Resonance-enhanced multiphoton ionization (REMPI) spectroscopy of bromobenzene and its perdeuterated isotopologue: assignment of the vibrations of the S_0, S_1 and D_0^+ states of bromobenzene and the S_0 and D_0^+ states of iodobenzene

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Abstract

We report vibrationally-resolved spectra of the $S_1 \leftarrow S_0$ transition of bromobenzene using resonance-enhanced multiphoton ionization (REMPI) spectroscopy. We study bromobenzene-h_5 as well as its perdeuterated isotopologue, bromobenzene-d_5. The form of the vibrational modes between the isotopologues and also between the S_0 and S_1 electronic states are discussed for each species, allowing assignment of the bands to be achieved and the activity between states and isotopologues to be established. Vibrational bands are assigned utilizing quantum chemical calculations, previous experimental results and isotopic shifts. Previous work and assignments of the S_1 spectra are discussed. Additionally, the vibrations in the ground state cation, D_0^+, are considered, since these have also been used by previous workers in assigning the excited neutral state spectra. We also examine the vibrations of iodobenzene in the S_0 and D_0^+ states and comment on previous assignments of these. In summary, we have been able to assign corresponding vibrations across the whole monohalobenzene series of molecules, in the S_0, S_1 and D_0^+ states, gaining insight into vibrational activity and vibrational couplings.

I. INTRODUCTION

The present work is a continuation of our previous work on fluorobenzene[1] and chlorobenzene,[2] in each case including the perdeuterated isotopologue. In those studies we recorded one-colour (1+1) resonance-enhanced multiphoton ionization (REMPI) spectra from 0–3000 cm^{-1} and assigned the vibrational structure observed. The spectra showed rich structure from both Franck-Condon allowed a_1 and vibronically-allowed b_2 vibrations, with higher-wavenumber features mainly consisting of overtones and combinations of vibrations seen to lower wavenumber. (Here, we position the molecule in the *yz* plane, to establish the b_1/b_2 labels unambiguously.) There were numerous Fermi resonances (FRs) observed, with these generally being different between the respective isotopologues, owing to vibrations moving in and out of resonance because of isotopic shifts. In the case of chlorobenzene, shifts arising from the presence of both ^{35}Cl and ^{37}Cl were extremely useful in establishing the assignment when there was more than one possibility. In the present work we shall denote the isotopologue of perhydrogenated bromobenzene as BrBz-h_5 and similarly for the fully-deuterated isotopologue, BrBz-d_5; we will only note the isotope of Br as required, but only little use is made of $^{79}Br/^{81}Br$ shifts in this work, as these were so small. When required, the other monohalogenated benzenes will be denoted in a similar manner, using FBz for fluorobenzene, ClBz for chlorobenzene and IBz for iodobenzene. We concentrate initially on BrBz and then at the end of this paper we shall briefly discuss IBz.

The infrared (IR) and Raman spectra of BrBz-h_5 have been reported by a number of workers,[3,4,5,6,7] with reasonable consistency between the reported values where these have been observed in more than one study. The assignment of the spectra has been achieved in terms of symmetry, by noting the band-type, and also in terms of expected positions of vibrations based upon various mass-scaling rules. Two main schemes for labelling the vibrations have been employed, with Wilson[8]-type labels being used by Varsányi[5] and, albeit with some (unexplained) switches, by Walter et al.[9]As noted and discussed in our previous work[10] the Varsányi (Wilson) labels are used inconsistently across the monohalobenzenes and so we use a different labelling scheme based on the Mulliken[11] labelling of the FBz S_0 modes, and we denote these M_i, with the motions available in ref. 10. This scheme maintains the same label for the same vibrational motion, and hence vibrational activity can be easily compared between molecules. (It should be noted that using the Mulliken labelling for the heavier monosubstituted halobenzenes will give some vibrations in a different order, owing to different mass shifts – see ref. 10.)

Very brief reports of the UV absorption spectrum of bromobenzene vapour have been given by Walerstein[12] and Sreeramamurty.[13] In addition, a study by Prakash and Singh[14] has reported a reasonably detailed UV absorption spectrum of BrBz vapour, predominantly at 0 °C. Klimusheva et al.[15] have reported absorption spectra of bromobenzene in both vapour (20 K) and crystals (4 K), but little experimental detail is given, nor are any spectra shown. We shall comment on these studies at appropriate points below.

Jet-cooled studies of the $S_1 \leftarrow S_0$ transition has been reported by Dietz et al.[16] and Boesl and coworkers[9,17] where Wilson/Varsańyi labelling was employed. The Wilson/Varsányi assignments between the two main studies[9,16] were not wholly consistent, and in part this results from the fact that many of these do not correspond to the correct vibrational motion. Such assignments can be made by analogy with spectra from similar molecules and a detailed consideration of mass and electronic shifts; however, the most robust assignment will come from comparison also with reliable quantum chemical calculations. In the below we shall discuss the previous assignments with those here. We shall establish assignments of the observed bands that are consistent with our previous monohalobenzene work, and so remove the ambiguity of the previous assignments for bromobenzene and provide a more coherent picture of the vibrational activity in the monohalobenzene species.

The vibrations of the cation have been probed via conventional photoelectron spectroscopy (PES),[18, 19] REMPI-PES[9] and one-photon MATI studies.[20] In the case of the REMPI-PES experiments, the assignment of the photoelectron spectrum and the resonant S_1 level are linked, and so these will be discussed as part of the present work in Section IV. C. 4

BrBz-d_5 has been much less studied compared to its non-deuterated isotopologue. Vibrationally-resolved IR and Raman spectra of the S_0 state have been reported by Nanney et al,[21] where assignments were given in Mulliken notation and (cautiously) in terms of an approximate description of the atomic motions; comparison was also made to the wavenumbers of the corresponding vibrations in ClBz-d_5 and FBz-d_5. The BrBz-d_5 vibrations were given Wilson-type labels by Varsányi[5] (see Table 1). To the best of our knowledge there have been no reports of the $S_1 \leftarrow S_0$ transition or any photoelectron spectrum for this isotopologue.

In the present work, we employ one-colour REMPI spectroscopy to record rotationally-cold, vibrationally-resolved electronic spectra of the $S_1 \leftarrow S_0$ transition in BrBz-h_5 and BrBz-d_5, for each of their ^{79}Br and ^{81}Br isotopologues. The spectra are assigned using: the observed experimental isotopic shifts; available previous experimental and theoretical results; and quantum chemical calculations for all of the isotopologues, carried out in the present work. The REMPI spectrum of BrBz-d_5 is reported here for the first time and, as with our previous work on FBz and ClBz,[1,2] we examine how the vibrations in the perdeuterated isotopologue compare to those of the perhydrogenated molecule. In addition, we consider the Duschinsky mixing of the vibrational modes that occurs between the S_0 and S_1 states for each isotopologue. In some cases, comparison between the activity seen in BrBz with that seen in FBz and ClBz is insightful. Since some of the assignments of the S_1 state vibrations depend on those of the cation via REMPI-PES spectra, we shall also examine the vibrations of the ground state cation of BrBz.

Towards the end of the paper, we shall also consider the vibrations of the S_0 state of IBz. We shall not consider the S_1 state vibrations, as this state is known to be extremely short lived and no fluorescence or REMPI spectrum has been reported (see later). We shall also consider the vibrations of the ground state cation, since

these have been observed by direct photoionization both using conventional PES[19, 22] and also mass-analyzed threshold ionization (MATI) spectroscopy.[20]

II. EXPERIMENT

The third harmonic (355 nm) of a neodymium-doped yttrium aluminium garnet laser (Nd:YAG, Surelite III, 10 Hz) was used to pump a tuneable dye laser (Sirah Cobra Stretch), operating on Coumarin 503. The fundamental output of the dye laser was frequency doubled by a beta-barium borate (BBO) crystal in order to obtain tuneable UV radiation across the wavenumber region of interest.

BrBz-h_5 (Aldrich, 99.8% purity) or BrBz-d_5 (Aldrich, 99 atom% D) vapour, each with the naturally-occurring ratio of ^{79}Br:^{81}Br, was seeded in ~5 bar of helium carrier gas and the gaseous mixture was passed through a General Valve pulsed nozzle (750 μm, 10 Hz, opening time of 180 μs) to create a free jet expansion. In our previous work on FBz and ClBz we employed Ar as the seeding gas, but we found the BrBz spectra were too warm (and hence broad) when this was used here; we attribute this to clustering and subsequent break-up; this also occurred even when using Ne. On the other hand, using He, we found it much easier to obtain cold spectra. The focused, frequency-doubled output of the dye laser passed through a vacuum chamber where it perpendicularly intersected the free jet expansion between two biased electrical grids located in the extraction region of a time-of-flight spectrometer. After (1+1) ionization occurred, the resulting ions were extracted and detected by a dual microchannel plate (MCP) detector. The signal was passed to an oscilloscope (LeCroy LT342 Waverunner) for monitoring, and a boxcar (SRS SR250) for integration and averaging; the averaged signal was then relayed to a computer for storage and analysis. The timing of the laser pulse relative to the opening time of the pulsed nozzle was controlled using a digital delay generator. The delays were varied to produce optimum conditions to ensure that the coldest part of the beam was probed. The calibration procedure is described in Section IV.

III. COMPUTATIONAL METHODOLOGY

In order to aid in the assignment of the spectra, the vibrational frequencies of each molecule were calculated using the GAUSSIAN 09 software package.[23] For the S_0 ($\tilde{X}\ ^1A_1$) state and the ground cation D_0^+($\tilde{X}\ ^2B_1$) state, (U)B3LYP/aug-cc-pVTZ calculations were used; whereas for the S_1 ($\tilde{A}\ ^1B_2$) state TD-B3LYP/aug-cc-pVTZ calculations were employed; for Br and I, these were the valence forms of these basis sets, used with the ECP10MDF and ECP28MDF small-core, relativistic effective core potentials. All of the harmonic vibrational wavenumbers were scaled by the widely used factor of 0.97, although this is only an approximate way of getting "anharmonic" values. For the unrestricted calculations $<S^2>$ values were all ~ 0.76 showing that spin contamination was minimal.

The vibrational modes of the BrBz-h_5 and IBz-h_5 S_0 states were labelled by comparing the molecular vibrational displacements with those of FBz-h_5 via a generalised Duschinsky matrix approach employing the FC-LabII program,[24] as discussed in ref. 10. This provided a clear assignment of the phenyl ring-localized vibrations. For BrBz-d_5 and IBz-d_5, the molecular vibrational motions were compared to those of BrBz-h_5 and IBz-h_5, respectively, in their S_0 states via a generalized Duschinsky approach using FC-LabII. Similarly, vibrations in the S_1 and D_0^+ states could be compared to those of the respective S_0 state, and those of the respective S_1 and D_0^+ states to each other.

IV. RESULTS AND ASSIGNMENTS

A. Overview of the $S_1 \leftarrow S_0$ spectra.

The (1+1) REMPI spectra of BrBz-h_5 (upright, top trace) and BrBz-d_5 (inverted, bottom trace) from 0 – 3050 cm^{-1} are shown in Figure 1 — the assignments are discussed below. Only the spectra for the ^{79}Br isotopologues are shown; the spectra of the ^{81}BrBz isotopologues exhibited only very small isotopic shifts compared to the ^{79}BrBz isotopologues, and will only be commented on occasionally. We have not corrected for laser intensity, as we believe this is not straightforward to do reliably.

We calibrate the ^{79}BrBz-h_5 spectrum to the band origin of 36991.5 ± 0.2 cm^{-1} by comparing with a simulation of the origin band origin using PGOPHER[25] and using the rotational constants taken from Ref. 26; additionally, this allowed a rotational temperature of 20–30 K to be established: warmer than we obtained for FBz and ClBz, but in line with the use of He rather than Ar. It was then found that the ^{81}BrBz-h_5 origin band was at the same position, within our experimental uncertainty, showing that the S_1 origin bands of the ^{79}Br and the ^{81}Br isotopologues are within 0.5 cm^{-1} of each other, consistent with the result of de la Cruz et al.,[27] who determined the difference to be < 0.02 cm^{-1}. For the BrBz-d_5 origin transition, an isotopic blue shift of 171.4 cm^{-1} is determined from our spectra, which locates the origin at 37162.9 ± 0.5 cm^{-1}. The two spectra presented in Figure 1 have been plotted on a relative scale, with the origin transitions each shifted to zero for straightforward comparison between the different isotopologues. Our vibrational bands are not fully rotationally resolved in either the BrBz-h_5 or BrBz-d_5 spectra and so we have employed the wavenumber of the most intense part of each vibrational band, in order to determine consistent vibrational spacings; although this may give small discrepancies with respect to the actual vibrational band origins, this is acknowledged to be the most consistent way of reporting these spacings. In any case, we have ascertained the reliability of this procedure by simulating different band profiles and comparing the position of the maxima in the rotational envelope relative to the band center. We find that these positions fall within the stepsize of our scans (0.5 cm^{-1}) and so any discrepancy in vibrational spacing arising from different band types will not introduce an error of more than 1 cm^{-1}; this will be similar to the error that would have been obtained employing band centers to derive the vibrational spacings.
We have checked our calibration against other spectra and although there are discrepancies, it does not seem that there are "bigger errors" to higher energy; we have checked our spectra in both wavenumber

and wavelength, and against spectra of other molecules, and our calibration appears to be sound across the spectral range cited.

The BrBz-h_5/ BrBz-d_5 isotopic shift of each vibration is clearly mode specific as participation of the hydrogen atoms is different – this will be more clearly seen in expanded spectral views presented later. The $^{79/81}$Br isotopic shift is very small, < 1 cm^{-1} for 29 of the 30 vibrational modes, apart from for M_{11}, which has an isotopic shift of 1.6 cm^{-1} for BrBz-h_5 and BrBz-d_5 isotopologues. (For the interested reader, calculated vibrational wavenumbers of the S_0, S_1 and D_0^+ states of ^{81}BrBz-$h_5^{(+)}$ and ^{81}BrBz-$d_5^{(+)}$ are given in Tables S1 and S2 of the Supplementary Material.[28])

In the following, we shall tackle the assignments of the BrBz-h_5 and BrBz-d_5 spectra simultaneously, considering spectral ranges separately. Our assignments are aided by previous work on BrBz-h_5 as well as the calculated vibrational frequencies, and use will also be made of previously-observed activity in our corresponding spectra of FBz and ClBz.[1,2] First we shall comment on the vibrational assignments of the S_0 state.

B. Calculated vibrational wavenumbers.

1. S_0 state

We shall only discuss vibrations for the ^{79}Br isotopologues here – those for the ^{81}Br one are very similar, and the calculated values are given as supplementary material.[28]

In ref. 10 we briefly discussed and assigned the S_0 vibrations of BrBz-h_5 in terms of the M_i vibrational modes; as such, we shall only note that the motions are very different to those of benzene, and so Wilson modes are inappropriate (Table 1 shows how mixed some of the modes are). On the other hand, correspondences between the vibrations of FBz-h_5 and BrBz-h_5 are very good (see Table 1 and Figure 2). As a consequence, we provide the Wilson/Varsányi mode labels used by other workers in Table 1, but only to aid the reader. In the text here we shall use M_i labels, when discussing our assignment and also when comparing to previous work. In Table 2 we compare our calculated vibrational wavenumbers for BrBz-h_5 with the experimental ones, where excellent agreement is seen. (We note that our calculated values are in very good agreement with the B3LYP/aug-cc-pVDZ values given in ref. 10, bearing in mind those were unscaled, as are the comparisons with the Wilson modes of benzene.)

For BrBz-d_5 we note that Nanney et al.[21] reported IR and Raman spectra, assigning the modes by virtue of the rotational band type and by comparison with vibrational wavenumbers for FBz-d_5 and ClBz-d_5; these trends were continued when assigning the corresponding spectra of IBz-d_5, which will be mentioned later. Wavenumbers for all 30 vibrational modes were obtained from fundamentals, overtones and combination bands, although a couple were uncertain. The assignment was given in terms of Mulliken nomenclature, and as noted

above this could lead to some discrepancies with the M_i labels owing to reordering following mass-dependent shifts across the monohalogenated benzene series. Since the agreement between the calculated and experimental values is excellent for both BrBz-h_5 and BrBz-d_5, then we can use the calculated values to confirm the assignment of Nanney et al.'s wavenumber values[21] to the M_i^d labels. (We note that while the appending of the ^{d} superscript to the M_i labels is often superfluous, it is maintained for consistency and clarity both within the present text, and with our earlier work.) The Duschinsky matrix in Figure 3 shows that the motions of the M_i^d vibrations are very similar to the M_i modes in most cases; however, the wavenumber ordering of the vibrations changes, as it does for FBz[1] and ClBz.[2] In particular, for FBz-h_5 the ordering is $M_9 < M_8 < M_7 < M_6$ (by construction), while for FBz-d_5 the ordering is $M_8^d < M_7^d < M_9^d < M_6^d$; for ClBz-$h_5$ the ordering is $M_9 < M_8 < M_6 < M_7$, while for ClBz-d_5 the ordering is again $M_8^d < M_7^d < M_9^d < M_6^d$. For BrBz, we find the same orderings in the S_0 states as for the respective ClBz isotopologues. The assignment from Nanney et al.'s wavenumber values is straightforward in most cases; we merely note that the estimated 2275 cm^{-1} value is consistent with our calculated value of 2269 cm^{-1} for M_3^d, the wavenumber of M_8^d is uncertain since in ref. 21 a band at 817 cm^{-1} was observed in the IR spectrum, but one at 826 cm^{-1} observed in the Raman one; these are close enough to our calculated value of 815 cm^{-1} that it is difficult to decide between them definitively.

2. S_1 state

The calculated wavenumbers for the S_1 state of the ^{79}BrBz-h_5 and ^{79}BrBz-d_5 are given in Table 3; these have been used to help in the assignment of the spectra, together with previously reported assignments of the ^{79}BrBz-h_5 spectra. Figure 4 shows the Duschinsky matrices for the S_1 vibrations in terms of the S_0 ones for each isotopologue. As was the case for FBz and ClBz, these indicate that there is more rotation of the vibrational coordinates for BrBz-h_5 than for BrBz-d_5, as such some of the vibrations in that S_1 state will be somewhat different to those in the S_0 state. In particular, we found that the M_8 and M_9 modes were significantly mixed (as we noted for ClBz), and have labelled these to be consistent with our previous work.

One other point of note is that in the Duschinsky matrix, the M_6^d and M_8^d modes are quite mixed in the S_0 state, with the coefficients suggesting their order has changed; however, it is clear from the spectra here and our previous assignments of these modes for FBz and ClBz, that in fact the M_8^d vibration has the lower wavenumber. (It is then clear from the $S_1 \leftarrow S_0$ Duschinsky matrix in Fig. 4b that the same ordering applies to the S_1 state.) We think this anomaly lies in the similarity of these two modes (see ref. 10), with the major difference being the stretching of the carbon–substituent bond. As the substituent gets heavier, this motion becomes smaller, and then determining the difference between these two modes in the Duschinsky procedure becomes less clear although these can be identified visually in animations. The comparison of the -h_5 and -d_5 spectra with the corresponding ones for FBz and ClBz does, however, make the assignment of these modes clear, as noted above and discussed below.

C. Assignment

We now move onto the assignment of the spectra, which we split into three main wavenumber regions. We shall discuss the assignment of the spectra for the ^{79}BrBz-h_5 and ^{79}BrBz-d_5,with the assignments for the ^{81}Br ones being the same. To assign the spectra, we have used the previous assignments as a guide, but have mainly relied on our calculated wavenumbers and our previous assignments of the FBz[1] and ClBz[2] spectra for both -h_5 and -d_5 variants. As low-wavenumber bands become assigned, the vibrational wavenumbers of these are used to assign the higher-wavenumber features; occasionally this process worked in reverse. We denote transitions by the upper vibrational level, since all transitions, unless noted, are from the zero point vibrational level in the ground electronic state.

1. Low wavenumber range (0- 750 cm^{-1})

a. BrBz-h_5

As may be seen from Figure 5, this region is dominated by the origin transition and that to the M_{29} level for both isotopologues. Concentrating first on BrBz-h_5, in the low-wavenumber region below 300 cm^{-1} we see a similar pattern of features we saw previously for FBz and ClBz, and so these mostly can be straightforwardly assigned as shown in Figure 5 and Table 4. We note that the M_{11} band is slightly red shifted in the ^{81}BrBz-h_5 spectrum (not shown), and indeed this is a signature that helps in the assignment of higher wavenumber combination bands. It is a peculiarity of the monohalobenzenes that the calculated wavenumber for the M_{14} vibration in the S_1 state is always in very poor agreement with the experimental value using the TD-B3LYP approach; indeed, in the present case, we did not even obtain a real value. As a consequence, we have relied on previous assignments and a process of elimination to assign features involving this vibration. First we note that at 462 cm^{-1}, we find a band whose assignment to the M_{14}^2 transition was considered. This assignment was rejected since it goes against the trend of falling wavenumber for the M_{14} vibration with substituent mass. Instead, we assign M_{14}^2 to the weak feature at 362 cm^{-1}, which has the added advantage that it allows us to identify the band at 278.5 cm^{-1} with the $M_{14}M_{20}$ combination transition – a corresponding band was seen in ClBz.[2] Further, as will be seen below, it is then straightforward to identify corresponding vibrations in BrBz-h_5 which also have expected trends when comparing with FBz and ClBz. We note that Prakash and Singh[14] attributed a band at 360 cm^{-1} to an overtone of a vibration with a_2 symmetry, which is consistent with the assignment offered here. This then leaves us requiring an assignment of the 462 cm^{-1} band. A clue to this comes from the calculated wavenumbers, the wavenumber value of M_{14}, and the corresponding spectrum of ClBz. In the latter, the M_{29} vibration is in FR with the $M_{14}M_{19}$ combination, which is almost isoenergetic, and two very close bands of almost the same intensity result. We assign the 462 cm^{-1} feature here to $M_{14}M_{19}$, which we assume is shifted from its non-perturbed value by FR. It is also possible to obtain a wavenumber for M_{19} from the calculations and comparing with the calculated and experimental values in ClBz. This leads us to expect the M_{19} vibration at ~ 310 cm^{-1}, and hence the $M_{14}M_{19}$ vibration should appear at ~491 cm^{-1}. With anharmonicity, FR and uncertainty in the values, we feel this assignment of the 462 cm^{-1} is reasonable, but clearly further evidence from dispersed fluorescence or ZEKE

spectroscopy is needed to confirm this assignment. As will be noted later, the estimated value of M_{19} suggests the overtone (seen for BrBz-d_5) may be obscured by the M_{10} transition.

At 521.5 cm^{-1} the intense, vibronically-allowed M_{29} transition appears and as noted above, this vibration is in Fermi resonance with the $M_{14}M_{19}$ combination in ClBz-h_5, but the mass effect has shifted the latter to lower wavenumber, but it still appears in the spectrum here. This is followed by a weak feature at 539.0 cm^{-1} that can be assigned to $M_{11}M_{30}$ and then the commonly-observed M_{10} at 623.0 cm^{-1}. The weak feature at 733.0 cm^{-1} is in the correct position to be the $M_{20}^2M_{29}$ transition, while the 741.0 cm^{-1} band is tentatively assigned to the $M_{13}M_{14}$ combination.

Walerstein[12] notes the appearance of a band with a value of 242 cm^{-1} (assigned to M_{30} here), which was thought to correspond to a totally-symmetric vibration. We also note that the M_{30} band was seen by Dietz et al. at 240.5 cm^{-1},[16] but they assigned this to an overtone in that work; interestingly, Prakash and Singh[14] offered a similar assignment. However, the calculated values and comparison with previous work on FBz and ClBz (confirmed by dispersed fluorescence and/or zero-kinetic energy, ZEKE, spectroscopy – see refs. 1 and 2) suggest the present assignment to M_{30} (b_2 symmetry) is the correct one.

Dietz et al.[16] and Prakash and Singh[14] also saw the M_{11} feature and assigned it to the ν_{6a} Wilson mode; however, as Table 1 shows the M_{11} mode is of very mixed Wilson-mode character and in fact it is the M_{10} mode that corresponds to the Wilson ν_{6a} mode. The M_{10} mode itself was reported in ref. 16 as Wilson mode 1 at 620.8 cm^{-1}, which is in agreement with our spectrum, and such a feature was also seen in ref. 14. In general, reasonable agreement is seen in this range with the results of Klimusheva et al.[15] for the vibrational wavenumbers that they were able to deduce from their 20 K vapour absorption spectrum, but the values for M_{11} M_{14} and M_{30} are somewhat higher than other reported values and those obtained here (see Table 3).

The assignment of the M_{29} band at ~520 cm^{-1} is consistent with the assignment in ref. 16 to the close-to-pure ν_{6b} Wilson mode and to a non-totally-symmetric vibration by Walerstein;[12] a vibration of ~520 cm^{-1} was also reported in ref. 13. The assignment of M_{29} has also been confirmed in the REMPI-photoelectron spectroscopy (REMPI-PES) study of Walter et al.,[9] which we shall comment on further below, and in the absorption study of Prakash and Singh.[14]

In a short report, Sreeramamurty[13] observed a difference wavenumber of 221 cm^{-1}, but did not assign this. The same spacing (albeit 225 cm^{-1}) was reported by Prakash and Singh[14] who attributed it to a 1–1 hot band, suggesting $M_{14}{}_1^1$, which is consistent with the ground and excited state values given here in Tables 2 and 3.

b. BrBz-d_5

As far as we are aware, there have been no previous studies of the BrBz-d_5 isotopologue, and so the assignment of this spectrum relies on the calculated vibrational wavenumbers/isotopic shifts and our previous assignments of the two lighter monohalobenzenes.[1,2] In the region below 300 cm^{-1} the three vibrations observed in BrBz-h_5 are present with relatively similar positions, consistent with the small calculated isotopic shifts for these. A band at 309.1 cm^{-1} is assigned as $(M_{14}^2)^d$, based on the expected large H/D isotopic shift and consistent with the behaviour seen previously for FBz and ClBz. This would give a predicted position for the $(M_{14}M_{20})^d$ combination as ~254 cm^{-1}, so the weak band at 249.1 cm^{-1} can be cautiously assigned to this band, with the difference attributable to anharmonicity. We note that the M_{11} band is slightly red shifted in the ^{81}BrBz-d_5 spectrum (not shown), consistent with the present calculated values (see supplementary material[28]).

The M_{29}^d feature appears strongly at 493.6 cm^{-1}, and we note that there is no obvious band that can be assigned to $(M_{14}M_{19})^d$ which is straightforwardly attributed to its being too separated in wavenumber, with the combination expected at ~419 cm^{-1}; a similar picture emerged for ClBz.[2]

To slightly higher wavenumber there is a small group of features, which we have marked α. From the calculated wavenumbers, and the spectrum of BrBz-h_5, we would expect the $(M_{11}M_{30})^d$ transition to appear here, and this would be expected at ~ 518 cm^{-1}. Since the $M_{11}M_{30}$ transition was weak in BrBz-h_5, we conclude there is a FR in BrBz-d_5 between $(M_{11}M_{30})^d$ and M_{29}^d. On the basis of the vibrations assigned thus far, the attribution of other vibrations close to 518 cm^{-1} seems not to be possible. Insight is achieved, however, with the assignment of the 560.1 cm^{-1} feature to $(M_{13}M_{14})^d$, consistent with the tentative assignment of a corresponding band in BrBz-h_5 and the calculated shifts upon deuteration; this gives a value for M_{13}^d of ~406 cm^{-1}. As a consequence of this, an assignment of a contributor to feature α of $(M_{13}M_{20})^d$ can be explored. Although the expected wavenumber of this transition based on half the value for the M_{20}^d overtone seems too low, it should be remembered that the latter vibration is likely to be quite anharmonic. In fact the calculated harmonic value of M_{20}^d is 112 cm^{-1}, giving an expected position of $(M_{13}M_{20})^d$ of 518 cm^{-1}, and so this is a plausible contributor to feature α. Additionally, we note that this combination is of b_2 symmetry and so could be in Fermi resonance with M_{29}^d and/or $(M_{11}M_{30})^d$, perhaps explaining why it is seen in the spectrum of BrBz-d_5 and not in that of BrBz-h_5. To slightly higher wavenumber is a band at 528.1 cm^{-1} whose assignment can be deduced from the equivalent spectrum for ClBz-d_5 where the $(M_{19}^2)^d$ transition was identified, giving a value for M_{19}^d that was also about 30 cm^{-1} lower than the calculated value. The calculated value of 297 cm^{-1} for BrBz-d_5 would suggest a M_{19}^d wavenumber of ~267 cm^{-1}, and hence a transition to the overtone, $(M_{19}^2)^d$, at ~ 528 cm^{-1} can be tentatively assigned. (With this assignment, we can use the differences in the calculated and experimental values for M_{19}^d to estimate the value for M_{19}, obtaining a value of 311 cm^{-1}, suggesting M_{19}^2 could be lying underneath the M_{10} feature, with there being some indication of a second feature there; this is also consistent with the position of the $M_{14}M_{19}$ mentioned above.)

The band at 604.1 cm^{-1} can be assigned to M_{10}^d and it is interesting to note that this is quite weak; in FBz-d_5 and ClBz-d_5 the same transition was also weak and this was attributed to its being involved in complex Fermi

resonances, but this seems not to be the case here. The only other band of note in this region is one at 714.1 cm^{-1}, with $(M_{29}M_{30})^d$ being our favoured assignment.

2. Medium wavenumber range (750-1050 cm^{-1})

a. BrBz-h_5

This region is dominated by three main features at ~934 cm^{-1}, ~963 cm^{-1} and ~1023 cm^{-1} and interestingly there is very little structure in the range 750–900 cm^{-1}. With regard to comparison with previous spectra and calculated fundamentals, the main expected contributors to these features are M_8, M_9 and M_6, respectively. The agreement between the calculated wavenumbers for the M_8 and M_9 vibrations and that observed is good, while that for M_6 is calculated to be ~ 30 cm^{-1} too low, as was seen previously for the two lighter monosubstituted benzenes.[1,2] The two higher-wavenumber features have a width consistent with a single contribution, and so these are safely assigned as labelled in Figure 6; the lowest wavenumber feature has a width suggestive of further contributors than M_8: we have marked this feature β. One obvious contributor to this feature, based on previous work, would be $M_{10}M_{11}$, which also has a_1 symmetry and so could be in FR with the M_8 vibration. It is expected at ~920 cm^{-1}, calculated from the sum of the wavenumbers of the two contributors, with both anharmonicity and FR expected to push the band lower in wavenumber. We conclude that this transition is associated with a weak feature on the low wavenumber (~918 cm^{-1}) side of region β, which is consistent with a small red shift seen for this feature in the ^{81}BrBz-h_5 spectrum (not shown). There is no obvious other fundamental of a_1 or b_2 symmetry that could contribute to region β, nor is there an overtone, but comparison with the corresponding FBz spectrum suggests the $M_{15}M_{20}$ combination band could be contributing to the central region at ~ 931 cm^{-1}, and that the corresponding vibration is in FR with the M_8 vibration. This would give a value for the M_{15} fundamental of ~ 825 cm^{-1}, which is in reasonable agreement with the calculated value of 843 cm^{-1}, considering that the calculated value in FBz was also not in such good agreement with experiment. The value is not in such good agreement with the value reported by Klimusheva et al.,[15] but the lack of detail and spectra, together with the discrepancies noted above, lead us to doubt their value. It is interesting to note that the $M_{15}M_{20}$ combination was also in FR with the M_8 vibration in FBz, while in ClBz this was not the case. Similarly, $M_{15}M_{20}$ was in FR with the M_9 in toluene-d_3,[29] indicating that this vibration can interact with the M_8 and M_9 modes if it happens to be in energetic proximity.

The three main bands corresponding to M_8, M_9 and M_6 were seen in the study by Dietz et al.[16] although the more complicated nature of the feature at ~ 935 cm^{-1} was not noted. These three bands were also employed to record REMPI-PES spectra by Walter et al.,[9] although the stated wavenumber for the M_8 feature seems to be incorrect, but the spectra suggest this was indeed the intermediate state employed (see later discussion of the photoelectron spectra). We note that the assignment of the 961 cm^{-1} band was given as the Wilson overtone ν_{18a}^2, which differs from the present assignment and that of ref. 16, but this seems to have been a typographical error (see

below), and this should be a transition to a fundamental vibration. We also note that different Wilson (Varsányi) labels were also used for the M_8, M_9 and M_6 modes between refs. 9 and 16 (see Table 1).

Both Walerstein[12] and Sreeramamurty[13] note vibrations with wavenumbers of 933, 963 and 1020 cm^{-1}, which correspond to M_8, M_9 and M_6, respectively, and very similar values are reported by Klimusheva et al.[15] Additionally, the latter study also reports a value for M_{12}, but this is in very poor agreement with our calculated value. We did not see any contributions from this vibration in the present work, and neither have any previous studies.

b. BrBz-d_5

We now move onto the spectrum of BrBz-d_5, which has more features in it. First, from our previous work[1,2] we expect there to be a significant red shift of the M_8 vibration upon deuteration, with smaller red shifts for the M_6 and M_9 vibrations. It is thus relatively straightforward to assign the band at 921.1 cm^{-1} to M_9^d and that at 996.6 cm^{-1} to M_6^d. Interestingly, the identification of the M_6^d and M_8^d vibrations from our calculations is not as transparent for BrBz-d_5 (see comments above), but fortunately, their wavenumbers and isotopic shifts are different enough for the assignment to be straightforward, particularly by comparison with our previous FBz and ClBz spectra. (Recall that the M_6 and M_8 motions are quite similar, with the main difference being the larger motion of the substituent in M_6, as the mass of the substituent approaches that of the ring.[10]) The calculated wavenumbers and comparison with the appearance of the two isotopologue spectra for each of FBz and ClBz then allowed the transition at 779.1 cm^{-1} to be assigned to M_8^d.

Moving onto the other features, a band at 796.1 cm^{-1} can be associated with $(M_{14}^2 M_{29})^d$, consistent with the appearance of such a band in the BrBz-h_5 spectrum. There are then two features to the red of the M_9^d band at 895.1 cm^{-1} and 906.6 cm^{-1}, the first is an excellent match for the expected position of the $(M_{10}M_{11})^d$ transition, and this feature also red shifts by ~ 1.5 cm^{-1} for ^{81}BrBz-d_5. The second band is then $(M_{10}M_{14}^2)^d$ and the corresponding vibration may be in FR with M_9^d. The band to the red of M_6^d at 977.1 cm^{-1} is in the correct position to be $(M_8 M_{20}^2)^d$ and the two vibrations could also form a FR.

3. High wavenumber range (1050-3000 cm^{-1})

As we move higher in wavenumber, more and more candidates arise for features, and there is the possibility of complications arising from anharmonic shifts and FR; for these reasons we refrain from a detailed discussion of the assignment of this higher region, but note the following points. It is relatively straightforward to pick out overtones and combinations involving the intense features, particularly with the M_8 and M_9 pair of features for BrBz-h_5. Indeed, once these are provisionally identified much of the main structure of the high-wavenumber regions is assigned. The assignments are summarized in Tables 4 and 5, and selected ones are also labelled in

Figure 1. Some high-wavenumber (< 1580 cm^{-1}) features were also identified in the work of Dietz et al.[16] using Wilson labels, and their assignments largely (but not completely) match those here, with the nomenclature change. A number of features occur close together, such as those involving the M_8^2, M_8M_9 and M_9^2 together with the M_6M_8 and M_6M_9; clearly combination bands of these with another vibration will also appear close together, and we have indicated two such in Figure 1. With regard to previous work, we note that Prakash and Singh[14] assigned a good number of the bands up to 4382 cm^{-1} and, although there are shifts of a few cm^{-1} from the present values, many assignments are consistent with those here. One interesting point is that a feature at 3082 cm^{-1} was observed, which has b_2 symmetry and it was hypothesised that this could be due to a totally-symmetric fundamental vibration of 2564 cm^{-1} that was in combination with M_{29}; such a spacing was also identified by Walterstein.[12] No such vibration is obvious from our calculations, but instead we suggest the 3082 cm^{-1} feature could be assigned to the b_2 mode, M_{22}.

Finally, Klimusheva et al.[15] reported values for M_7, M_{23}, M_{24}, M_{25} and M_{27} that are in moderately good agreement with our calculated values, but we did not see any contributions from these vibrations in the present work, nor have they been reported by others.

By analogy, even though the M_8 and M_9 pair does not appear for BrBz-d_5, we can pick out the corresponding combinations involving M_9^d and have labelled these in the inverted trace of Figure 1. Clearly many other contributions are appearing in these regions of the spectrum.

4. Cation

The Duschinsky matrix for the -h_5 isotopologue showing the relationship between S_0 and D_0^+ vibrations for BrBz is shown in Figure 7a, and that for the S_1 and D_0^+ vibrations in Figure 7b. The appearance of these suggests that the vibrational motion in the cation is largely the same as in each of the two neutral states, although some of these will show deviation. Based on this and previous work, for most cases we would expect a $\Delta v = 0$ propensity rule to work well for the $D_0^+ \leftarrow S_1$ ionization, so that the selected intermediate vibrational level in a REMPI-PES experiment would correspond to that of the most intense cation band.

We have calculated the vibrational wavenumbers of BrBz-h_5^+ and present these in Table 6; for completeness, we also present the BrBz-d_5^+ values. Referring to Walter et al.'s paper,[9] we have noted above that some of the assignments they offered are neither consistent with those here, nor with those in ref. 16; however, the observed structure in the REMPI-PES spectra should help elucidate this. First we note that exciting via the origin yielded a progression of bands with a spacing of 320 cm^{-1}, which matches our calculated 323 cm^{-1} value for M_{11}^+ extremely well. Walter et al. assigned this as Wilson mode ν_{6a}, but we have noted above (see Table 1) and elsewhere[10] that M_{11} is quite mixed in the monosubstituted benzenes, and that ν_{6a} is essentially M_{10} for the heavier species. When exciting via the M_{29} level a series of bands with a spacing of 540 cm^{-1} was observed,[9] which matches very well our calculated value of 534 cm^{-1} for M_{29}^+. They also observed a spacing of 950 cm^{-1}, which is in best agreement with our value for M_8^+. Progressions of 950 cm^{-1} and 320 cm^{-1} were seen when

exciting via the M_8 intermediate level (recall we noted there seems to have been an error in the reporting of the wavenumber of that transition), which match the spacings given above; additionally, another spacing of 1530 cm^{-1} was observed, which best matches our calculated M_4^+ value. Excitation of the M_9 mode (erroneously given as an overtone in Table 1 of ref. 9, but as a fundamental, ν_{18a}, in the text and in the caption of Figure 7) gives progressions involving spacings of 320 and 980 cm^{-1}, with the latter being assignable as M_9^+ from our calculated values in Table 6.

There is much confusion with the excitation of the intermediate level at what Walter et al.[9] cite as 1060 cm^{-1} above the S_1 origin, which Dietz et al.[16] locate at 1019 cm^{-1}, in excellent agreement with our position (Table 4). Further, owing to a lack of structure below the $\Delta v = 0$ region in their REMPI-PES spectrum, Walter et al.[9] tentatively reassign this level as Wilson mode ν_{9b} (but maintain a ν_{9a} label in other places in the paper). However, the spacings (134 meV) they see of 1080 cm^{-1} (but mistyped as 1180 cm^{-1} therein) are in best agreement with those for M_6^+ and so confirm an assignment of the intermediate level to M_6 and not to a b_2 symmetry vibration

Kwon et al.[20] recorded one-photon, mass-analyzed threshold ionization (MATI) spectra of BrBz, noting largest shifts of only a few cm^{-1} between some of the vibrations between the ^{79}Br and ^{81}Br isotopologues. Rich structure was seen in the spectrum and assigned to various vibrational modes using Wilson notation, with the derived wavenumbers included in Table 6. In including these, we have associated them with an M_i^+ label on the basis of previous discussion and on the basis of the symmetry. As can be seen, for many of the modes good agreement is seen with the calculated values, but there are some anomalies. The M_{29}^+ value of 593 cm^{-1} seems far from the REMPI-PES value and our calculated value, and the M_{23}^+ value of 1523 cm^{-1} is also far from our calculated value. The proposed value of 3083 cm^{-1} agrees best with our M_3^+ value. The assignment of the 1008 cm^{-1} feature to M_9^+ is unclear because it does not match the REMPI-PES value well. Since the resolution is much better in the MATI study, and the latter value is also closer to the value from the conventional PES studies by Potts et al. and Holland et al.,[18,19] then we take this value as the more reliable. We also note that the conventional PES studies give values for M_{11}^+ that match other experimental and the present calculated values well.

D. Iodobenzene

There is a trend for the lifetimes of the S_1 state to shorten with increasing mass of the halogen, attributable to intersystem crossing (ISC) and predissociation in the cases of FBz, ClBz and BrBz. Additionally, no LIF or REMPI spectrum appears to have been achievable for IBz, attributed to this short lifetime,[16] caused by internal conversion (IC) to a repulsive region of a singlet $n\sigma^*$ state (in contrast to ISC for the other monohalobenzenes);[30,31] however, it was possible for Kwon et al.[20] to record a one-colour MATI spectrum of iodobenzene, since the predissociating S_1 state is bypassed. We did not attempt to record a REMPI spectrum of IBz in the present work; however, we here briefly consider the vibrational assignment of the S_0 and D_0^+ states.

The S_0 state vibrational wavenumbers have been reported by Whiffen[6] and Griffiths and Thompson,[7] and were assigned Wilson-like labels by Varsańyi[5] (with some changes in assignments); we briefly discussed the assignments in terms of the M_i nomenclature in ref. 10, noting there that Wilson labels are inappropriate for many of the vibrations, and the inconsistency in assigning labels through the monohalobenzene series by Varsányi. In Table 7 we summarize the experimental vibrational wavenumbers, together with the present B3LYP/aug-cc-pVTZ values. As can be seen, the agreement between experiment and the present calculated values is extremely good in all cases; there is also agreement with the assignment presented in ref. 10. The only point worth emphasising is the switch in the wavenumber ordering of modes M_6 and M_7, which also occurs for ClBz and BrBz (see above), noted in ref. 10, but the motion of the corresponding vibrations for the series FBz $\rightarrow$ IBz being very similar in all cases.

Moving onto the vibrations for S_0 IBz-d_5, again we see that there is very good agreement with the experimental values presented by Nanney et al.[21] (which were given Wilson-like labels by Varsányi,[5] but these are inappropriate and do not match those given to FBz-d_5). The assignment in terms of M_i labels is relatively clear, as may be seen by the close-to-diagonal form of the Duschinsky matrix in Figure 8a and also the fact that the M_i labels have been shown to be appropriate for the S_0 state of IBz-h_5 in ref. 10. As with BrBz (and ClBz), there is some change in the motion of some vibrations as a result of the deuteration; however, the majority of the motions are close to those of IBz-h_5. The agreement between the calculated and experimental wavenumber values is again very good in all cases.

We present the calculated values for the cation in Table 8 for both IBz-h_5^+ and IBz-d_5^+. There seems to be no experimental data or previous calculations available for IBz-d_5^+, so these are presented for the first time and for completeness. There have been a couple of studies on IBz-h_5^+ employing both conventional PES and MATI spectroscopy. The PES studies of Holland et al.[22] and Potts et al.[19] each measured two vibrational separations (see Table 8) that are both expected to be of a_1 symmetry and are straightforwardly associated with the M_{11}^+ and M_9^+ vibrations, respectively.

In the MATI study of Kwon et al.,[20] a number of different vibrations were observed, including the two vibrations seen in the conventional PES studies[19,22] just discussed. We note that an error appears to have been made in the conversion of the value for M_{11}^+, where a value of 331 cm^{-1} is cited as coming from ref. 22 whereas in fact this should be 280 cm^{-1}, and thus in excellent agreement with the 284 cm^{-1} value obtained from the MATI study, and also in very good agreement with the present calculated value; the Potts et al.[19] value is not cited in that work. The values for M_8^+ agree in the two studies. In Table 8 we have tabulated the vibrational wavenumbers obtained by Kwon et al.[20] As can be seen, very good agreement is obtained in most cases, with the values for M_{17}^+ and M_{24}^+ being in slightly poorer agreement.

V. CONCLUDING REMARKS

In this paper we have reported the REMPI spectrum of both BrBz-h_5 and BrBz-d_5 and assigned these in detail up until ~ 1050 cm^{-1}, and then the major features thereafter. The present assignment gives a consistent picture of the spectra of FBz, ClBz and BrBz and their -d_5 isotopologues and suggests a number of future studies to unpick various Fermi resonances. It is interesting that it is rather straightforward to obtain a good-quality REMPI spectrum of BrBz given the short lifetime that precludes the possibility of obtaining an LIF spectrum; on the other hand, obtaining such a spectrum of IBz appears not to be possible as discussed above, owing to rapid internal conversion.

Our assignments are the first such for BrBz-d_5, while for BrBz-h_5 we have discussed the previous suggested assignments, noting some disagreements between them, and presenting our new assignments based on our previous work and quantum chemical calculations. We have also discussed the vibrations of the cations, reassigning where required.

Finally, for IBz we have presented calculated vibrations for the S_0 and D_0^+ states and briefly discussed previous work on these.

In summary, via the present and our previous work on the fluorobenzenes and chlorobenzenes, we have been able to assign corresponding vibrations across the whole monohalobenzene series of molecules, in the S_0, S_1 and D_0^+ states, gaining insight into vibrational activity and vibrational couplings.

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Table 1. Labels for BrBz-h_5 S_0 state vibrations.

Mode Label	In terms of FBz[a]	Wilson/Varsányi		
		Ref. 5	Ref. 9[b]	In Terms of benzene[c]
			a_1	
M_1	$\boldsymbol{M_1}$	20a	2	**2,**(7a,13)
M_2	$\boldsymbol{M_2}$	2	20a	**20a**,(2,13)
M_3	$\boldsymbol{M_3}$	13	13	**13**,7a
M_4	$\boldsymbol{M_4}$	8a	8a	**9a**
M_5	$\boldsymbol{M_5}$	19a	19a	**18a**
M_6	$\boldsymbol{M_6}$, M_8 (M_{10})	1	7a	**19a**, (1)
M_7	$\boldsymbol{M_7}$, M_6	9a	9a	**8a**
M_8	$\boldsymbol{M_8}$, (M_{10}, M_6)	18a	18a	**1,**19a,12
M_9	$\boldsymbol{M_9}$	12	1	**12,**1
M_{10}	$\boldsymbol{M_{10}}$, M_{11} (M_6)	6a	12	**6a**
M_{11}	$\boldsymbol{M_{11}}$, (M_{10}, M_6)	7a	6a	(7a, 20a,6a,13,2)
			a_2	
M_{12}	$\boldsymbol{M_{12}}$	17a	17a	**17a**
M_{13}	$\boldsymbol{M_{13}}$	10a	10a	**10a**
M_{14}	$\boldsymbol{M_{14}}$	16a	16a	**16a**
			b_1	
M_{15}	$\boldsymbol{M_{15}}$	5	5	**5**, 17b
M_{16}	$\boldsymbol{M_{16}}$	17b	17b	10b,17b
M_{17}	$\boldsymbol{M_{17}}$	11	10b	**11**, (10b,4)
M_{18}	$\boldsymbol{M_{18}}$	4	4	**4** (11)
M_{19}	$\boldsymbol{M_{19}}$	16b	16b	**16b**, (11)
M_{20}	$\boldsymbol{M_{20}}$	10b	11	(16b, 10b, 17b)
			b_2	
M_{21}	$\boldsymbol{M_{21}}$	20b	20b	**20b**
M_{22}	$\boldsymbol{M_{22}}$	7b	7b	**7b**,(20b)
M_{23}	$\boldsymbol{M_{23}}$	8b	8b	**9b**
M_{24}	$\boldsymbol{M_{24}}$	19b	19b	**18b**, 3
M_{25}	$\boldsymbol{M_{25}}$, (M_{26})	14	3	**3**, (15)
M_{26}	$\boldsymbol{M_{26}}$, (M_{25})	3	14	**15**, (8b,3)
M_{27}	$\boldsymbol{M_{27}}$	9b	9b	**14**, 8b
M_{28}	$\boldsymbol{M_{28}}$	18b	15	**19b**, 8b, 14
M_{29}	$\boldsymbol{M_{29}}$	6b	6b	**6b**
M_{30}	$\boldsymbol{M_{30}}$	15	18b	(8b, 19b)

[a] M_i modes of BrBz-h_5 expressed in terms of those of FBz-h_5. 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.

[b] Vibrational assignment is taken from Ref. 9 – although attributed to the original Varsányi work therein, the assignments are actually different for a number of the vibrations.

[c] M_i modes of BrBz-h_5 expressed in terms of those of benzene. 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. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the S_0 state of ^{79}BrBz-h_5 and ^{79}BrBz-d_5.

^{79}BrBz-h_5				^{79}BrBz-d_5		
Mode Label	Calculated		Experimental	Mode Label	Calculated	Experimental
	This work[a]	Ref. 10[b]	IR/Raman[c]		This work[a]	IR/Raman[d]
			a_1			
M_1	3109	3212	3069	M_1^d	2304	2296
M_2	3097	3200	3050	M_2^d	2291	2275[e]
M_3	3077	3178	3029	M_3^d	2269	2270
M_4	1567	1616	1580	M_4^d	1530	1551
M_5	1463	1489	1473	M_5^d	1328	1346
M_6	1052	1080	1070	M_6^d	995	1020
M_7	1164	1191	1176	M_7^d	853	865
M_8	1009	1036	1020	M_8^d	815	817 or 826[f]
M_9	988	1003	1001	M_9^d	948	958
M_{10}	662	676	669	M_{10}^d	633	644
M_{11}	305	312	315	M_{11}^d	298	305
			a_2			
M_{12}	961	977	963	M_{12}^d	783	760
M_{13}	825	836	832	M_{13}^d	642	680
M_{14}	401	415	409	M_{14}^d	348	350
			b_1			
M_{15}	980	1000	988	M_{15}^d	816	817
M_{16}	902	914	903	M_{16}^d	742	743
M_{17}	732	746	735	M_{17}^d	607	614
M_{18}	677	701	681	M_{18}^d	538	543
M_{19}	456	472	458	M_{19}^d	401	403
M_{20}	162	168	181	M_{20}^d	152	172
			b_2			
M_{21}	3106	3210	3069	M_{21}^d	2299	2280
M_{22}	3085	3186	3056	M_{22}^d	2278	2270
M_{23}	1573	1623	1577	M_{23}^d	1538	1541
M_{24}	1432	1458	1445	M_{24}^d	1304	1316
M_{25}	1306	1341	1323	M_{25}^d	1017	1012
M_{26}	1275	1316	1264	M_{26}^d	1271	1278
M_{27}	1146	1172	1159	M_{27}^d	831	841
M_{28}	1064	1092	1068	M_{28}^d	809	800[e]
M_{29}	608	621	615	M_{29}^d	583	586
M_{30}	240	249	254	M_{30}^d	226	238

[a] B3LYP/aug-cc-pVTZ values, scaled by 0.97

[b] B3LYP/aug-cc-pVDZ, unscaled.

[c] From ref. 6 (see text).

[d] Ref. 21.

[e] Estimated value from ref. 21.

[f] In ref. 21, a band at 817 cm^{-1} was observed in the IR spectrum, but one at 826 cm^{-1} was observed in the Raman one.

Table 3. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the S_1 states of ^{79}BrBz-h_5 and ^{79}BrBz-d_5.

^{79}BrBz-h_5							^{79}BrBz-d_5		
Mode Label	Calculated	Experimental					Mode Label	Calculated	Experimental
	This work[a]	This work	Ref. 16[b]	Ref. 9[c]	Ref. 15[d]	Ref. 14		This work[a]	This work
a_1									
M_1	3135						M_1[d]	2320	
M_2	3115						M_2[d]	2301	
M_3	3079						M_3[d]	2271	
M_4	1445				1447		M_4[d]	1394	
M_5	1401						M_5[d]	1239	
M_6	993	1022.5	1019.1	1020	1017	1019	M_6[d]	965	996.6
M_7	1125				1141		M_7[d]	833	
M_8	949	934.5	931.4		929	931	M_8[d]	787	779.1
M_9	974	963.0	960.3	961	959	961	M_9[d]	917	921.1
M_{10}	641	623.0	620.8		650	620	M_{10}[d]	614	604.1
M_{11}	295	297.0	294.1		(333)		M_{11}[d]	289	290.6
a_2									
M_{12}	612				709		M_{12}[d]	511	
M_{13}	511	560[e]					M_{13}[d]	412	405.5[e]
M_{14}	--[f]	181.0[g]			231	296	M_{14}[d]	--[f]	154.6[g]
b_1									
M_{15}	843	825.4[e]			871		M_{15}[d]	711	
M_{16}	680					678[h]	M_{16}[d]	581	
M_{17}	575	579[g]					M_{17}[d]	449	
M_{18}	486	486.8[e]					M_{18}[d]	393	
M_{19}	344	311[i]					M_{19}[d]	297	264.1[g]
M_{20}	119	105.6[g]				120	M_{20}[d]	112	99.1[g]
b_2									
M_{21}	3130						M_{21}[d]	2310	
M_{22}	3106					3082[j]	M_{22}[d]	2285	
M_{23}	1426				1476		M_{23}[d]	1316	
M_{24}	1360				1328		M_{24}[d]	1199	
M_{25}	1253				1257		M_{25}[d]	996	
M_{26}	1372						M_{26}[d]	1401	
M_{27}	1121				1199		M_{27}[d]	816	
M_{28}	973						M_{28}[d]	775	
M_{29}	511	521.5	518.9	517	519	518	M_{29}[d]	491	493.6
M_{30}	242	242.0			282	234	M_{30}[d]	228	227.1

[a] TDDFT, B3LYP/aug-cc-pVTZ, scaled by 0.97

[b] Dietz et al. REMPI study.

[c] Walter et al. REMPI-PES study.

[d] All values in the vapour phase at 20 K, except for the parenthesised value which was from a 4 K crystalline sample.

[e] Derived from a combination band and so there may be an anharmonic shift..

[f] The M_{14} mode in the S_1 state is calculated to give unrealistic values, as for the lighter monohalobenzenes, and so is not reported here – see text.

[g] Derived from an overtone band and so there may be an anharmonic shift...

[h] Assigned in the present work from hot bands seen in refs. 13 and 14 – see text.

[i] Tentatively assigned from assuming the overtone is contributing to the feature at 623 cm^{-1} – see text.

[j] Reassigned (tentatively) in the present work – see text.

Table 4. A summary of the assigned vibrational features from the present work for the $S_1 \leftarrow S_0$ transition of ^{79}BrBz-h_5

	Experimental band (cm^{-1})[a]	Assignment[b]	This work B3LYP	From experimental fundamental [c]	Overall symmetry
	0.0	0^0	-	-	a_1
	211.5	M_{20}^2	239	211.5[d]	a_1
	242.0	M_{30}	242	242.0[d]	b_2
	278.5	$M_{14}M_{20}$	-[e]	286.6	b_2
	297.0	M_{11}	295	297.0[d]	a_1
	362.0	M_{14}^2	-[e]	362.0[d]	a_1
	462.0	$M_{14}M_{19}$	-[e]	492.0	b_2
	501.5	$M_{11}M_{20}^2$	533	508.4	a_1
	521.5	M_{29}	511	521.5[d]	b_2
	539.0	$M_{11}M_{30}$	537	539.0	b_2
	592.5	$M_{18}M_{20}$	606	592.5[d]	a_1
	623.0	M_{10}	641	623.0[d]	a_1
	669.5	$M_{14}M_{18}$	-[e]	667.0	b_2
	733.0	$M_{20}^2M_{29}$	750	732.7	b_2
	741.0	$M_{13}M_{14}$	691	741.0	a_1
	880.0	$M_{14}^2M_{29}$	-[e]	883.5	b_2
	905.5	$M_{14}M_{18}M_{30}$ $M_{10}M_{14}M_{20}$	-[e] -[e]	909.0 909.6	a_1 b_2
Region β	918.0	$M_{10}M_{11}$	936	920.0	a_1
	931[f]	$M_{15}M_{20}$	963	931.0[d]	a_1
	934[f]	M_8	949	934.0[d]	a_1
	963.0	M_9	974	963.0[d]	a_1
	985.0	$M_{10}M_{14}^2$	-[e]	985.0	a_1
	1022.5	M_6	994	1022.5[d]	a_1
	1107.5	$M_{10}M_{30}^2$	1126	1107.0	a_1
	1143.5	$M_{10}M_{29}$	1153	1144.5	b_2
	1150.0	$M_8M_{20}^2$	1187	1146.0	a_1
	1157.5	M_{17}^2	1150	1157.5	a_1
	1174.5	$M_9M_{20}^2$	1212	1174.5	a_1
	1176.5	M_8M_{30}	1191	1176.6	b_2
	1203.5	M_9M_{30}	1216	1205.0	b_2
	1211.0	$M_{18}^2M_{30}$	1198	1214.0	b_2
	1231.5	M_8M_{11}	1243	1231.6	a_1
	1258.5	M_9M_{11}	1268	1260.0	a_1
	1455.0	M_8M_{29}	1460	1456.1	b_2
	1474	$M_8M_{11}M_{30}$	1486	1473.6	b_2
	1482	M_9M_{29}	1485	1484.5	b_2
	1498	$M_9M_{11}M_{30}$	1510	1502.0	b_2
	1542	M_6M_{29}	1505	1544.0	b_2
	1868	M_8^2	1897	1869.2	a_1
	1898	M_8M_9	1922	1897.6	a_1
	1926	M_9^2	1947	1926.0	a_1
	1956	M_6M_8	1942	1957.1	a_1
	1986	M_6M_9	1967	1985.5	a_1
	2386	$M_8^2M_{29}$	2409	2390.7	b_2
	2414	$M_8M_9M_{29}$	2434	2419.1	b_2
	2440	$M_9^2M_{29}$	2459	2447.5	b_2
	2474	$M_6M_8M_{29}$	2454	2478.6	b_2
	2500	$M_6M_9M_{29}$	2478	2507.0	b_2

	2892	$M_6M_8^2$	2891	2891.7	a_1
	2948	$M_6M_9^2$	2941	2948.5	a_1
	2974	$M_6^2M_8$	2936	2979.6	a_1

[a] Features above 1460 cm^{-1} are quoted to the nearest 1 cm^{-1} only since only scans with 2 cm^{-1} stepsize were undertaken for this isotopologue.

[b] Selected assignments given for the region > 1000 cm^{-1}. If more than one option is given, the assignment is not known definitely.

[c] All values have been computed from experimental fundamentals.

[d] An experimental fundamental is taken from this feature.

[e] M_{14} calculated B3LYP frequency was unrealistic; see text for details.

[f] Overlapped bands, and so the position is an estimate.

Table 5. A summary of the assigned vibrational features from the present work for the $S_1 \leftarrow S_0$ transition of ^{79}BrBz-d_5

	Experimental band (cm^{-1})[a]	Assignment[b]	This work B3LYP	From experimental fundamentals [c]	Overall symmetry
	0.0	0^0	-	-	-
	198.1	$(M_{20}^2)^d$	224	198.1[d]	a_1
	227.1	M_{30}^d	228	227.1[d]	b_2
	249.1	$(M_{14}M_{20})^d$	-[e]	253.7	b_2
	290.6	M_{11}^d	289	290.6[d]	a_1
	309.1	$(M_{14}^2)^d$	-[e]	309.2[d]	a_1
	487.6	$(M_{11}M_{20}^2)^d$	513	488.7	a_1
	493.6	M_{29}^d	491	493.6[d]	b_2
α	515.6	$(M_{13}M_{20})^d$	524	504.6	b_2
	518.1	$(M_{11}M_{30})^d$	517	517.7	b_2
	528.1	$(M_{19}^2)^d$	-[e]	528.1[d]	a_1
	560.1	$(M_{13}M_{14})^d$	-[e]	560.1[d]	a_1
	604.1	M_{10}^d	615	604.1[d]	a_1
	714.1	$(M_{29}M_{30})^d$	719	720.7	a_1
	779.1	M_8^d	787	779.1[d]	a_1
	796.1	$(M_{14}^2M_{29})^d$	-[e]	802.8	b_2
	895.1	$(M_{10}M_{11})^d$	898	894.7	a_1
	906.6	$(M_{10}M_{14}^2)^d$	-[d]	915.7	a_1
	921.1	M_9^d	917	921.1[d]	a_1
	977.1	$(M_8M_{20}^2)$	1011	977.3	a_1
	996.6	M_6^d	965	996.6[d]	a_1
	1086.6	$(M_8M_{14}^2)^d$	-[e]	1088.3	a_1
	1093.6	$(M_{10}M_{29})^d$	1106	1097.7	b_2
	1117.1	$(M_9M_{20}^2)^d$	1141	1119.3	a_1
	1147.6	$(M_9M_{30})^d$	1145	1148.2	b_2
	1209.1	$(M_9M_{11})^d$	1206	1211.7	a_1
	1222.6	$(M_6M_{30})^d$	1193	1223.7	b_2
	1225.1	$(M_9M_{14}^2)^d$	-[e]	1230.1	a_1
	1286.1	$(M_6M_{11})^d$	1253	1287.2	a_1
	1415.1	$(M_9M_{29})^d$	1408	1414.7	a_2
	1439.6	$(M_9M_{11}M_{30})^d$	1434	1438.8	b_2
	1464.6	$(M_8M_{18}M_{19})^d$	-[e]	1468.1	b_2
	1484.6	$(M_6M_{29})^d$	1456	1490.2	b_2
	1843	$(M_9^2)^d$	1834	1842.2	a_1
	2057	$(M_8^2M_{29})^d$	2065	2051.8	b_2
	2067	$(M_6M_8M_{11})^d$	2041	2066.3	a_1
	2277	$(M_6M_8M_{29})^d$	2243	2269.2	b_2
	2335	$(M_9^2M_{29})^d$	2326	2335.8	b_2
	2385	$(M_6M_8M_{10})^d$	2366	2379.8	a_1
	2457	$(M_9^2M_{10})^d$	2449	2446.3	a_1

[a] Features above 1500 cm^{-1} are quoted to the nearest cm^{-1} as only 2 cm^{-1} step size scans were taken of the high wavenumber region for this isotopologue.

[b] Selected assignments given for the region > 1000 cm^{-1}.

[c] All values come from experimental fundamentals.

[d] An experimental fundamental is taken from this feature.

[e] M_{14}^d calculated B3LYP frequency is unphysical; see text for details.

Table 6. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the ground state cation, D_0^+, of ^{79}BrBz-h_5 and ^{79}BrBz-d_5.

^{79}BrBz-h_5^+					^{79}BrBz-d_5^+	
Mode Label	Calculated	Experimental			Mode Label	Calculated
	This work[a]	Walter et al.[b]	Kwon et al.[c]	PES[d]		This work[a]
			a_1			
M_1^+	3121				M_1^{d+}	2316
M_2^+	3111				M_2^{d+}	2299
M_3^+	3098		3083[e]		M_3^{d+}	2289
M_4^+	1573	1530	1577		M_4^{d+}	1532
M_5^+	1425				M_5^{d+}	1251
M_6^+	1040	1080[f]	1073		M_6^{d+}	1016
M_7^+	1181		1193		M_7^{d+}	854
M_8^+	966	950			M_8^{d+}	801
M_9^+	981	980	1008	1020 (1016)	M_9^{d+}	933
M_{10}^+	669		678		M_{10}^{d+}	639
M_{11}^+	323	320	331	330 (330)	M_{11}^{d+}	315
			a_2			
M_{12}^+	988				M_{12}^{d+}	802
M_{13}^+	792				M_{13}^{d+}	616
M_{14}^+	346		396		M_{14}^{d+}	301
			b_1			
M_{15}^+	998				M_{15}^{d+}	840
M_{16}^+	944				M_{16}^{d+}	765
M_{17}^+	758		791		M_{17}^{d+}	637
M_{18}^+	587				M_{18}^{d+}	328
M_{19}^+	378				M_{19}^{d+}	472
M_{20}^+	131		126		M_{20}^{d+}	122
			b_2			
M_{21}^+	3119				M_{21}^{d+}	2312
M_{22}^+	3108				M_{22}^{d+}	2294
M_{23}^+	1479		1523[g]		M_{23}^{d+}	1244
M_{24}^+	1341				M_{24}^{d+}	1381
M_{25}^+	1254				M_{25}^{d+}	1019
M_{26}^+	1380		1307		M_{26}^{d+}	1313
M_{27}^+	1129				M_{27}^{d+}	827
M_{28}^+	1074				M_{28}^{d+}	823
M_{29}^+	534	540	593		M_{29}^{d+}	517
M_{30}^+	246		257		M_{30}^{d+}	232

[a] UB3LYP/aug-cc-pVTZ, scaled by 0.97
[b] Ref. 9
[c] Ref.20
[d] Ref. 18 and, in parentheses, ref. 19.
[e] Reassigned in the present work.
[f] Reassigned vibrational band.
[g] Assigned to a fundamental in ref. 20, but the value is far from any calculated b_2 symmetry vibration here.

Table 7. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the S_0 state of IBz-h_5 and IBz-d_5.

IBz-h_5				IBz-d_5		
Mode Label	Calculated		Experimental	Mode Label	Calculated	Experimental
	This work[a]	Ref. 10[b]	IR/Raman[c]		This work[a]	IR/Raman[d]
a_1						
M_1	3105	3210	3064	M_1^d	2301	2290
M_2	3095	3199	3050	M_2^d	2289	2273
M_3	3073	3177	3031	M_3^d	2266	2270[e]
M_4	1562	1611	1575	M_4^d	1524	1550
M_5	1461	1487	1473	M_5^d	1323	1330
M_6	1046	1074	1060	M_6^d	983	992
M_7	1168	1194	1178	M_7^d	855	862
M_8	1004	1032	1015	M_8^d	817	815 or 826[f]
M_9	986	997	998	M_9^d	946	952
M_{10}	649	662	654	M_{10}^d	622	623
M_{11}	258	264	266	M_{11}^d	252	256
a_2						
M_{12}	963	978	963	M_{12}^d	785	757
M_{13}	828	839	835	M_{13}^d	644	680
M_{14}	398	411	398	M_{14}^d	345	350
b_1						
M_{15}	982	1000	987	M_{15}^d	816	815
M_{16}	904	915	904	M_{16}^d	739	735
M_{17}	728	739	730	M_{17}^d	602	607
M_{18}	672	699	684	M_{18}^d	535	537
M_{19}	448	460	448	M_{19}^d	396	397
M_{20}	147	151	181	M_{20}^d	137	158
b_2						
M_{21}	3103	3207	3064	M_{21}^d	2296	2273
M_{22}	3081	3185	3048	M_{22}^d	2275	2258
M_{23}	1569	1618	1575	M_{23}^d	1533	1535
M_{24}	1428	1454	1435	M_{24}^d	1298	1305
M_{25}	1307	1338	1321	M_{25}^d	1267	1273
M_{26}	1271	1316	1261	M_{26}^d	1016	999
M_{27}	1147	1173	1159	M_{27}^d	831	837
M_{28}	1063	1091	1068	M_{28}^d	811	800
M_{29}	608	620	613	M_{29}^d	583	587
M_{30}	212	218	220	M_{30}^d	198	202

[a] B3LYP/aug-cc-pVTZ values, scaled by 0.97

[b] B3LYP/aug-cc-pVDZ, unscaled.

[c] From ref. 6

[d] From ref. 21

[e] Estimated value from ref. 21.

[f] In ref. 21, a band at 815 cm^{-1} was observed in the IR spectrum, but one at 826 cm^{-1} was observed in the Raman one.

Table 8. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the ground state cation, D_0^+, of IBz-h_5 and IBz-d_5.

IBz-h_5				IBz-d_5	
Mode Label	Calculated	Experimental		Mode Label	Calculated
	This work[a]	PES[b]	Ref. 20[c]		This work[a]
a_1					
M_1^+	3119			M_1^{d+}	2314
M_2^+	3110			M_2^{d+}	2298
M_3^+	3098			M_3^{d+}	2288
M_4^+	1554		1575	M_4^{d+}	1511
M_5^+	1431			M_5^{d+}	1259
M_6^+	1007		1036	M_6^{d+}	980
M_7^+	1181			M_7^{d+}	858
M_8^+	973		990	M_8^{d+}	805
M_9^+	988	1020 (1010)	1015	M_9^{d+}	935
M_{10}^+	651		661	M_{10}^{d+}	624
M_{11}^+	273	280 (285)	284	M_{11}^{d+}	266
a_2					
M_{12}^+	986			M_{12}^{d+}	801
M_{13}^+	804			M_{13}^{d+}	625
M_{14}^+	352		357	M_{14}^{d+}	306
b_1					
M_{15}^+	998			M_{15}^{d+}	837
M_{16}^+	943		903	M_{16}^{d+}	760
M_{17}^+	746		808	M_{17}^{d+}	619
M_{18}^+	588			M_{18}^{d+}	477
M_{19}^+	387		406	M_{19}^{d+}	338
M_{20}^+	121		127	M_{20}^{d+}	112
b_2					
M_{21}^+	3117			M_{21}^{d+}	2309
M_{22}^+	3105			M_{22}^{d+}	2292
M_{23}^+	1393			M_{23}^{d+}	1253
M_{24}^+	1478		1517[d]	M_{24}^{d+}	1371
M_{25}^+	1333			M_{25}^{d+}	1020
M_{26}^+	1263			M_{26}^{d+}	1335
M_{27}^+	1140			M_{27}^{d+}	831
M_{28}^+	1077			M_{28}^{d+}	825
M_{29}^+	554		538	M_{29}^{d+}	535
M_{30}^+	216		242	M_{30}^{d+}	203

[a] UB3LYP/aug-cc-pVTZ, scaled by 0.97

[b] Conventional photoelectron study: ref. 22 and, in parentheses, ref. 19.

[c] One-photon MATI study.

[d] Assigned to a fundamental in ref. 20, but the value is far from any calculated b_2 symmetry vibration here.

Figure Captions

Figure 1. Complete 0–3050 cm^{-1} spectral range scan of the $S_1 \leftarrow S_0$ (1+1) REMPI spectra of BrBz-h_5 (top trace, upright) and BrBz-d_5 (bottom trace, inverted).
(The final vibrational level is given with all transitions emanating from the ground state zero point vibrational level; M_i^n represents a transition to n quanta of the M_i vibration.) The assignments are discussed in the text: in detail for the region < 1050 cm^{-1}, and in more general terms for the higher wavenumber features. The "combs" indicate regions of the spectrum whose contributors also appear to higher wavenumber in combination with another vibration, although the precise assignment of the individual features is not necessarily clear.

Figure 2. Generalized Duschinsky matrix between vibrational modes of the S_0 states of FBz-h_5 and BrBz-h_5. Shadings indicate the mixing coefficient values, with black = 1.00 while white = 0.00, with the level of the grey shading indicating intermediate values. The numbers are the i values for each M_i mode.

Figure 3. Generalized Duschinsky matrix between the vibrational modes of the S_0 states of BrBz-h_5 and BrBz-d_5. Shadings indicate the mixing coefficient values, with black = 1.00 while white = 0.00, with the level of the grey shading indicating intermediate values. The numbers are the i values for each M_i or M_i^d mode. See text for details. Note that the M_6^d and M_8^d modes mix significantly, with the Duschinsky approach suggesting an incorrect dominant contribution in each case; however, the identification of the modes is clear from the form of the modes, and the spectrum – see text.

Figure 4. Generalized Duschinsky matrices between the vibrational modes of the S_0 and S_1 states for: (a) BrBz-h_5 and (b) BrBz-d_5. Shadings indicate the mixing coefficient values, with black = 1.00 while white = 0.00, with the level of the grey shading indicating intermediate values. The numbers are the i values for each M_i or M_i^d mode. See text for details.

Figure 5. Expanded views of the low wavenumber regions (0–750 cm^{-1}) of the $S_1 \leftarrow S_0$ (1+1) REMPI spectra of BrBz-h_5 (top trace, upright) and BrBz-d_5 (bottom trace, inverted). Assignments are discussed in the text and summarized in Tables 4 and 5; suggested assignments for some of the weaker features and the region marked α are also given in these tables. (The final vibrational level is given with all transitions emanating from the ground state zero point vibrational level; M_i^n represents a transition to n quanta of the M_i vibration.)

Figure 6. Expanded views of the medium wavenumber regions (750–1050 cm^{-1}) of the $S_1 \leftarrow S_0$ (1+1) REMPI spectra of BrBz-h_5 (top trace, upright) and BrBz-d_5 (bottom trace, inverted). Assignments are discussed in the text and summarized in Tables 4 and 5; suggested assignments for some of the weaker features and the region marked β are also given in these tables. (The final vibrational level is given with all transitions emanating from the ground state zero point vibrational level; M_i^n represents a transition to n quanta of the M_i vibration.)

Figure 7. Generalized Duschinsky matrices between the vibrational modes of: (a) the S_0 and D_0^+ states for BrBz-h_5 and (b) the S_1 and the D_0^+ states for BrBz-h_5. Shadings indicate the normalized coefficient values, with black = 1.00 while white = 0.00, with the level of the grey shading indicating intermediate values. The numbers are the i values for each M_i/M_i^+ mode. See text for details.

Figure 8. Generalized Duschinsky matrices between the vibrational modes of: (a) the S_0 for IBz-h_5 and S_0 IBz-d_5 and (b) the S_0 and the D_0^+ states for IBz-h_5. Shadings indicate the normalized coefficient values, with black = 1.00 while white = 0.00, with the level of the grey shading indicating intermediate values. The numbers are the i values for each $M_i/ M_i^d/ M_i^+$ mode. As can be seen from (a), the M_6^d and M_8^d modes mix significantly, with the Duschinsky approach suggesting an incorrect dominant contribution in each case; however, the identification of the modes is clear from the form of the modes, and by comparison with BrBz-d_5 – see text.

Figure 1.

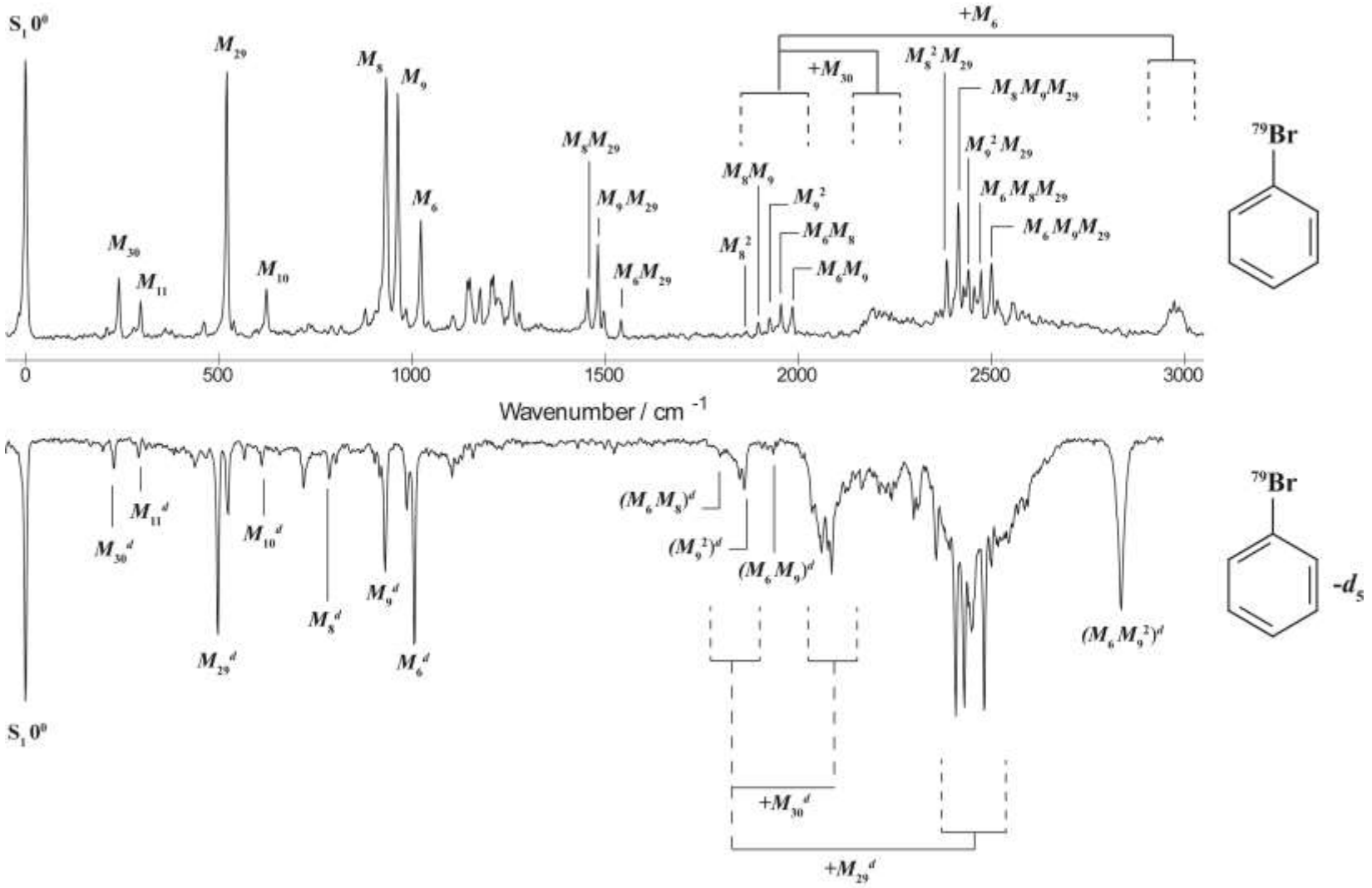

S1 0⁰
M29
M8
M9
M30
M11
M10
M6
M8M29
M9M29
M6M29
+M6
+M30
M8²M29
M8M9M29
M9²M29
M6M8M29
M6M9M29
M8M9
M9²
M6M8
M6M9
M8²
79Br
0
500
1000
1500
2000
2500
3000
Wavenumber / cm -1
M30d
M11d
M10d
M8d
M9d
M29d
M6d
(M6M8)d
(M9²)d
(M6M9)d
(M6M9²)d
+M30d
+M29d
79Br
-d5
S1 0⁰

Figure 2.

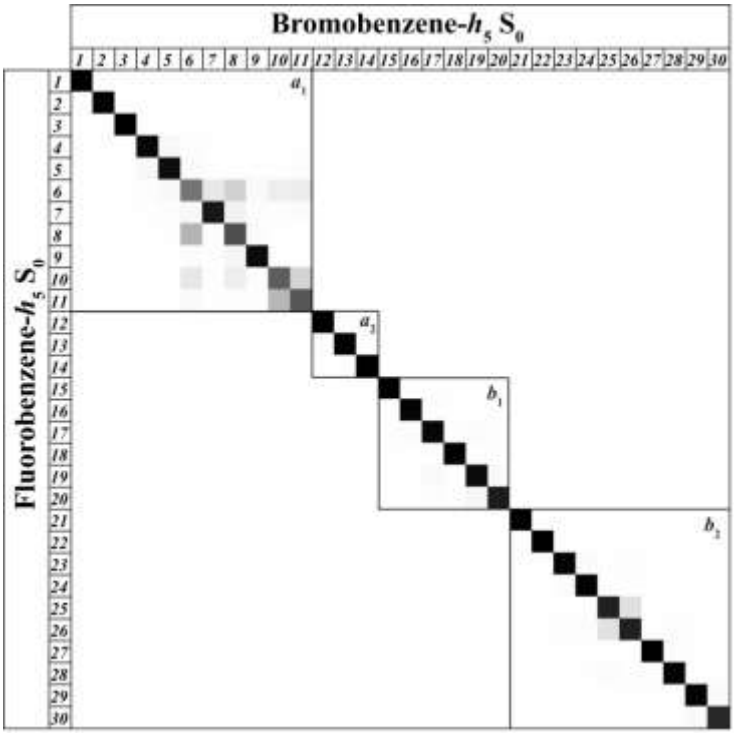


Figure 3.

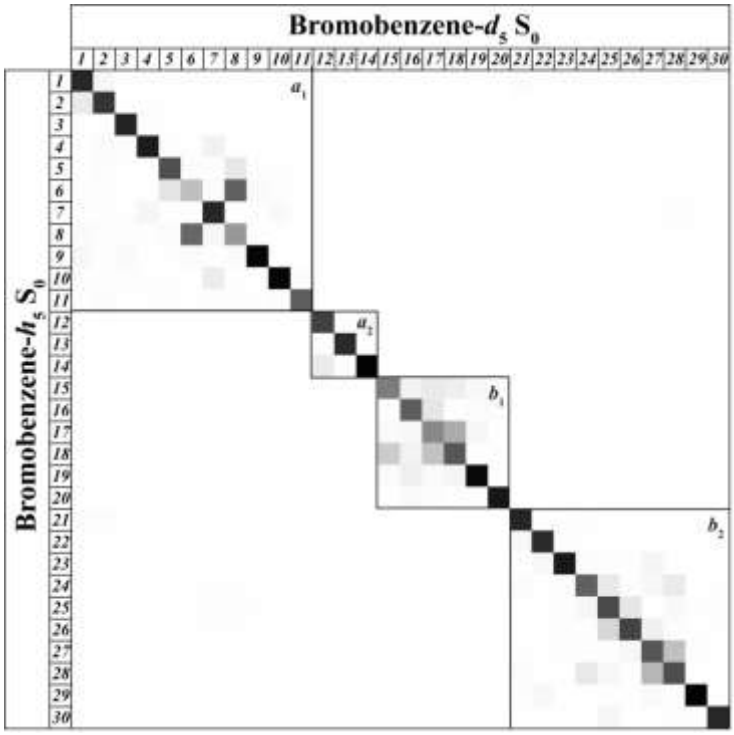


Figure 4.

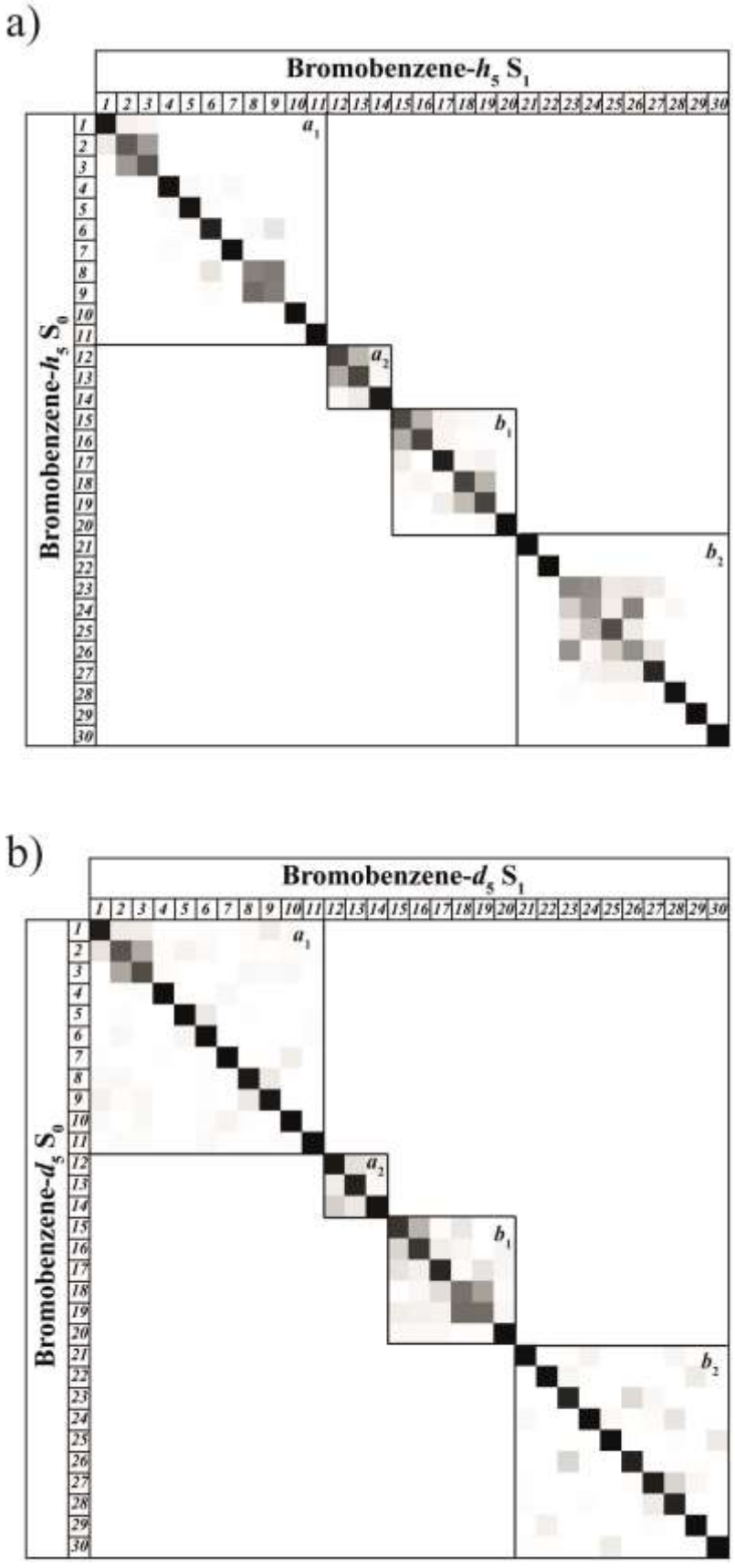

a)
Bromobenzene-h_5 S_1
Bromobenzene-h_5 S_0
a_1
a_2
b_1
b_2
b)
Bromobenzene-d_5 S_1
Bromobenzene-d_5 S_0
a_1
a_2
b_1
b_2

Figure 5.

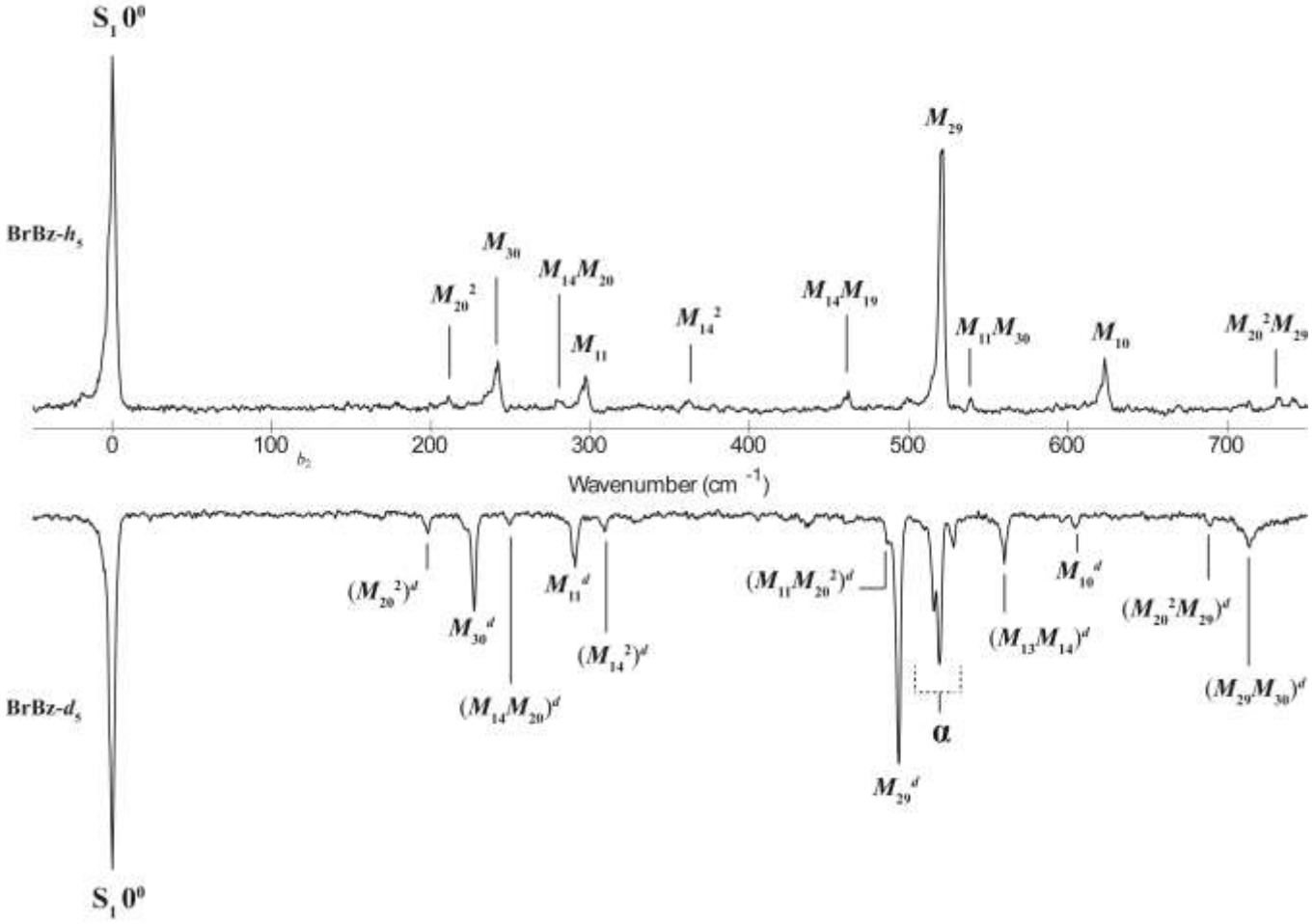

S1 0⁰
BrBz-h5
M29
M30
M14M20
M20²
M11
M14²
M14M19
M11M30
M10
M20²M29
0
100
200
300
400
500
600
700
b2
Wavenumber (cm -1)
(M20²)d
M30d
M11d
(M14²)d
(M11M20²)d
M10d
(M20²M29)d
(M13M14)d
(M14M20)d
(M29M30)d
α
M29d
BrBz-d5
S1 0⁰

Figure 6.

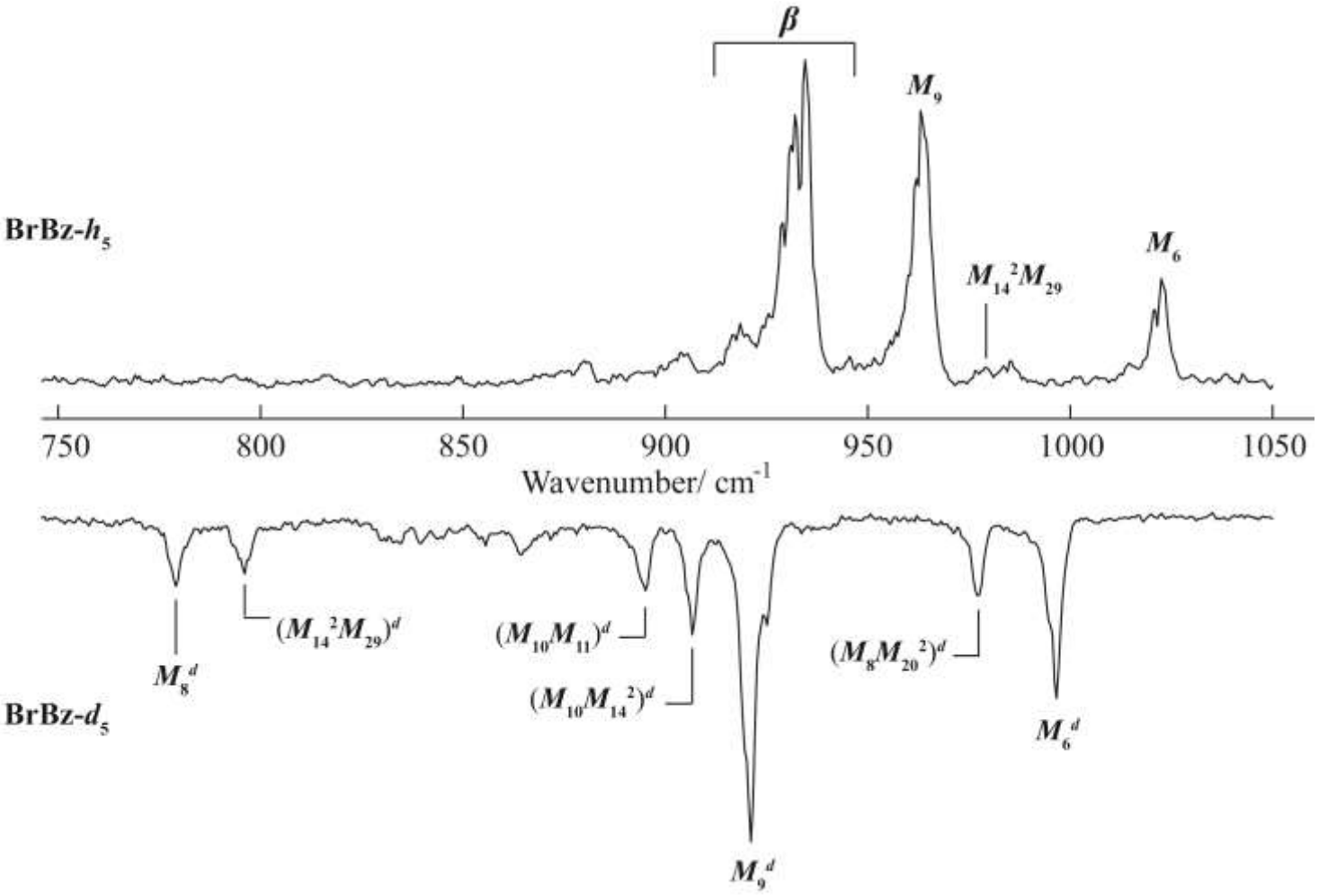

β
M9
M6
M14 2M29
BrBz-h5
750
800
850
900
950
1000
1050
Wavenumber/ cm-1
M8 d
(M14 2M29)d
(M10M11)d
(M10M14 2)d
M9 d
(M8M20 2)d
M6 d
BrBz-d5

Figure 7.

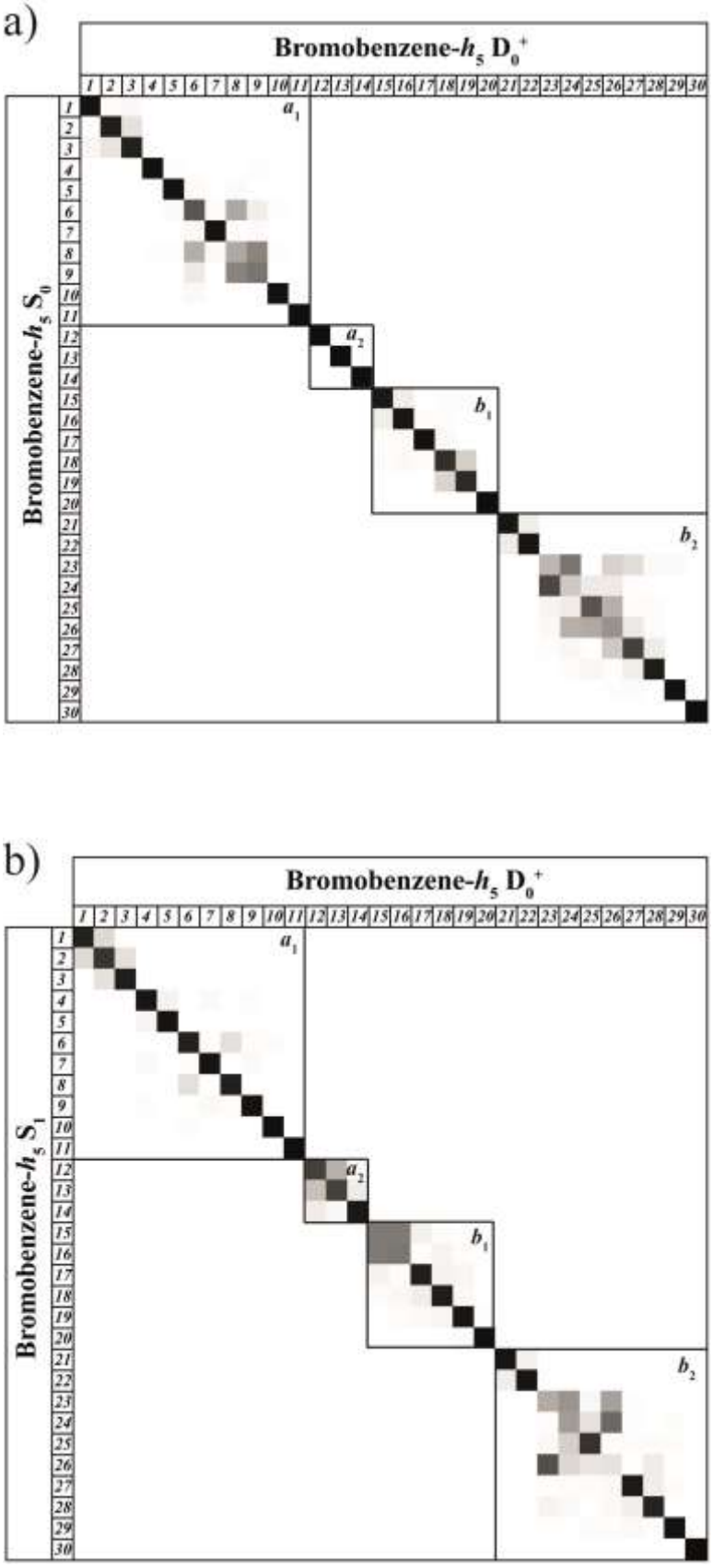
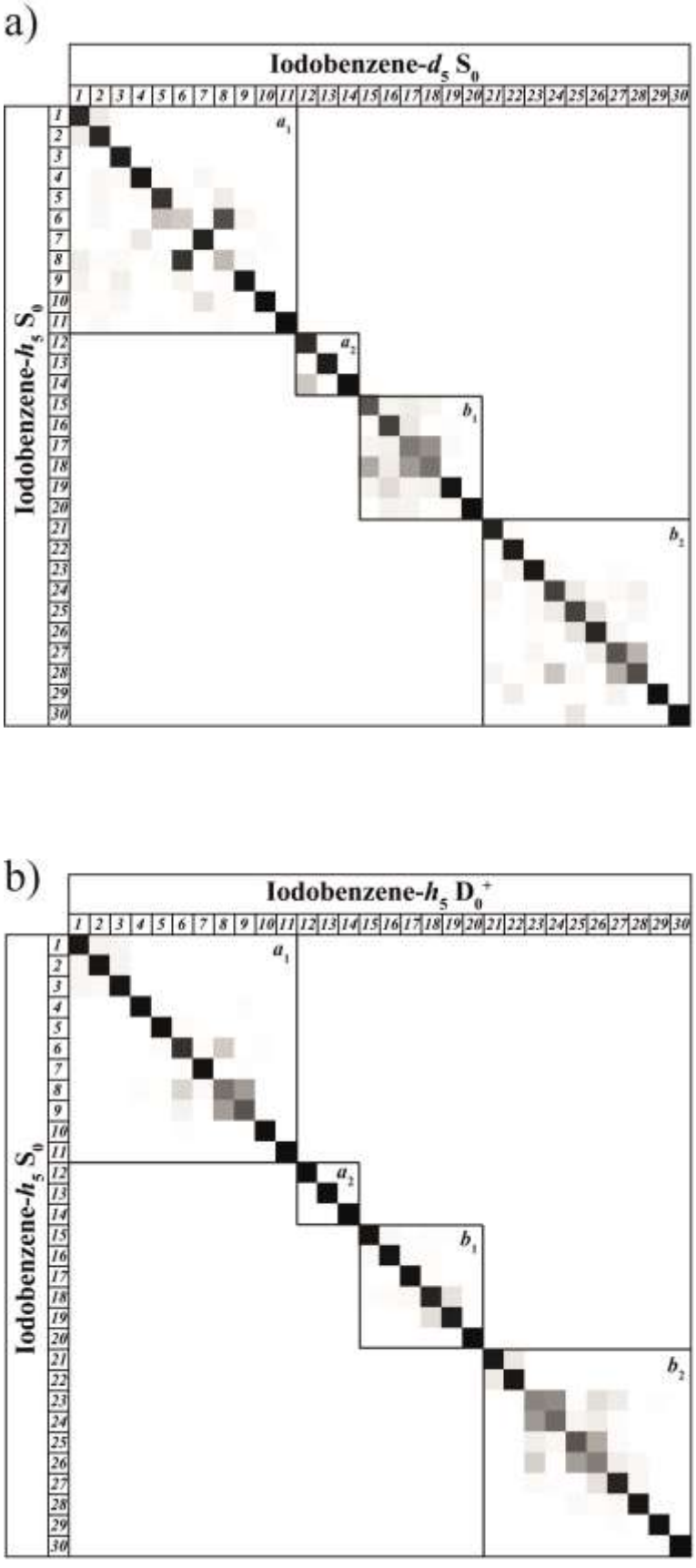

a)
Bromobenzene-h_5 D_0^+
Bromobenzene-h_5 S_0
a_1
a_2
b_1
b_2
b)
Bromobenzene-h_5 D_0^+
Bromobenzene-h_5 S_1
a_1
a_2
b_1
b_2

Figure 8.


a)
Iodobenzene-d_5 S_0
Iodobenzene-h_5 S_0
a_1
a_2
b_1
b_2
b)
Iodobenzene-h_5 D_0^+
Iodobenzene-h_5 S_0
a_1
a_2
b_1
b_2

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