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## 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 cancerogenic 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.<sup>1-4</sup> 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 ( $D_0$ ).<sup>1,5-13</sup> 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  $S_1$ ,<sup>14</sup> 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  $b_{2g}$ -symmetric mode 11 shows an unusual strong activity in the form of a long progression ( $v_{11}^{2n}$ ). 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<sup>1</sup> were reconsidered and compared to the newly gained knowledge.

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## 2. Experimental setup

The experimental setup consists of a homemade time-of-flight (TOF) mass spectrometer as described in detail previously.<sup>1,15,16</sup> Briefly, the spectrometer consists of a standard second order corrected reflectron 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 opto-galvanic spectrum with a neon hollow cathode lamp yielding accuracy better than  $2\text{ cm}^{-1}$ . 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  $\text{cm}^{-1}$  by a subsequent delay ( $\sim 100\text{ ns}$ ) to multi-photon excitation. Finally, a high voltage pulse (890 V  $\text{cm}^{-1}$ ) 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<sup>17–20</sup> was used for all quantum chemical calculations. Geometry optimizations and subsequent frequency analyses for molecules in the electronic ground state ( $S_0$ ) and the cationic ground state ( $D_0$ ) were conducted at the density functional theory (DFT) level of theory with both the gradient corrected functional BP86<sup>21a</sup> and the hybrid functional B3LYP.<sup>21b</sup> The triple basis set TZVPP<sup>21c</sup> has been applied to all DFT calculations. Calculations for the  $S_1$  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  $S_0$ - and  $S_1$ -state using the Ahlrichs basis set cc-pVTZ.<sup>21d</sup> The nomenclature used for assignment of vibrational bands is according to

Varsanyi and Szoke,<sup>22</sup> which is derived from Wilson's notation of the Benzene modes.<sup>23</sup>

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  ${}^1\text{B}_2\text{S}_1(\pi^* \leftarrow \pi)$  in 1,3,2-DCFB is allowed ( $\gamma$ -polarized). For benzene, the corresponding transition  ${}^1\text{B}_{2u} \leftarrow {}^1\text{A}_{1g}$  is dipole forbidden under  $D_{6h}$  symmetry. The reduced symmetry in 1,3,2-DCFB ( $C_{2v}$ ) 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  $1300\text{ cm}^{-1}$ . The excitation energy of the first excited state  $S_1$  could be determined for the first time to be  $36\,460 \pm 2\text{ cm}^{-1}$ .

Normal coordinate analysis for 1,3,2-DCFB yields following distribution of fundamental modes under  $C_{2v}$  symmetry:  $\Gamma_{\text{vib}} = 11 \times a_1, 10 \times b_2, 3 \times a_2, 6 \times b_1$ . Clearly, the spectrum is dominated by the total symmetric modes  $1^1$  ( $565\text{ cm}^{-1}$ ) and  $18a$  ( $977\text{ cm}^{-1}$ ). Moreover the  $a_1$ -symmetric modes  $9a^1, 6a^1, 7a^1, 12^1$  ( $186\text{ cm}^{-1}, 349\text{ cm}^{-1}, 792\text{ cm}^{-1}, 1104\text{ cm}^{-1}$ ) 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  $120\text{ cm}^{-1}$ . 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  $52\text{ cm}^{-1}$  calculated with the coupled cluster method is in reasonable agreement with the experimental value for the half of the overtone for  $17b^2$ . The bands at  $247\text{ cm}^{-1}$  ( $15^1$ ),  $337\text{ cm}^{-1}$  ( $6b^1$ ),  $500\text{ cm}^{-1}$  ( $3^1$ ) and  $1236\text{ cm}^{-1}$  ( $18b^1$ ) 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  $15^1$  and  $6b^1$  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  $9a^1, 6a^1, 1^1, 7a^1, 18a^1, 12^1, 16a^1$ , whereas the best results were obtained with the CC2 level of theory (see Table 1).

**4.1.2. MATI spectra.** The MATI spectra *via* the  $S_1$  intermediate states  $0^0, 17b^1, 9a^1, 1^1$  are shown in Fig. 2. The origin of the  $D_0({}^2\text{B}_1)$  state and with that the adiabatic ionization energy was found to be  $75.242 \pm 6\text{ cm}^{-1}$  ( $9.3288 \pm 0.0007\text{ eV}$ ). This value is in good accordance with the previously by conventional photoelectron spectroscopy determined value of  $9.32 \pm 0.02\text{ eV}$ .<sup>25</sup>



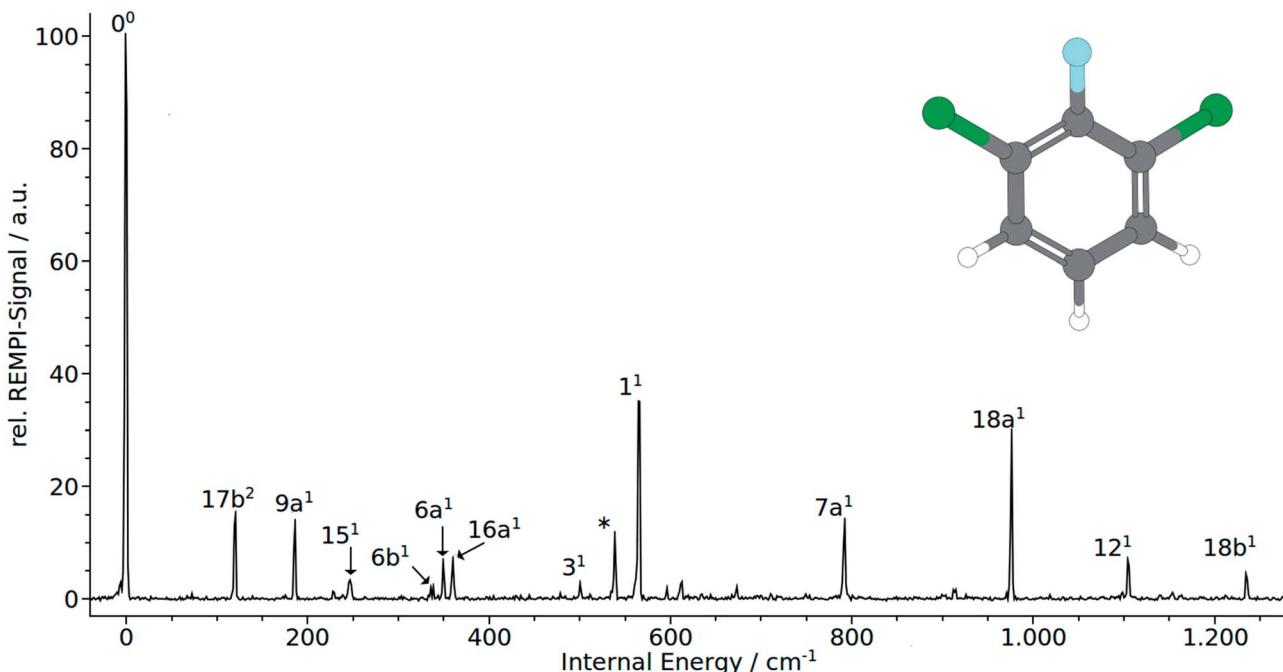


Fig. 1 (1 + 1') REMPI spectrum of 1,3-dichloro-2-fluoro-benzene (1,3,2-DCFB).

Table 1 Comparison experimental and calculated normal modes observed in the S<sub>0</sub>, S<sub>1</sub> and D<sub>0</sub> state of 1,3,2 DCFB

S <sub>0</sub> (C <sub>2v</sub> )						S <sub>1</sub>	(C <sub>2v</sub> )	(C <sub>2v</sub> )	(C <sub>S</sub> )	D <sub>0</sub>	(C <sub>2v</sub> )	
Wilson	Sym.	exp.	B3LYP	BP86	CC2	exp.	B3LYP	BP86	CC2	exp.	B3LYP	BP86
9a	a <sub>1</sub>	256 <sup>a</sup>	192	186	189	186	241	232	183	190	195	189
6a	a <sub>1</sub>	376 <sup>a</sup>	379	369	380	349	355	361	343	361	381	372
1	a <sub>1</sub>	597 <sup>a</sup>	601	584	596	565	538	522	558	578	603	586
7a	a <sub>1</sub>	803 <sup>a</sup>	839	813	829	792	831	815	791	798	820	797
18a	a <sub>1</sub>	1058 <sup>a</sup>	1092	1061	1080	977	1013	998	991		1047	1027
12	a <sub>1</sub>	1112 <sup>a</sup>	1116	1083	1124	1104	1077	1046	1079		1143	1104
13	a <sub>1</sub>	1205 <sup>a</sup>	1277	1240	1277		1314	1320	1242		1339	1295
19a	a <sub>1</sub>	1462 <sup>a</sup>	1490	1444	1485		1213	1229	1383		1459	1412
8a	a <sub>1</sub>	1572 <sup>a</sup>	1613	1564	1608		1509	1476	1512		1618	1567
20a	a <sub>1</sub>	3084 <sup>a</sup>	3189	3119	3220		3159	3080	3210		3197	3126
2	a <sub>1</sub>		3212	3142	3243		3220	3147	3246		3218	3147
10a	a <sub>2</sub>	215 <sup>a,b</sup>	208	201	207		120	123	71	174	180	173
16a	a <sub>2</sub>	530 <sup>a,b</sup>	553	534	518	360	458	495	313	512	498	476
17a	a <sub>2</sub>	894 <sup>a</sup>	921	876	890		1045	1060	616		936	897
17b	b <sub>1</sub>	115 <sup>a,b</sup>	107	103	107	60 <sup>c</sup>	31	38	52	95	88	85
10b	b <sub>1</sub>	260 <sup>a,b</sup>	282	271	278	270 <sup>c</sup>	263	259	178	264	274	265
16b	b <sub>1</sub>	513 <sup>a</sup>	533	512	542		502	454	364	452	455	441
4	b <sub>1</sub>	705 <sup>a</sup>	732	699	680		766	755	460	732	743	715
11	b <sub>1</sub>	770 <sup>a</sup>	794	758	771		847	827	601	678	826	792
5	b <sub>1</sub>	965 <sup>a</sup>	983	937	949		1004	966	782		1009	966
15	b <sub>2</sub>	279 <sup>a</sup>	258	248	252	247	62	61	227	242	233	253
6b	b <sub>2</sub>	401 <sup>a</sup>	404	393	401	337	202	209	319	331	300	331
3	b <sub>2</sub>	539 <sup>a</sup>	545	528	538	500	500	498	519	471	513	504
7b	b <sub>2</sub>	829 <sup>a</sup>	798	779	810		698	683	759	827	812	796
9b	b <sub>2</sub>	1154 <sup>a</sup>	1180	1145	1170		1177	1144	1105		1083	1104
18b	b <sub>2</sub>	1205 <sup>a,b</sup>	1233	1193	1223	1236	1250	1185	1170		1330	1192
14	b <sub>2</sub>	1255 <sup>a</sup>	1313	1322	1421		1413	1360	1497		1226	1296
19b	b <sub>2</sub>	1446 <sup>a</sup>	1481	1432	1465		1446	1407	1389		1514	1466
8b	b <sub>2</sub>	1583 <sup>a</sup>	1615	1566	1608		1574	1545	1683		1371	1384
20b	b <sub>2</sub>	3084 <sup>a</sup>	3207	3137	3235		3188	3177	3141		3215	3144

<sup>a</sup> IR-band.<sup>24</sup> <sup>b</sup> From combination band. <sup>c</sup> From overtone.

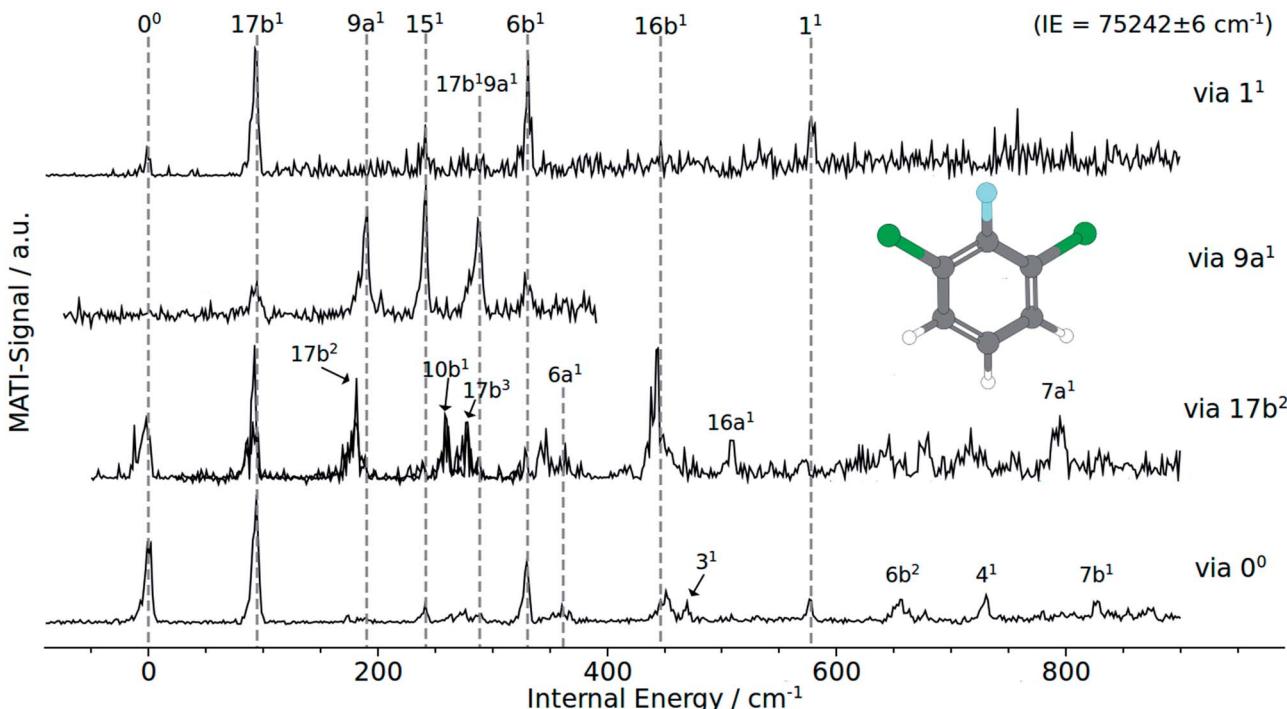


Fig. 2 MATI spectra of 1,3,2-DFCB of different vibrational intermediate states of the first excited electronic state: (a) via  $1^1$ , (b) via  $9a^1$ , (c) via  $17b^2$ , (d) via the electronic origin ( $0^0$ ).

Besides the  $0^0$  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  $17b^1$  at  $95\text{ cm}^{-1}$  appears as a combination band ( $17b^19a^1$ ) at  $288\text{ cm}^{-1}$ . Moreover the spectrum is conspicuously rich in  $b_1$ -symmetric modes. In addition to  $17b^1$  we assigned the  $10b^1$  ( $264\text{ cm}^{-1}$ ),  $16b^1$  ( $452\text{ cm}^{-1}$ ),  $11^1$  ( $678\text{ cm}^{-1}$ ) and  $4^1$  ( $732\text{ cm}^{-1}$ ). Another out-of-plane vibration ( $10a^1$ ) with  $a_2$ -symmetry and low intensity has been assigned to the band at  $174\text{ cm}^{-1}$ . The bands at  $361\text{ cm}^{-1}$ ,  $578\text{ cm}^{-1}$  have been assigned to the total symmetric modes  $6a^1$  and  $1^1$ , respectively.  $b_2$  symmetric modes were identified at  $242\text{ cm}^{-1}$  ( $15^1$ ),  $331\text{ cm}^{-1}$  ( $6b^1$ ),  $471\text{ cm}^{-1}$  ( $3^1$ ) and  $827\text{ cm}^{-1}$  ( $7b^1$ ). The band at  $657\text{ cm}^{-1}$  fits the overtone  $6b^1$ .

The MATI spectrum obtained *via* the  $S_117b^2$  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  $17b^19a^1$  ( $288\text{ cm}^{-1}$ ) and  $16b^16b^1$  ( $423\text{ cm}^{-1}$ ). Also apparent is the richness in  $b_1$ -symmetric modes, first and foremost the intense  $16b^1$  ( $448\text{ cm}^{-1}$ ), but also the  $10b^1$  ( $264\text{ cm}^{-1}$ ),  $11^1$  ( $680\text{ cm}^{-1}$ ),  $4^1$  ( $728\text{ cm}^{-1}$ ). The MATI spectrum obtained *via* the  $S_19a^1$  mode also shows a breakdown of the  $\Delta\nu = 0$  propensity rule. Not the vertical transition into the  $D_09a^1$  state is the dominating one, but the band at  $242\text{ cm}^{-1}$  ( $15^1$ ). In addition the  $17b$  mode appears again, also as a combination in  $17b^19a^1$ . A further band at  $331\text{ cm}^{-1}$  could be identified with  $6b^1$ . The measured values

are in good accordance with the calculated values ( $195$  and  $189\text{ cm}^{-1}$  for the  $9a^1$ ,  $233$  and  $253\text{ cm}^{-1}$  for the  $15^1$  and also  $300$  and  $331\text{ cm}^{-1}$  for the  $6b^1$ ).

The MATI spectrum *via*  $S_11^1$  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  $D_017b^1$  state. Further active modes that could be assigned in the recorded range up to  $750\text{ cm}^{-1}$  are the  $15^1$  ( $241\text{ cm}^{-1}$ ),  $6b^1$  ( $331\text{ cm}^{-1}$ ) and  $1^1$  ( $578\text{ cm}^{-1}$ ). The experimentally determined frequency for the  $1^1$  mode is in good accordance with the calculated values of  $578\text{ cm}^{-1}$  or  $603\text{ cm}^{-1}$  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  $578\text{ cm}^{-1}$  to the mode  $6a$  is excluded since it was already doubtlessly assigned to the band at  $361\text{ cm}^{-1}$ .

#### 4.2. 1,3-Difluoro-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  ${}^1A_1S_1(\pi^* \leftarrow \pi)$  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  $800\text{ cm}^{-1}$ . The excitation energy of the first excited state  $S_1$  could be determined for the first time to be  $37\ 449 \pm 2\text{ cm}^{-1}$ .



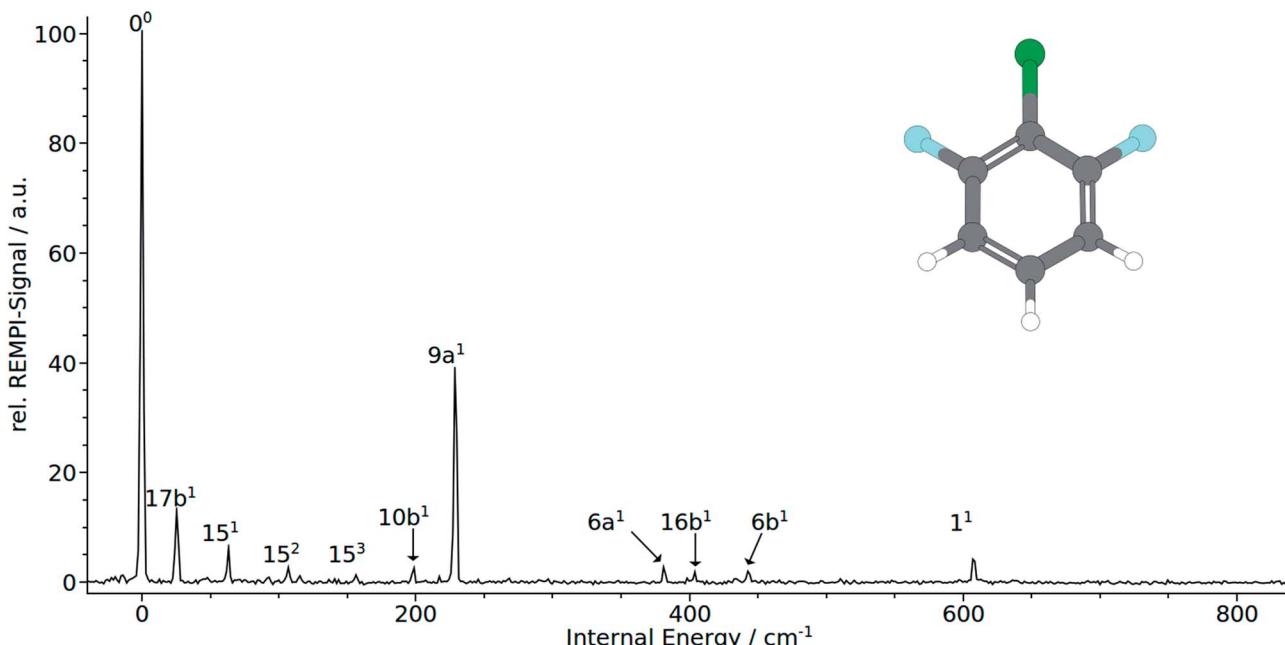


Fig. 3 (1 + 1') REMPI spectrum of 1,3-difluoro-2-chloro-benzene (1,3,2-DFCB).

The electronic origin and the total symmetric mode  $9a^1$  at  $228\text{ cm}^{-1}$  dominates clearly the measured REMPI spectrum. It should be noted that the remaining bands at  $381\text{ cm}^{-1}$  and  $607\text{ cm}^{-1}$  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  $188\text{ cm}^{-1}$  to  $202\text{ cm}^{-1}$  and  $488\text{ cm}^{-1}$  to  $517\text{ cm}^{-1}$ , respectively. The  $9a^1$  has been overestimated with  $364\text{ cm}^{-1}$  to  $374\text{ cm}^{-1}$ . 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  $710\text{ cm}^{-1}$  and  $750\text{ cm}^{-1}$ . 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  $404\text{ cm}^{-1}$  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

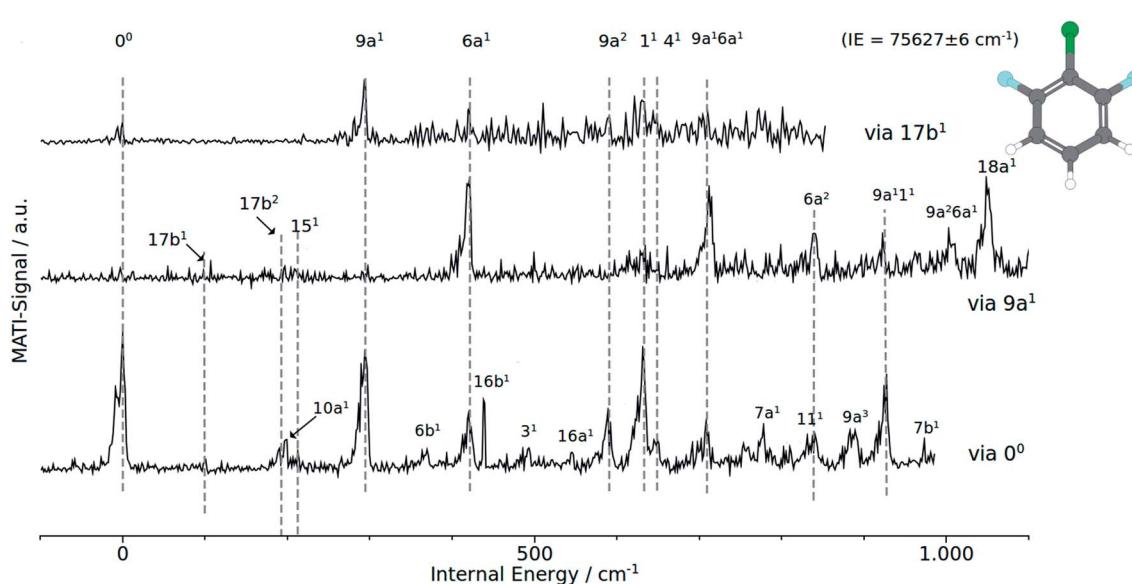


Fig. 4 MATI spectra of 1,2,6 DCFB of different vibrational intermediate states of the first excited electronic state: (a) via  $9a^1$ , (b) via  $17b^2$ , (c) via the electronic origin ( $0^0$ ).

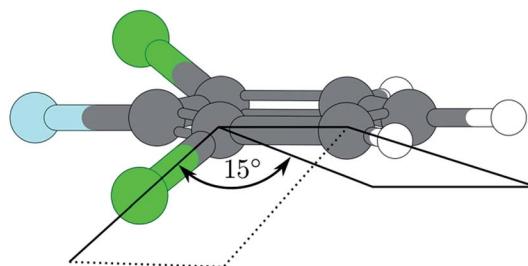


Fig. 5 Excited state geometry of 1,3,2-DCFB obtained by CC2-optimization.

$17b^1$  has been predicted to appear between  $31\text{ cm}^{-1}$  and  $51\text{ cm}^{-1}$ , the  $10b^1$  between  $176\text{ cm}^{-1}$  and  $215\text{ cm}^{-1}$  and the  $16b^1$  between  $351\text{ cm}^{-1}$  and  $428\text{ cm}^{-1}$ . 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  $443\text{ cm}^{-1}$  for  $6b^1$  and  $63\text{ cm}^{-1}$  for  $15^1$  are well reproduced by the B3LYP calculation with  $439$  and  $64\text{ cm}^{-1}$ . The BP86 calculation predicts the  $15^1$  correctly with  $67\text{ cm}^{-1}$ , while it slightly overestimates the  $6b^1$  with  $463\text{ cm}^{-1}$ . The CC2

calculation gives good results in predicting the  $6b^1$  with  $439\text{ cm}^{-1}$ , while it overestimates the  $15^1$  with  $154\text{ cm}^{-1}$ .

**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  $D_0(^2B_1)$  state and with that the adiabatic ionization energy was found to be  $75.627 \pm 6\text{ cm}^{-1}$  ( $9.3765 \pm 0.0007\text{ eV}$ ). This value is in good accordance the previously by photoelectron spectroscopy determined value of  $9.37 \pm 0.02\text{ eV}$ .<sup>25</sup>

In accordance with the  $\Delta\nu = 0$  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  $1000\text{ cm}^{-1}$ , the spectrum exhibits a progression in  $9a$  composed of the first three overtones  $9a^1$  ( $293\text{ cm}^{-1}$ ),  $9a^2$  ( $588\text{ cm}^{-1}$ ) and  $9a^3$  ( $882\text{ cm}^{-1}$ ). The  $6a$  appears as ground vibration  $6a^1$  ( $418\text{ cm}^{-1}$ ), first overtone  $6a^2$  ( $839\text{ cm}^{-1}$ ) as well as combination vibration  $9a^16a^1$  ( $706\text{ cm}^{-1}$ ).

Additionally we assigned the band at  $925\text{ cm}^{-1}$  to a combination band of modes  $9a^11^1$ . The relative intensive band at  $630\text{ cm}^{-1}$  has been identified with the mode  $1^1$ . The shoulder at  $649\text{ cm}^{-1}$  in the peak labeled with  $1^1$  has been assigned to the mode  $4^1$ . Exhibiting a similar weak intensity as the  $4^1$ , another  $b_1$ -symmetrical mode ( $7a^1$ ) could be identified at  $778\text{ cm}^{-1}$ . In the view of previous work,<sup>1</sup> the assignment of the bands at  $95\text{ cm}^{-1}$

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

$S_0(C_{2v})$						$S_1$	$(C_{2v})$		$(C_{2v})$		$(C_S)$	$D_0$	$(C_{2v})$	
Wilson	Sym.	exp.	B3LYP	BP86	CC2	exp.	B3LYP	BP86	CC2	exp.	B3LYP	BP86		
9a	$a_1$	301	290	295	228	374	364	367	293	304	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		1506	1462	1360		1360	1318			
18a	$a_1$	1121	1042	1065		1113	1083	1059		1045	1021			
12	$a_1$	1314	1275	1317		1005	984	949		1150	1114			
13	$a_1$	1494	1448	1491		1294	1252	1268		1413	1372			
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	766	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	94			
10b	$b_1$	275	264	273	198	215	214	176	280	289	277			
16b	$b_1$	530	510	521	404	428	407	351	439	434	415			
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	212			
6b	$b_2$	509	494	501	443	451	463	439	367	386	369			
3	$b_2$	555	534	543		511	501	492	489	539	522			
7b	$b_2$	1020	990	1014		979	958	948	982	1018	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	1331	1424		1380	1393	1456		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			



Table 3 B3LYP/TZVPP calculated geometries of 1,3,2-DCFB

B3LYP/TZVPP	$C_{2v}$			$C_2$			$C_{2v}$		
	$S_0$	$S_1$	$D_0$	$S_0$	$S_1$	$D_0$	$S_0$	$S_1$	$D_0$
<b>Bond length [Å]</b>									
C1–C2	1.391	1.364	1.438	C1–C2	1.400	1.377	1.444		
C2–C3	1.391	1.445	1.438	C2–C3	1.400	1.445	1.444		
C3–C4	1.389	1.403	1.373	C3–C4	1.396	1.411	1.382		
C4–C5	1.389	1.370	1.407	C4–C5	1.395	1.379	1.411		
C5–C6	1.389	1.370	1.407	C5–C6	1.395	1.434	1.411		
C6–C1	1.389	1.380	1.373	C6–C1	1.396	1.395	1.382		
C1–Cl7	1.739	2.358	1.698	C1–Cl7	1.740	2.325	1.701		
C2–F8	1.334	1.325	1.290	C2–F8	1.341	1.335	1.300		
C3–Cl9	1.739	1.700	1.698	C3–Cl9	1.740	1.708	1.701		
C4–H10	1.080	1.080	1.081	C4–H10	1.088	1.088	1.089		
C5–H11	1.081	1.082	1.082	C5–H11	1.089	1.090	1.090		
C6–H12	1.080	1.085	1.081	C6–H12	1.088	1.094	1.089		
<b>Bond angles [°]</b>									
C1–C2–C3	120.125	123.523	122.001	C1–C2–C3	120.007	123.861	121.791		
C2–C3–C4	119.972	119.825	118.077	C2–C3–C4	120.019	120.100	118.195		
C3–C4–C5	119.648	117.525	119.488	C3–C4–C5	119.613	117.257	119.447		
C4–C5–C6	120.635	120.436	122.869	C4–C5–C6	120.728	120.361	122.865		
C5–C6–C1	119.648	123.643	119.488	C5–C6–C1	119.613	124.461	119.477		
C6–C1–C2	119.972	115.049	118.077	C6–C1–C2	120.019	113.959	118.195		
Cl7–C1–C2	119.336	131.346	118.378	Cl7–C1–C2	119.198	130.690	118.269		
C1–C2–F8	119.938	121.023	118.996	C1–C2–F8	119.938	121.023	118.996		
C4–C3–Cl9	120.692	120.051	123.541	C4–C3–Cl9	120.783	119.621	123.535		
<b>Dihedral angle [°]</b>									
Cl7–C1–C6–H12	0	-0.018	0	Cl7–C1–C6–H12	0	-0.030	0		
Cl7–C1–C2–F8	0	0.016	0	Cl7–C1–C2–F8	0	0.038	0		
Cl9–C3–C4–H10	0	-0.005	0	Cl9–C3–C4–H10	0	-0.006	0		

and  $196\text{ cm}^{-1}$  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  $439\text{ cm}^{-1}$  and  $839\text{ cm}^{-1}$ . The  $a_2$ -symmetrical modes  $10a^1$  and  $16a^1$  are assigned to the weak bands at  $201\text{ cm}^{-1}$  and  $546\text{ cm}^{-1}$ . With exception of  $4^1$  all calculated frequencies are in good accordance with the experimentally determined ones.

Provided the validity of the  $\Delta\nu = 0$  propensity rule, the MATI spectrum obtained *via* the  $S_117b^1$  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

Table 4 BP86/TZVPP calculated geometries of 1,3,2-DCFB

BP86/TZVPP	$C_{2v}$			$C_2$			$C_{2v}$		
	$S_0$	$S_1$	$D_0$	$S_0$	$S_1$	$D_0$	$S_0$	$S_1$	$D_0$
<b>Bond length [Å]</b>									
C1–C2	1.400	1.377	1.444	C1–C2	1.400	1.445	1.444		
C2–C3	1.400	1.445	1.444	C2–C3	1.396	1.411	1.382		
C3–C4	1.396	1.411	1.382	C3–C4	1.395	1.379	1.411		
C4–C5	1.395	1.379	1.411	C4–C5	1.395	1.434	1.411		
C5–C6	1.395	1.434	1.411	C5–C6	1.396	1.395	1.382		
C6–C1	1.396	1.395	1.382	C6–C1	1.740	2.325	1.701		
C1–Cl7	1.740	2.325	1.701	C1–Cl7	1.341	1.335	1.300		
C2–F8	1.341	1.335	1.300	C2–F8	1.740	1.708	1.701		
C3–Cl9	1.740	1.708	1.701	C3–Cl9	1.088	1.088	1.089		
C4–H10	1.088	1.088	1.089	C4–H10	1.089	1.090	1.090		
C5–H11	1.089	1.090	1.090	C5–H11	1.088	1.094	1.089		
C6–H12	1.088	1.094	1.089	C6–H12	1.088	1.094	1.089		
<b>Bond angles [°]</b>									
C1–C2–C3	120.007	123.861	121.791	C1–C2–C3	120.019	120.100	118.195		
C2–C3–C4	120.019	120.100	118.195	C2–C3–C4	119.613	117.257	119.447		
C3–C4–C5	119.613	117.257	119.447	C3–C4–C5	120.728	120.361	122.865		
C4–C5–C6	120.728	120.361	122.865	C4–C5–C6	119.613	124.461	119.477		
C5–C6–C1	119.613	124.461	119.477	C5–C6–C1	120.019	113.959	118.195		
C6–C1–C2	120.019	113.959	118.195	C6–C1–C2	119.198	130.690	118.269		
Cl7–C1–C2	119.198	130.690	118.269	Cl7–C1–C2	119.938	121.023	118.996		
C1–C2–F8	119.938	121.023	118.996	C1–C2–F8	120.783	119.621	123.535		
C4–C3–Cl9	120.783	119.621	123.535	C4–C3–Cl9	120.783	119.621	123.535		
<b>Dihedral angle [°]</b>									
Cl7–C1–C6–H12	0	-0.030	0	Cl7–C1–C6–H12	0	-0.030	0		
Cl7–C1–C2–F8	0	0.038	0	Cl7–C1–C2–F8	0	0.038	0		
Cl9–C3–C4–H10	0	-0.006	0	Cl9–C3–C4–H10	0	-0.006	0		

shown in Fig. 4. Instead, the spectrum shows the  $9a^1$  at  $291\text{ cm}^{-1}$  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  $586\text{ cm}^{-1}$  as well. The signals at  $419\text{ cm}^{-1}$  and  $629\text{ cm}^{-1}$  are identified as the  $6a^1$  and  $1^1$  total symmetric modes. Obviously, the signals for the  $11$ -vibration is broadened. Based on the MATI spectrum of the  $0^0$  transition, we assigned this signal both to the  $1^1$  and  $4^1$  vibrations, the latter of which gives rise to the shoulder. The MATI spectrum obtained *via* the  $S_19a^1$  shows three prominent peaks: the  $6a^1$ , the  $9a^16a^1$  and the  $18a^1$ . Without folding the spectrum with the laser

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

BP86/TZVPP		
	$C_{2v}$	$C_2$
Bond length [ $\text{\AA}$ ]	$S_0$	$S_1$
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–Cl7	1.725	1.719
C2–F8	1.333	1.326
C3–Cl9	1.725	1.719
C4–H10	1.080	1.079
C5–H11	1.081	1.082
C6–H12	1.080	1.079
<b>Bond angles [°]</b>		
C1–C2–C3	119.992	121.970
C2–C3–C4	120.078	118.706
C3–C4–C5	119.618	118.910
C4–C5–C6	120.617	122.532
C5–C6–C1	119.618	118.910
C6–C1–C2	120.078	118.706
Cl7–C1–C2	119.105	118.817
C1–C2–F8	120.004	119.015
C4–C3–Cl9	110.817	120.760
<b>Dihedral angle [°]</b>		
Cl7–C1–C6–H12	0	–17.842
Cl7–C1–C2–F8	0	17.222
Cl9–C3–C4–H10	0	–17.842

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  $6a^1$  and  $9a^16a^1$  are at least as same as intensive while the vertical transition into the  $D_09a^1$  state is scarcely visible in the spectrum. Nevertheless the mode  $9a$  appears in a series of overtones  $9a^16a^1$  ( $710 \text{ cm}^{-1}$ ),  $9a^11$  ( $924 \text{ cm}^{-1}$ ) and  $9a^26a^1$  ( $1003 \text{ cm}^{-1}$ ).

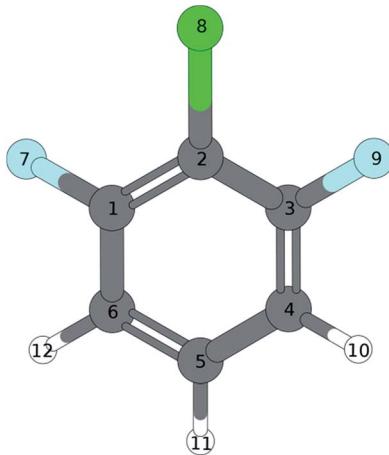
Table 6 B3LYP/TZVPP calculated geometries of 1,3,2-DFCB

B3LYP/TZVPP		
	$C_{2v}$	$C_{2v}$
Bond length [ $\text{\AA}$ ]	$S_0$	$S_1$
C1–C2	1.393	1.365
C2–C3	1.393	1.365
C3–C4	1.384	1.444
C4–C5	1.389	1.384
C5–C6	1.389	1.384
C6–C1	1.384	1.444
C1–F7	1.340	1.326
C2–Cl8	1.729	2.361
C3–F9	1.340	1.326
C4–H10	1.081	1.081
C5–H11	1.081	1.080
C6–H12	1.081	1.081
<b>Bond angles [°]</b>		
C1–C2–C3	117.528	111.693
C2–C3–C4	121.919	126.328
C3–C4–C5	118.997	118.962
C4–C5–C6	120.640	117.726
C5–C6–C1	118.997	118.962
C6–C1–C2	117.528	126.328
F7–C1–C2	118.843	120.164
C1–C2–Cl8	121.236	124.155
C4–C3–F9	119.237	113.508
<b>Dihedral angle [°]</b>		
F7–C1–C6–H12	0	0.027
F7–C1–C2–Cl8	0	–0.204
F9–C3–C4–H10	0	–0.032

Remarkably, the spectrum exhibits a strong activity in  $6a$  modes: the bands assigned to the modes  $6a^1$  and  $9a^16a^1$  are among the three most intense bands in the spectrum. The  $6a^1$  vibration shows progression activity ( $6a^1$  and  $6a^2$  in the recorded range). In addition, the  $6a^1$  mode contributes to overtone bands as already discussed above. The weak features at 97, 193 and  $213 \text{ cm}^{-1}$  have been assigned on the basis of our previous



Table 7 BP86/TZVPP calculated geometries of 1,2,3-DFCB



BP86/TZVPP	$C_{2v}$	$C_{2v}$	$C_{2v}$
Bond length [Å]	$S_0$	$S_1$	$D_0$
C1–C2	1.401	1.378	1.446
C2–C3	1.401	1.378	1.446
C3–C4	1.391	1.446	1.374
C4–C5	1.396	1.391	1.414
C5–C6	1.396	1.391	1.414
C6–C1	1.391	1.446	1.374
C1–F7	1.348	1.337	1.318
C2–Cl8	1.730	2.332	1.671
C3–F9	1.348	1.337	1.318
C4–H10	1.089	1.089	1.089
C5–H11	1.089	1.087	1.090
C6–H12	1.089	1.089	1.089
<b>Bond angles [°]</b>			
C1–C2–C3	117.514	110.326	118.508
C2–C3–C4	121.885	127.177	120.727
C3–C4–C5	118.999	118.870	118.543
C4–C5–C6	120.718	117.579	122.956
C5–C6–C1	118.999	118.870	118.543
C6–C1–C2	117.514	127.177	120.727
F7–C1–C2	118.763	119.276	117.392
C1–C2–Cl8	121.242	124.836	120.740
C4–C3–F9	119.349	113.548	121.870
<b>Dihedral angle [°]</b>			
F7–C1–C6–H12	0	0.041	0
F7–C1–C2–Cl8	0	-0.191	0
F9–C3–C4–H10	0	-0.032	0

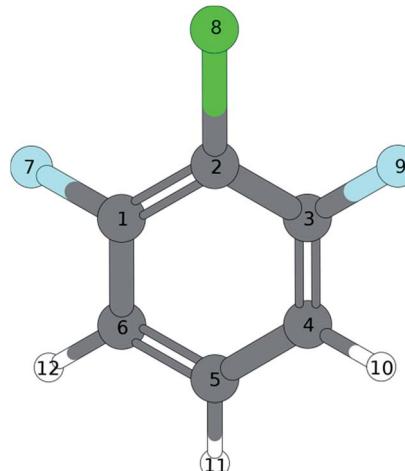
studies<sup>7,8</sup> to the out-of-plane modes  $17b^1$ ,  $17b^2$  and in-plane mode  $15^1$ .

## 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

Table 8 CC2/cc-pVTZ calculated geometries of 1,2,3-DFCB



CC2/cc-pVTZ	$C_{2v}$	$C_{2v}$
Bond length [Å]	$S_0$	$S_1$
C1–C2	1.396	1.416
C2–C3	1.396	1.416
C3–C4	1.387	1.431
C4–C5	1.394	1.407
C5–C6	1.394	1.407
C6–C1	1.387	1.431
C1–F7	1.339	1.337
C2–Cl8	1.716	1.825
C3–F9	1.339	1.337
C4–H10	1.080	1.825
C5–H11	1.081	1.337
C6–H12	1.080	1.083
<b>Bond angles [°]</b>		
C1–C2–C3	117.753	110.391
C2–C3–C4	121.786	125.833
C3–C4–C5	118.972	120.624
C4–C5–C6	120.732	116.095
C5–C6–C1	118.972	120.624
C6–C1–C2	121.786	125.833
F7–C1–C2	118.680	118.508
C1–C2–Cl8	121.124	118.556
C4–C3–F9	119.534	115.651
<b>Dihedral angle [°]</b>		
F7–C1–C6–H12	0	0.912
F7–C1–C2–Cl8	0	46.945
F9–C3–C4–H10	0	-0.912

from  $S_0$  to  $S_1$  or from  $D_0$  to  $S_1$ , respectively. As considered earlier by Tsuchiya *et al.*<sup>14</sup> for difluorobenzene it is highly suggested that this phenomenon is the result of strong vibronic coupling between the  $S_1$  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  $17b^2$ . 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  $S_1$  and  $D_0$ , the fact that the transition from  $D_0 17b^1 \leftarrow S_1 17b^2$  is favored could be interpreted as a



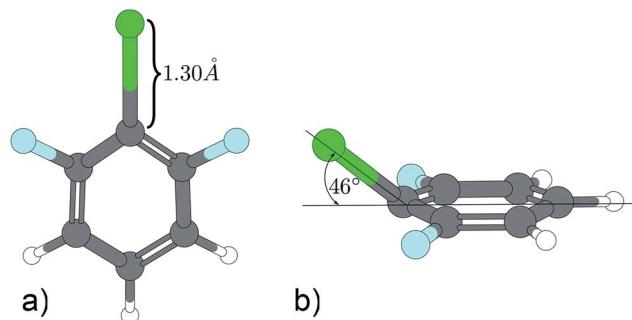


Fig. 6 Excited state geometry of 1,3,2-DFCB obtained by different quantum mechanical methods. (a) TDDFT, (b) CC2.

replanarisation of the molecular geometry in going from  $S_1$  to  $D_0$  along that mode.

Also during ionization *via* the vibrationless level of the first excited state, the transition  $D_0 17b^1 \leftarrow S_0 0^0$  is clearly favored over  $D_0 0^0 \leftarrow S_1 0^0$  (see MATI *via*  $0^0$  Fig. 2). A major role of the  $17b$  mode during ionization is aggravated by the fact the  $17b$  also appears as combination bands ( $17b^1 9a^1$  in each of the recorded MATI spectra,  $17b^1 6b^1$  in the MATI *via*  $17b^2$ ). The strong activity of the mode  $16b^1$  in the MATI *via*  $17b^2$  and the general, unusual appearance of multiple other out-of-plane modes throughout the MATI spectra give rise to the assumption that the geometry in the  $S_1$  is a product of a distortion along several modes. The CC2 computed geometry optimization seem to support the statements derived from the experimental data: the geometry shown in Fig. 5 is obviously not just the product of a distortion along a single (out-of-plane) normal mode (Table 2).

The quantum chemical calculations predict a  $S_1(\pi^* \leftarrow \pi)$  transition into the first excited state for 1,3,2-DFCB. However, due to  $\sigma^*$ -orbitals localized on the Halogen–Carbon bond, it is possible for modes of appropriate symmetry to induce coupling to  $(\pi\sigma^*)$ -states. In accordance with the assumption of a vibronic coupling effect we prevalently observed a substantial decrease in frequency comparing the  $S_0$  state and the  $S_1$  state of the neutral for formal forbidden modes with strong influence of halogen atoms on their displacement pattern. For the modes 15, 6b, 3 ( $b_2$  symmetry) and 16a ( $a_2$  symmetry) we observed such a decrease.

The decrease in frequency for the modes 15, 6b, 3 is explainable in accordance with the Herzberg–Teller (HT) effect. However, the frequency lowering of the symmetry allowed mode  $17b^2$  could not be described in terms of the HT effect in a sufficient way. It seems that the distortion along  $17b$  blurs the symmetry differences between the  $(\pi\sigma^*)$ - and  $(\pi\pi^*)$ -states which would be an indication for a pseudo Jahn–Teller effect.

## 5.2. 1,3,2-DFCB

In 1,3,2-DFCB the vibration 15 appears in the REMPI spectrum as a progression-forming and largely frequency lowered mode. Remarkably, the progression reveals a negative anharmonicity. The occurrence of the 15 as a  $b_2$  symmetric mode is explained in terms of the Herzberg–Teller effect. Besides the mode 15, also the modes 6a and 9a exhibit a largely lowered frequency in the

first excited state  $S_1$ . Both modes are likely to contribute in pseudo Jahn–Teller distortion in going from the electronic ground to excited state or from excited state to ionic ground state, respectively. This is seen from the different MATI spectra as well as the different calculated structures given in Tables 3–8. The MATI spectrum *via* the electronic origin exhibits a harmonic, three-membered progression of mode 9a ( $9a^1$ ,  $9a^2$ ,  $9a^3$ ), whereby the band  $9a^1$  is almost as intense as the  $0-0$  transition. Such a shift of the Franck–Condon maximum is a clear indication for a distortion along the eigenvector of this mode during ionization.

A similar situation is found in the MATI spectrum *via*  $9a^1$ . Here, in contradiction to the  $\Delta\nu = 0$  propensity rule, the transition into the  $S_1 6a^1$  state is the most favorable while the vertical transition into the  $9a^1$  is scarcely observable. Nevertheless the mode 9a is strongly present in overtones ( $9a^1 6a^1$ ,  $9a^1 1^1$ ,  $9a^2 6a^1$ ). 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  $a_1$ -symmetrical  $S_1$ -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,<sup>1</sup> the increasing number of fluorine 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 fluorine 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 fluorine atoms.<sup>12</sup> It can be concluded that the fluorine atoms contribute a significant share in form of  $\sigma^* \leftarrow \pi$  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 TDDFT 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  $S_1 \leftarrow S_0$  electronic excitation energies (EE) and  $D_0 \leftarrow S_0$  adiabatic ionization energies (IE) could be determined very exactly:

$$\text{EE}(1,3,2\text{-DFCB}) = 36\ 460 \pm 2 \text{ cm}^{-1}, \text{IE}(1,3,2\text{-DFCB}) = 75.242 \pm 6 \text{ cm}^{-1};$$

$$\text{EE}(1,3,2\text{-DCFB}) = 37\ 449 \pm 2 \text{ cm}^{-1}, \text{IE}(1,3,2\text{-DCFB}) = 75.627 \pm 6 \text{ cm}^{-1}.$$

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