DFB expressed in terms of those of benzene via a Duschinsky matrix approach. This method allows one set of vibrations to be fully expressed as linear combinations of another set of vibrations. The shading, noted in the figure caption, indicates the degree of similarity between the vibrations in the two molecules, with black meaning the vibrations are identical, and shades of grey quantitatively representing the degree of similarity. The data we extract from the Duschinsky matrix is also presented in a different form in Table 1. We have previously noted that there are some caveats regarding setting up the Duschinsky matrix, in terms of which axis system is chosen, and the reader is directed to Ref. [7] for these; here we shall move onto the results of our comparisons. The key conclusion from both Fig. 1 and Table 1 is that in many cases the modes of one molecule can only be expressed as significant mixtures of those of the other. Hence, in the majority of cases, it is not possible to associate a single Wilson label with a particular mode of *m*DFB leading us to, once again, conclude that the Wilson labels are not suitable.

We then move on to compare the modes of *m*DFB with those of monofluorobenzene (FBz) (with the latter using the M_i labels of Ref. [5]) using the same approach. Fig. 2 once again shows a Duschinsky matrix, allowing us to ascertain the degree of mixing between the vibrational modes. We have placed both molecules in the *yz* plane with the *z* axis passing through the C—F bond in FBz and passing through the same C—H bond in *m*DFB as before, this is shown in Fig. 2. This separates the vibrations of both molecules into the a_1, a_2, b_1 and b_2 C_{2v} symmetry classes, and no mixing occurs between different classes. We present a breakdown of the *m*DFB vibrations in terms of those of the monosubstituted vibrations, employing the M_i labels, in Table 1. As can be seen from both Fig. 2 and Table 1, many of the *m*DFB vibrations are formed from significant mixtures of the FBz vibrations, with only a small number of vibrations remaining largely unchanged and therefore, unsurprisingly given the conclusions for this approach for both the *para*- and *ortho*-disubstituted benzene molecules, it is apparent that one cannot use the monosubstituted benzene vibrational labels to describe the vibrations in *m*DFB.

We now consider how the vibrations of benzene evolve into those of *m*DFB as we artificially change the mass of two hydrogen atoms in the *meta*- positions stepwise, from 1 amu through 19 amu. This mass correlation approach maintains a constant force field and hence neglects any electronic effects on the vibrational wavenumbers. We may, therefore, obtain a mass-only view of any changes to the benzene vibrations. We once again align the molecules (as we did above) so that the vibrations are separated into the C_{2v} symmetry classes. Fig. 3 shows the plot for the

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