Mass-analyzed-threshold-ionization (MATI) spectroscopy of 1,2,3-substituted halogenated benzenes via different intermediate vibrational states in the $S_1$ state

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For the first time, two color resonant mass analyzed threshold ionization (MATI) spectroscopy has been applied in order to investigate the ionic properties of 1,3-dichloro-2-fluoro-benzene (1,3,2-DFCB) and 1,3-difluoro-2-chloro-benzene (1,3,2-DFCB) radical cations in their electronic ground state. The ionic ground state of the different samples has been investigated via different $S_1$ intermediate states and compared to 1,2,3-trichlorobenzene measured in previous work. Additionally quantum chemical calculations at DFT (density functional theory) and TD DFT (time-dependent density functional theory) level of theory have been performed to support experimental findings. From the MATI spectra the adiabatic ionization energies of 1,3-dichloro-2-fluorobenzene and 1,3-fluoro-2-chlorobenzene could be determined to be 75.242 ± 6 cm$^{-1}$ and 75.627 ± 6 cm$^{-1}$, respectively. Several vibrational modes of both compounds have been assigned by comparison of the experimental and theoretical results.

1. Introduction

Halogenated aromatic molecules became a topic of great interest due to their widespread presence in industrial processes and hence presence in the environment as potentially toxic and carcinogenic pollutants. Moreover halogenated benzenes are important model substances to validate theoretical concepts, such as vibronic coupling and others. As one of the spectroscopically best-investigated molecules of all, benzene can serve as an outstanding reference system to study the influence of tailored perturbations, such as careful choice of substitution pattern, to the (ro)vibronic structure. As an immediate effect a shift in transition energies, ionization energy, molecular geometry and vibrational frequencies can be observed. The characteristics of these effects strongly depend on the number, type and localization of the substituents. As the magnitude of these effects are rather small (from a few wavenumbers up to a hundred wavenumbers), high resolution techniques, such as mass analyzed threshold ionization (MATI) or zero kinetic energy (ZEKE) spectroscopy are ideally suited to investigate such phenomena. Chloro- and fluoro-benzenes have been subject to various studies investigating the vibronic properties of the first electronic excited state ($S_1$) as well as cationic ground state ($D_0$). In this paper we will focus particularly on out-of-plane $b_1$-symmetric modes. Modes of this symmetry are connected to interesting phenomena observed in a whole variety of halobenzenes. For example, difluorobenzenes exhibit large frequency lowering of $b_1$ ($b_{3u}$ under $D_{2h}$ in case of p-DFB) symmetric modes in going from $S_0$ to $S_1$ or from $D_0$ to $S_1$, respectively. The intensity gain of this symmetry forbidden mode was interpreted in terms of the pseudo-Jahn–Teller effect (PJTE). The PJTE is based on the idea that a geometrical distortion blurs the difference in symmetry between two or more electronic states of virtually equal energy. In 1,2,4,5-tetrafluorobenzene ($D_{2h}$) it was found that the $b_{3u}$-symmetric mode 11 shows an unusual strong activity in the form of a long progression ($v_{11}^{14}$). Recent results show that the planarity of this molecule is distorted along the eigenvector of the 11 mode during excitation to $^1B_{2u}S_1$ state. It is an interesting question to elucidate if these phenomena can be extended to further congeners and identified as a general feature. In particular in the case of the molecular geometry change it is crucial to determine the involved vibrational modes and participating electronic states. For this purpose, the experimental data are compared to theoretical calculations, which enable the possibility of assigning the observed vibrational modes. In this paper we present mass-selected two color two photon Resonance Enhanced Multi Photon Ionization (2C2P-REMPI) spectra of the $S_1 \leftarrow S_0$ transition and MATI spectra via different $S_1$-intermediate states of 1,3-dichloro-2-fluorobenzene and 1,3-dichloro-2-fluorobenzene. Some assignments of 1,2,3-trichlorobenzene reported previously were reconsidered and compared to the newly gained knowledge.
2. Experimental setup

The experimental setup consists of a homemade time-of-flight (TOF) mass spectrometer as described in detail previously.\textsuperscript{1,15,16} Briefly, the spectrometer consists of a standard second order corrected reflection time-of-flight mass spectrometer equipped with single stage ion source. The laser system used for excitation and ionization consists of two dye lasers (Laser Analytical Systems LDL 205, Lambda Physics FL 3002). Each dye laser is pumped by a dedicated Nd:YAG laser (Lumonics HY-1200, Continuum Surelite II). A Quantum Composers 9600+ delay pulse generator fed by an external clock operated at 10 Hz controls flash lamp and Q-switch delays. The output of each dye laser is frequency-doubled by a BBO-I crystal yielding tunable ranges from 245 to 285 nm. Wavelength calibration of both dye lasers is performed by recording an optogalvanic spectrum with a neon hollow cathode lamp yielding accuracy better than 2 cm\textsuperscript{-1}. Initially a supersonic molecular beam of sample molecules and seed gas (argon) with a backing pressure of approximately 2 bar is expanded via a pulsed jet valve (General Valves Series 9) into the ion source. To obtain a sufficient vapor pressure the sample is heated to approximately 80 °C. Excitation or ionization is accomplished by multi photon absorption under field-free conditions. In the MATI modus, promptly generated ions are discriminated against Rydberg neutrals through the application of a weak electrical field of 1–2 V cm\textsuperscript{-1} by a subsequent delay (100 ns) to multi-photon excitation. Finally, a high voltage pulse (890 V cm\textsuperscript{-1}) switched by a Behlke HS56-01 fast thyristor ionizes the Rydberg neutrals and accelerates them into the mass spectrometer. In REMPI modus, the generated ions are accelerated directly into the TOF without the retarding field. The ion signal is detected by a conventional dual micro-channel-plate detector and transferred to a LeCroy 534M digital oscilloscope. A computer, linked to the oscilloscope by a GPIB connection performs the data acquisition and processing. The 123-DCFB was purchased from Aldrich, 126-DFCB from ABCR and were used without further purification.

3. Quantum-chemical calculations

Quantum chemical calculations were performed in order to assign the observed vibrational bands and to support the experimental findings. The software package Turbomole\textsuperscript{17–20} was used for all quantum chemical calculations. Geometry optimizations and subsequent frequency analyses for molecules in the electronic ground state (S\textsubscript{0}) and the cationic ground state (D\textsubscript{0}) were conducted at the density functional theory (DFT) level of theory with both the gradient corrected functional BP86\textsuperscript{21a} and the hybrid functional B3LYP.\textsuperscript{21b} The triple basis set TZVPP\textsuperscript{21c} has been applied to all DFT calculations. Calculations for the S\textsubscript{1} were done analogously using the time dependent density functional theory (TDDFT). For comparison reasons, geometry calculations and frequency analyses were also treated at the coupled cluster (CC2) level of theory for the S\textsubscript{0} and S\textsubscript{1} state using the Ahlrichs basis set cc-pVTZ.\textsuperscript{21d} The nomenclature used for assignment of vibrational bands is according to Varsanyi and Szoke,\textsuperscript{22} which is derived from Wilson’s notation of the Benzene modes.\textsuperscript{23}

We refrained from the use of scaling factors to fit the calculated frequencies.

4. Experimental results

4.1. 1,3-Dichloro-2-fluorobenzene (1,3,2-DCFB)

4.1.1. REMPI spectrum. According to electric dipole selection rules the transition to first excited singlet state \( ^1\text{B}_2S_1(\pi^* \leftarrow \pi) \) in 1,3,2-DCFB is allowed (\( \gamma \)-polarized). For benzene, the corresponding transition \( ^1\text{A}_1S_1 \leftarrow X^1\text{A}_1G \) is dipole forbidden under D\textsubscript{0h} symmetry. The reduced symmetry in 1,3,2-DCFB \( (C_\text{v}) \) leads to an electronically as well as vibronically allowed transition. Starting from the premise that the molecules are sufficiently cooled with regards to their degrees of freedom, only total symmetric \( (a_1) \) vibrations are allowed according to the Franck-Condon (FC) principle. Due to vibronic coupling to intensive, nearby states, vibrations of \( a_2 \) and \( b_2 \) symmetry can gain intensity as well. The REMPI spectrum shown in Fig. 1 in units of internal energy could be recorded in the range up to 1300 cm\textsuperscript{-1}. The excitation energy of the first excited state \( S_1 \) could be determined for the first time to be 36 460 ± 2 cm\textsuperscript{-1}.

Normal coordinate analysis for 1,3,2-DCFB yields following distribution of fundamental modes under \( C_{\text{2v}} \) symmetry: \( \nu_{\text{ vib}} = 11 \times a_1, 10 \times b_2, 3 \times a_2, 6 \times b_1 \). Clearly, the spectrum is dominated by the total symmetric modes \( 1 \) \( (565 \text{ cm}^{-1}) \) and \( 18a \) \( (977 \text{ cm}^{-1}) \). Moreover the \( a_1 \)-symmetric modes \( 9a_1, 6a_1, 7a_1, 12b \) \( (186 \text{ cm}^{-1}, 349 \text{ cm}^{-1}, 792 \text{ cm}^{-1}, 1104 \text{ cm}^{-1}) \) could be identified with lower intensity. With \( 16a_1 \) \( (360 \text{ cm}^{-1}) \) also an \( a_2 \)-symmetric mode could be assigned. As expected, no modes of \( b_1 \)-symmetry could be assigned to the spectrum in accordance with selection rules. Particular attention should be paid to the low frequency band at 120 cm\textsuperscript{-1}. A band with such a low frequency can with certainty be assigned to an out-of-plane mode. Based on correlation with MATI spectra we assigned the first even overtone of the \( b_1 \)-symmetric mode 17b to this band. The frequency of 52 cm\textsuperscript{-1} calculated with the coupled cluster method is in reasonable agreement with the experimental value for the half of the overtone for 17b.\textsuperscript{2} The bands at 247 cm\textsuperscript{-1} \( (15\text{a}) \), 337 cm\textsuperscript{-1} \( (6b) \), 500 cm\textsuperscript{-1} \( (3\text{b}) \) and 1236 cm\textsuperscript{-1} \( (18b) \) were assigned to \( b_2 \)-symmetric modes. The latter two experimental values are in excellent agreement with both calculated values (TDDFT, CC2) for the first excited singlet state of 1,2,3-DCFB. Comparing the calculated values for the \( 15\text{a} \) and \( 6\text{b} \) mode a major deviation becomes apparent, just like in the case of 17b. All performed calculations show good agreement with the experiment for the modes \( 9a_1, 6a_1, 7a_1, 18a_1, 12\text{a}, 16a_1 \), whereas the best results were obtained with the CC2 level of theory (see Table 1).

4.1.2. MATI spectra. The MATI spectra \textit{via} the \( S_1 \) intermediate states \( 0\text{a} \), 17b, 9a1, 11 are shown in Fig. 2. The origin of the \( D_0(\text{B}_2) \) state and with that the adiabatic ionization energy was found to be 75.242 ± 6 cm\textsuperscript{-1} (9.3288 ± 0.0007 eV). This value is in good accordance with the previously by conventional photoelectron spectroscopy determined value of 9.32 ± 0.02 eV.\textsuperscript{25}
Fig. 1 (1 + 1’) REMPI spectrum of 1,3-dichloro-2-fluoro-benzene (1,3,2-DCFB).

Table 1 Comparison experimental and calculated normal modes observed in the $S_0$, $S_1$ and $D_0$ state of 1,3,2 DCFB

| S_0(C_{2v}) | Wilson | Sym. | B3LYP | BP86 | CC2 | exp. | B3LYP | BP86 | CC2 | exp. | B3LYP | BP86 |
|-------------|--------|------|-------|------|-----|------|-------|------|-----|------|-------|------|
| 9a          | $a_1$  | 256  | 192   | 186  | 189 | 186  | 241   | 232  | 183 | 190 | 195   | 189  |
| 6a          | $a_1$  | 376  | 379   | 369  | 380 | 349  | 355   | 361  | 343 | 361 | 381   | 372  |
| 1           | $a_1$  | 597  | 601   | 584  | 596 | 565  | 538   | 522  | 558 | 578 | 603   | 586  |
| 7a          | $e$    | 803  | 839   | 813  | 829 | 792  | 831   | 815  | 791 | 798 | 820   | 797  |
| 18a         | $a_1$  | 1058 | 1092  | 1061 | 1080| 977  | 1013  | 998  | 991 | 1047| 1027  |      |
| 12          | $a_1$  | 1112 | 1116  | 1083 | 1124| 1104 | 1077  | 1046 | 1079| 1143| 1104  |      |
| 13          | $a_1$  | 1205 | 1277  | 1240 | 1277| 1314 | 1320  | 1242 | 1242| 1339| 1295  |      |
| 19a         | $a_1$  | 1462 | 1490  | 1444 | 1485| 1213 | 1229  | 1383 | 1459| 1412|       |      |
| 8a          | $a_1$  | 1572 | 1613  | 1564 | 1608| 1509 | 1476  | 1512 | 1618| 1567|       |      |
| 20a         | $a_1$  | 3084 | 3189  | 3119 | 3220| 3159 | 3080  | 3210 | 3197| 3126|       |      |
| 2           |        |      | 3212  | 3142 | 3243| 3220 | 3147  | 3246 | 3218| 3147|       |      |
| 10a         | $e$    | 215  | 208   | 201  | 207 | 120  | 123   | 71   | 174 | 180 | 173   |      |
| 16a         | $e$    | 530  | 553   | 534  | 518 | 360  | 458   | 495  | 313 | 512 | 498   | 476  |
| 17a         | $e$    | 894  | 921   | 876  | 890 | 1045 | 1060  | 616  | 936 | 897 |       |      |
| 17b         | $b_1$  | 115  | 107   | 103  | 107 | 60   | 31     | 52   | 95  | 88  | 85    |      |
| 10b         | $b_1$  | 260  | 282   | 271  | 278 | 270  | 263   | 259  | 178 | 264 | 274   | 265  |
| 16b         | $b_1$  | 513  | 533   | 512  | 542 | 502  | 454   | 364  | 452 | 455 | 441   |      |
| 4           | $e$    | 705  | 732   | 699  | 680 | 766  | 755   | 460  | 732 | 743 | 715   |      |
| 11b         | $e$    | 770  | 794   | 758  | 771 | 847  | 827   | 601  | 678 | 826 | 792   |      |
| 5           | $b_1$  | 965  | 983   | 937  | 949 | 1004 | 966   | 782  | 1009| 966 |       |      |
| 15          | $b_1$  | 279  | 258   | 248  | 252 | 247  | 62     | 61   | 227 | 243 | 253   |      |
| 6b          | $b_1$  | 401  | 404   | 393  | 401 | 337  | 202   | 209  | 319 | 331 | 300   | 331  |
| 3           | $b_1$  | 539  | 545   | 528  | 538 | 500  | 500   | 498  | 519 | 471 | 513   | 504  |
| 7b          | $b_1$  | 829  | 798   | 779  | 810 | 698  | 683   | 759  | 827 | 812 | 796   |      |
| 9b          | $b_1$  | 1154 | 1180  | 1145 | 1170| 1177 | 1144  | 1105 | 1083| 1104|       |      |
| 18b         | $b_1$  | 1205 | 1233  | 1193 | 1223| 1236 | 1250  | 1185 | 1170| 1330| 1192  |      |
| 14          | $b_1$  | 1255 | 1313  | 1322 | 1421| 1413 | 1360  | 1497 | 1226| 1296|       |      |
| 19b         | $b_1$  | 1446 | 1481  | 1432 | 1465| 1446 | 1407  | 1389 | 1514| 1466|       |      |
| 8b          | $b_1$  | 1583 | 1615  | 1566 | 1608| 1574 | 1545  | 1683 | 1371| 1384|       |      |
| 20b         | $b_1$  | 3084 | 3207  | 3137 | 3235| 3188 | 3177  | 3141 | 3215| 3144|       |      |

* IR-band, $^{24}$ From combination band. $^a$ From overtone.
Besides the $^0 \nu$ transition, the MATI spectrum obtained via the electronic origin exhibits several more additional resonances. The most prominent peak in the spectrum is the band assigned to the 17b mode, which is constituting a violation of the $\Delta \nu = 0$ propensity rule. Additionally, the mode 17b at 95 cm$^{-1}$ appears as a combination band (17b$^9$a$^1$) at 288 cm$^{-1}$. Moreover the spectrum is conspicuously rich in b$^1$-symmetric modes. In addition to 17b$^1$ we assigned the 10b$^1$ (264 cm$^{-1}$), 16b$^1$ (452 cm$^{-1}$), 11$^1$ (678 cm$^{-1}$) and 4$^1$ (732 cm$^{-1}$). Another out-of-plane vibration (10a$^1$) with a$_2$-symmetry and low intensity has been assigned to the band at 174 cm$^{-1}$. The bands at 361 cm$^{-1}$, 578 cm$^{-1}$ have been assigned to the total symmetric modes 6a$^1$ and 1$^1$, respectively. b$^1$ symmetric modes were identified at 242 cm$^{-1}$ (15$^1$), 331 cm$^{-1}$ (6b$^1$), 471 cm$^{-1}$ (3$^1$) and 827 cm$^{-1}$ (7b$^1$). The band at 657 cm$^{-1}$ fits the overtone 6b$^1$.

The MATI spectrum obtained via the S$^1$7b$^2$ shows a short, three-membered regular progression with transitions corresponding to the excitation of one, two and three quanta. In contradiction to the $\Delta \nu = 0$ propensity rule, the band labeled 17b$^1$ is the most prominent peak in the spectrum. It is notable that the 17b mode also appears in the combination bands 17b$^9$9a$^1$ (288 cm$^{-1}$) and 16b$^1$6b$^1$ (423 cm$^{-1}$). Also apparent is the richness in b$^1$-symmetric modes, first and foremost the intense 16b$^1$ (448 cm$^{-1}$), but also the 10b$^1$ (264 cm$^{-1}$), 11$^1$ (680 cm$^{-1}$), 4$^1$ (728 cm$^{-1}$). The MATI spectrum obtained via the S$^1$9a$^1$ mode also shows a breakdown of the $\Delta \nu = 0$ propensity rule. Not the vertical transition into the D$^0$9a$^1$ state is the dominating one, but the band at 242 cm$^{-1}$ (15$^1$). In addition the 17b mode appears again, also as a combination in 17b$^9$9a$^1$. A further band at 331 cm$^{-1}$ could be identified with 6b$^1$. The measured values are in good accordance with the calculated values (195 and 189 cm$^{-1}$ for the 9a$^1$, 233 and 253 cm$^{-1}$ for the 15$^1$ and also 300 and 331 cm$^{-1}$ for the 6b$^1$).

The MATI spectrum via S$^1$1$^1$ continues the series of MATI spectra characterized by a breakdown of the $\Delta \nu = 0$ propensity rule in favor for the vibronic transition into the D$^0$17b$^1$ state. Further active modes that could be assigned in the recorded range up to 750 cm$^{-1}$ are the 15$^1$ (241 cm$^{-1}$), 6b$^1$ (331 cm$^{-1}$) and 1$^1$ (578 cm$^{-1}$). The experimentally determined frequency for the 1$^1$ mode is in good accordance with the calculated values of 578 cm$^{-1}$ or 603 cm$^{-1}$ respectively. It should be noticed that, owing to the heavy substituents, the displacement pattern of the ‘ring-breathing-mode’ shows a striking deviation from the original benzene pattern. It resembles clearly the pattern of mode 6a found for benzene. The assignment of the band at 578 cm$^{-1}$ to the mode 6a is excluded since it was already doubtlessly assigned to the band at 361 cm$^{-1}$.

4.2. 1,3-Difuoro-2-chloro-benzene (1,3,2-DFCB)

4.2.1. REMPI spectrum. 1,3,2-DFCB belongs to C$_{2v}$ point group and has a dipole allowed transition to the $^1A_1$S$_0$(\pi* $\rightarrow$ \pi) first excited state. According to FC-principle only transitions in total symmetric (a$_1$) modes are allowed, b$_1$ and b$_2$ can gain intensity due to vibronic coupling mechanism, a$_2$ modes are symmetry forbidden. The REMPI spectrum shown in Fig. 3 in units of internal energy could be recorded in the range up to 800 cm$^{-1}$. The excitation energy of the first excited state S$_1$ could be determined for the first time to be 37 449 ± 2 cm$^{-1}$.
The electronic origin and the total symmetric mode $9a^1$ at 228 cm$^{-1}$ dominates clearly the measured REMPI spectrum. It should be noted that the remaining bands at 381 cm$^{-1}$ and 607 cm$^{-1}$ that were both assigned to the total symmetric modes $6^1$ and $1^1$, respectively. Quite unusual for total symmetric modes we found poor consistency between calculated and observed bands: calculation substantially underestimate the $6a^1$ and $1^1$ with 188 cm$^{-1}$ to 202 cm$^{-1}$ and 488 cm$^{-1}$ to 517 cm$^{-1}$, respectively. The $9a^1$ has been overestimated with 364 cm$^{-1}$ to 374 cm$^{-1}$. Nevertheless the correlation with MATI spectra backups the assignment of the total symmetric modes. Moreover, the calculations suggest the mode $7a^1$, that cannot be seen in the spectrum, to appear in the spectrum between 710 cm$^{-1}$ and 750 cm$^{-1}$. As expected, no modes of $a_2$ symmetry could be assigned to the spectrum in accordance with selection rules. In contrast to 1,2,3-TCB and 1,3,2-DCFB, transitions to $b_1$-symmetric modes are allowed in 1,3,2-DFCB. The bands at 25, 98 and 404 cm$^{-1}$ could be identified with the $b_1$-symmetric modes $17b^1$, $10b^1$ and $16b^1$. In this case, the calculated frequencies are in good agreement with the observed ones. The

![Fig. 3](image-url)  
Fig. 3  $(1 + 1')$ REMPI spectrum of 1,3-difluoro-2-chloro-benzene (1,3,2-DFCB).

![Fig. 4](image-url)  
Fig. 4  MATI spectra of 1,2,6 DCFB of different vibrational intermediate states of the first excited electronic state: (a) via $9a^1$, (b) via $17b^2$, (c) via the electronic origin ($0^0$).
17b\(^1\) has been predicted to appear between 31 cm\(^{-1}\) and 51 cm\(^{-1}\), the 10b\(^1\) between 176 cm\(^{-1}\) and 215 cm\(^{-1}\) and the 16b\(^1\) between 351 cm\(^{-1}\) and 428 cm\(^{-1}\). With 15\(^1\) and 6b\(^1\) two a\(^2\)\(-\)symmetric modes could be assigned. Noteworthy is the appearance of the 15 mode as a short, three-membered progression of overtones (15\(^1\), 15\(^2\), 15\(^3\)). The measured frequencies of 443 cm\(^{-1}\) for 6b\(^1\) and 63 cm\(^{-1}\) for 15\(^1\) are well reproduced by the B3LYP calculation with 439 and 64 cm\(^{-1}\). The BP86 calculation predicts the 15\(^1\) correctly with 67 cm\(^{-1}\), while it slightly overestimates the 6b\(^1\) with 463 cm\(^{-1}\). The CC2 calculation gives good results in predicting the 6b\(^1\) with 439 cm\(^{-1}\), while it overestimates the 15\(^1\) with 154 cm\(^{-1}\).

### 4.2.2. MATI spectra.

The MATI spectra via the S\(_1\) intermediate states 0\(^0\), 17b\(^1\), 9a\(^1\) are shown in Fig. 4. The origin of the D\(_0\)(B\(_1\)) state and with that the adiabatic ionization energy was found to be 75.627 (+6 cm\(^{-1}\) (9.3765 ± 0.0007 eV). This value is in good accordance the previously by photoelectron spectroscopy determined value of 9.37 ± 0.02 eV.\(^{25}\)

In accordance with the D\(_v=0\) propensity rule, the MATI spectrum obtained via the electronic origin is dominated by the 0\(^0\)-band. Furthermore the spectrum is characterized by strong activity of the two total symmetric modes 9a\(^1\) and 6a\(^1\). Within the recorded range of 1000 cm\(^{-1}\), the spectrum exhibits a progression in 9a composed of the first three overtones 9a\(^1\) (293 cm\(^{-1}\)), 9a\(^2\) (588 cm\(^{-1}\)) and 9a\(^3\) (882 cm\(^{-1}\)).

Additionally we assigned the band at 925 cm\(^{-1}\) to a combination band of modes 9a\(^1\)11. The relative intensive band at 630 cm\(^{-1}\) has been identified with the mode 11. The shoulder at 649 cm\(^{-1}\) in the peak labeled with 11 has been assigned to the mode 41. Exhibiting a similar weak intensity as the 41, another b\(^1\)\(-\)symmetrical mode (7a\(^1\)) could be identified at 778 cm\(^{-1}\).

The assignment of the bands at 95 cm\(^{-1}\) and 124 cm\(^{-1}\) is consistent with the previous work,\(^1\)

### Table 2

| S\(_0\)(C\(_{2v}\)) | S\(_i\) (C\(_{2v}\)) | S\(_1\) (C\(_{2v}\)) | S\(_2\) (C\(_{2v}\)) | S\(_3\) (C\(_{2v}\)) | S\(_4\) (C\(_{2v}\)) |
|---|---|---|---|---|---|
| Wilson | Sym. | exp. | B3LYP | BP86 | CC2 | exp. | B3LYP | BP86 | CC2 | exp. | B3LYP | BP86 |
| 9a | a\(_1\) | 301 | 290 | 295 | 228 | 374 | 364 | 367 | 293 | 294 |
| 6a | a\(_1\) | 437 | 425 | 436 | 381 | 198 | 202 | 188 | 418 | 435 | 422 |
| 1 | a\(_1\) | 617 | 602 | 618 | 607 | 517 | 500 | 488 | 630 | 636 | 620 |
| 7a | a\(_1\) | 783 | 760 | 776 | 748 | 729 | 713 | 778 | 784 | 761 |
| 19a | a\(_1\) | 1072 | 1142 | 1124 | 1056 | 1462 | 1360 | 1360 | 1318 | 1318 |
| 18a | a\(_1\) | 1121 | 1102 | 1065 | 1113 | 1103 | 1059 | 1045 | 1021 |
| 12 | a\(_1\) | 1314 | 1275 | 1317 | 1005 | 1194 | 1288 | 1141 | 1372 |
| 13 | a\(_1\) | 1494 | 1448 | 1491 | 1294 | 1252 | 1268 | 1265 | 1613 |
| 8a | a\(_1\) | 1637 | 1587 | 1635 | 1577 | 1542 | 1507 | 1665 | 1613 |
| 20a | a\(_1\) | 3191 | 3121 | 3224 | 3201 | 3133 | 3212 | 3199 | 3128 |
| 2 | a\(_1\) | 3212 | 3143 | 3248 | 3223 | 3155 | 3266 | 3217 | 3148 |
| 10a | a\(_2\) | 249 | 239 | 247 | 194 | 189 | 183 | 201 | 218 | 209 |
| 16a | a\(_2\) | 597 | 573 | 588 | 762 | 754 | 519 | 546 | 565 | 541 |
| 17a | a\(_2\) | 893 | 850 | 873 | 1043 | 1107 | 788 | 920 | 880 |
| 17b | b\(_1\) | 124 | 119 | 125 | 25 | 31 | 41 | 51 | 97 | 98 |
| 10b | b\(_1\) | 275 | 264 | 273 | 198 | 215 | 214 | 176 | 280 | 289 |
| 16b | b\(_1\) | 530 | 510 | 521 | 404 | 428 | 407 | 351 | 439 | 434 |
| 4 | b\(_1\) | 717 | 684 | 675 | 805 | 779 | 649 | 649 | 729 | 700 |
| 11 | b\(_1\) | 792 | 754 | 772 | 640 | 632 | 548 | 839 | 837 | 802 |
| 5 | b\(_1\) | 968 | 922 | 944 | 979 | 946 | 781 | 1000 | 954 |
| 15 | b\(_2\) | 212 | 204 | 208 | 63 | 64 | 67 | 154 | 213 | 221 |
| 6b | b\(_2\) | 509 | 494 | 501 | 443 | 451 | 463 | 439 | 367 | 386 |
| 3 | b\(_2\) | 555 | 534 | 543 | 511 | 501 | 492 | 489 | 539 | 522 |
| 7b | b\(_2\) | 1020 | 990 | 1014 | 979 | 958 | 948 | 982 | 1081 | 986 |
| 9b | b\(_2\) | 1179 | 1088 | 1167 | 1137 | 1128 | 1133 | 1110 | 1087 |
| 18b | b\(_2\) | 1266 | 1226 | 1262 | 1208 | 1171 | 1194 | 1303 | 1259 |
| 14 | b\(_2\) | 1322 | 1311 | 1424 | 1380 | 1393 | 1356 | 1354 | 1316 |
| 19b | b\(_2\) | 1503 | 1456 | 1495 | 1441 | 1382 | 1381 | 1548 | 1500 |
| 8b | b\(_2\) | 1626 | 1577 | 1623 | 1477 | 1451 | 1680 | 1381 | 1370 |
| 20b | b\(_2\) | 3206 | 3137 | 3242 | 3207 | 3139 | 3215 | 3214 | 3145 |
and 196 cm\(^{-1}\) to the modes 17b\(^1\) and 17b\(^2\) respectively seems appropriate. Assignments that are more tentative are the 16b\(^1\) and 11\(^1\) to the bands at 439 cm\(^{-1}\) and 839 cm\(^{-1}\). The a\(^2\) symmetrical modes 10a\(^1\) and 16a\(^1\) are assigned to the weak bands at 201 cm\(^{-1}\) and 546 cm\(^{-1}\). With exception of 4\(^1\) all calculated frequencies are in good accordance with the experimentally determined ones.

Provided the validity of the \(\Delta v = 0\) propensity rule, the MATI spectrum obtained \(\text{via}\) the S\(_1\)7b\(^1\) mode ought to be characterized by a towering 17b\(^1\) band. Contrary to expectations, the band 17b\(^1\) could not be observed in the spectrum shown in Fig. 4. Instead, the spectrum shows the 9a\(^1\) at 291 cm\(^{-1}\) as the most intensive resonance absorption. As can be seen from the correlation between the MATI spectra in Fig. 4, the first overtone 9a\(^2\) appears at 586 cm\(^{-1}\) as well. The signals at 1 as the most intensive resonance absorption. As can be seen from the correlation between the MATI spectra in Fig. 4, the first overtone 9a\(^2\) appears at 586 cm\(^{-1}\) as well. The signals at 11a\(^1\) and 629 cm\(^{-1}\) are identical with the bands at 7 339 cm\(^{-1}\) and 143 cm\(^{-1}\) showing a prominent shoulder. The MATI spectrum obtained \(\text{via}\) the S\(_1\)9a\(^3\) shows three prominent peaks: the 6a\(^1\), the 9a\(^6\)a\(^1\) and the 18a\(^1\). Without folding the spectrum with the laser
power, no absolute statement can be made in regards to the peak intensities. The three peaks are of nearly equal intensity (approx. 5% difference), so it is hard to tell which one is the highest in intensity. Nevertheless it can be stated that in contrary to the predictions of the propensity rule, transitions to 6a1 and 9a16a1 are at least as same as intensive while the vertical transition into the D09a1 state is scarcely visible in the spectrum. Nevertheless the mode 9a appears in a series of overtones 9a16a1 (710 cm⁻¹), 9a111 (924 cm⁻¹) and 9a16a1 (1003 cm⁻¹).

Remarkably, the spectrum exhibits a strong activity in 6a modes: the bands assigned to the modes 6a1 and 9a16a1 are among the three most intense bands in the spectrum. The 6a1 vibration shows progression activity (6a1 and 6a2 in the recorded range). In addition, the 6a1 mode contributes to overtone bands as already discussed above. The weak features at 97, 193 and 213 cm⁻¹ have been assigned on the basis of our previous

### Table 5 CC2/cc-pVTZ calculated geometries of 1,3,2-DCFB

| Bond length [Å] | C2v | C2 |
|-----------------|-----|-----|
| C1–C2           | 1.395 | 1.432 |
| C2–C3           | 1.395 | 1.432 |
| C3–C4           | 1.393 | 1.426 |
| C4–C5           | 1.393 | 1.421 |
| C5–C6           | 1.393 | 1.421 |
| C6–C1           | 1.393 | 1.426 |
| C1–C17          | 1.725 | 1.719 |
| C2–F8           | 1.333 | 1.326 |
| C3–Cl9          | 1.081 | 1.079 |
| C4–H10          | 1.081 | 1.079 |
| C5–H11          | 1.081 | 1.079 |
| C6–H12          | 1.080 | 1.079 |

### Table 6 B3LYP/TZVPP calculated geometries of 1,3,2-DFCB

| Bond length [Å] | C2v | C2v | C2v |
|-----------------|-----|-----|-----|
| C1–C2           | 1.393 | 1.365 | 1.440 |
| C2–C3           | 1.393 | 1.365 | 1.440 |
| C3–C4           | 1.384 | 1.365 | 1.444 |
| C4–C5           | 1.393 | 1.365 | 1.444 |
| C5–C6           | 1.393 | 1.365 | 1.444 |
| C6–C1           | 1.393 | 1.365 | 1.444 |
| C1–Cl8          | 1.729 | 2.361 | 1.665 |
| C4–Cl9          | 1.081 | 1.081 | 1.082 |
| C5–H11          | 1.081 | 1.080 | 1.082 |
| C6–H12          | 1.081 | 1.081 | 1.082 |

### Bond angles [°]

| C1–C2–C3        | 119.992 | 121.970 |
| C2–C3–C4        | 120.078 | 118.706 |
| C3–C4–C5        | 119.618 | 118.910 |
| C4–C5–C6        | 119.618 | 118.902 |
| C5–C6–C1        | 119.618 | 118.910 |
| C6–C1–C2        | 119.105 | 118.817 |
| C7–C1–C2–Cl8    | 110.817 | 120.760 |
| C7–C1–C2–C3     | 0       | −17.842 |
| C8–C1–C2–C3     | 0       | 17.222  |
| C9–C3–C4–Cl9    | 0       | −17.842 |

| Bond angles [°] |
|-----------------|
| C1–C2–C3        | 117.528 | 111.693 | 118.393 |
| C2–C3–C4        | 121.191 | 126.328 | 120.838 |
| C3–C4–C5        | 118.997 | 118.962 | 118.528 |
| C4–C5–C6        | 120.640 | 117.726 | 122.876 |
| C5–C6–C1        | 118.997 | 118.962 | 118.528 |
| C6–C1–C2        | 117.528 | 126.328 | 120.838 |
| C7–C1–C2–Cl8    | 118.843 | 120.164 | 117.338 |
| C1–C2–Cl8       | 121.236 | 124.155 | 120.803 |
| C4–C3–F9        | 119.237 | 113.508 | 121.823 |

| Dihedral angle [°] |
|--------------------|
| C7–C1–C6–H12      | 0       | 0.027   | 0       |
| C7–C1–C2–F8       | 0       | −0.032  | 0       |
| C9–C3–C4–H10      | 0       | −0.204  | 0       |

studies\textsuperscript{7,8} to the out-of-plane modes 17b\textsuperscript{1}, 17b\textsuperscript{2} and in-plane mode 15\textsuperscript{1}.

5. Discussion

5.1. 1,3,2-DFCB

Compared to electronic and cationic ground states the 17b exhibits a drastically decreased frequency in the first electronic excited state (see Table 1). Such a frequency lowering suggests a geometrical distortion along the eigenvector of 17b in going from S\textsubscript{0} to S\textsubscript{1} or from D\textsubscript{0} to S\textsubscript{1}, respectively. As considered earlier by Tsuchiya et al.\textsuperscript{14} for difluorobenzene it is highly suggested that this phenomenon is the result of strong vibronic coupling between the S\textsubscript{1} and nearby states. But the most important indication for such a distortion shows up in the MATI spectra via the electronic origin and, first and foremost, via the 17b\textsuperscript{2}.

The latter exhibits a three-membered progression of the mode 17b. Not just that this progression shows a shift of the Franck–Condon maximum between S\textsubscript{1} and D\textsubscript{0} the fact that the transition from D\textsubscript{0}17b\textsuperscript{1} \rightleftharpoons S\textsubscript{1}17b\textsuperscript{2} is favored could be interpreted as a
The occurrence of the 15 as a \( b_2 \) symmetric mode is explained in accordance with the Herzberg–Teller effect. Here, in contradiction to the \( \Delta v = 0 \) propensity rule, the transition into the \( S_1 \) state is the most favorable while the vertical transition into the \( S_0 \) is scarcely observable. Nevertheless the mode 9a is strongly present in overtones (9a\(^6\)a\(^1\), 9a\(^1\)1\(^1\), 9a\(^3\)a\(^1\)). The geometry found by the TDDFT calculations (Fig. 6a; Tables 6 and 7) support the experimental findings in predicting a \( C_{2v} \)-symmetric structure distorted along the 6a. The CC2 calculation suggests a 17b-like distorted structure (Fig. 6b; Table 8).

The CC2 calculation suggests a 17b-like distorted structure (Fig. 6b). Considering the vanishing low activity of 17b in the MATI spectra, the suggestion seems incorrect. Nevertheless the substantial decrease in frequency for 6a\(^1\) and 9a\(^1\) comparing the \( D_0 \) state and the \( S_1 \) state is accurately reproduced by all quantum chemical methods employed. Comparing experimental and calculated results for 1,3,2-DFCB, the unusual, striking deviation (up to 49\%) for \( a_\gamma \)-symmetrical \( S_0 \)-frequencies was particularly noticeable. A poor reproduction of the molecular equilibrium structure in the \( S_1 \) (wrong minimum on the PES) could be one possible explanation.

A contrary indication is the fact that we find very similar frequencies for widely differing structures predicted by TDDFT (planar structure) and CC2 method (out-of-plane-structure). The planar structure resembles the experimental observations well, but since all frequency analyses were performed in harmonic approximation, a strong anharmonicity for this particular vibrations could be another explanation for this findings.

6. Conclusion

Comparing the results from two compounds presented in this paper with results obtained from different isomeric trichlorobenzenes, the increasing number of fluorne atoms lead to a progressive decrease in some of the observed frequencies in going from \( S_0 \) to \( S_1 \) and from \( D_0 \) to \( S_1 \), respectively. This is especially true for modes with a strong fluoride participation in their vibrational pattern like 17b (cf. Table 1). We interpreted this as a strong indication for an out-of-plane distortion during excitation or a replanarisation during ionization along the eigenvector of those modes. This phenomenon could be attributed to an above, bounding \( S(\pi\sigma^*) \) state which is stabilized by an increasing number of fluorne atoms. It can be concluded that the fluorne atoms contribute a significant share in form of \( \sigma^* \leftrightarrow \pi \) character to the transition.

For 1,3,2-DFCB the quantum chemical calculations gave excitation energies (EE) of 5.06 eV (B3LYP/TZVPP), 4.71 eV...
(BP86/TZVPP) and 4.44 eV (CC2/cc-pVTZ). The CC2 value reproduces the experimental value of 4.52 eV with a deviation of 0.08 eV best.

The experimental value for the ionization energy (IE) of 9.32 eV is underestimated by both DFT methods with 9.00 eV (B3LYP/TZVPP) and 8.97 eV (BP86/TZVPP). (The coupled cluster method CC2 is not suited for the ionic species!) In this case the frequency analysis performed by the CC2 method showed to be most appropriate to reproduce the experimental frequencies.

For 1,3,2-DFCB the quantum chemical calculations gave excitation energies (EE) of 5.23 eV (B3LYP/TZVPP), 4.90 eV (BP86/TZVPP) and 3.88 eV (CC2/cc-pVTZ). The TD-DFT value reproduces the experimental value of 4.64 eV best, whereas BP86 underestimates and B3LYP overestimates the experimental value. Both DFT methods with 9.03 eV (B3LYP/TZVPP) and 9.02 eV (BP86/TZVPP) underestimate the experimental value for the ionization energy (IE) of 9.38 eV. Contrary to the 1,3,2 DCFB the frequency analysis performed by the DFT methods results in a better reproduction of the experimental frequencies for the 1,3,2 DFCB.

Furthermore the Sg ← S0 and Dg ← S0 adiabatic ionization energies (IE) could be determined very exactly:

\[
\text{EE}(1,3,2-\text{DFCB}) = 36.460 \pm 2 \text{ cm}^{-1}, \quad \text{IE}(1,3,2-\text{DCFB}) = 75.242 \pm 6 \text{ cm}^{-1}.
\]

\[
\text{EE}(1,3,2-\text{DFCB}) = 37.449 \pm 2 \text{ cm}^{-1}, \quad \text{IE}(1,3,2-\text{DCFB}) = 75.627 \pm 6 \text{ cm}^{-1}.
\]

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