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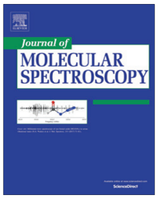

Consistent assignment of the vibrations of symmetric and asymmetric *ortho*-disubstituted benzenes

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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, 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, 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.

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

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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 [6–8] 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 *o*DFB

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

As a first step, we compare the vibrations of *o*DFB with those of benzene. There is an immediate problem, since a choice of axis system must be made. The C_2 axis in *o*DFB 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 *o*DFB with both molecules lying in the *yz* plane; further, to compare motions the atoms in the molecules need to be aligned, and we

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