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Mass analyzed threshold ionization (MATI) spectroscopy of trichlorobenzenes via different intermediate vibrational states in the S_1 state

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ABSTRACT

Two color resonant mass analyzed threshold ionization (MATI) spectroscopy was applied in order to investigate the ionic properties of the structural isomers of trichlorobenzene (TCB) above the ionization threshold. For the first time, vibrational spectra of the $^{35}Cl_3$ and $^{35}Cl_2{}^{37}Cl$ isotopomers of 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene cations in their electronic ground state have been measured via different S_1 intermediate states by mass analyzed threshold ionization (MATI) spectroscopy. Additionally *ab initio* calculations at DFT (density functional theory) and TDDFT (time-dependent density functional theory) have been performed to compare experimental findings with theory. From the MATI spectra the adiabatic ionization energies of the three isomers 1,2,3-TCB, 1,2,4-TCB and 1,3,5-TCB could be determined to $74289 \pm 6\,\mathrm{cm}^{-1}$, $72779 \pm 6\,\mathrm{cm}^{-1}$ and $74900 \pm 100\,\mathrm{cm}^{-1}$, respectively. Several vibrational modes of the isotopomers have been assigned by comparison of the experimental and theoretical results.

1. Introduction

Chlorinated aromatic molecules are a topic of great interest due to their widespread presence and their potentially toxic and carcinogenic properties. Chlorobenzene has been subject of various investigations studying the first excited state as well as the cation ground state [1–3]. The substitution of hydrogen atoms of the aromatic ring by other substituents in general changes the electron distribution of the molecule. This can cause alterations in the transition energies, ionization energies, and the molecular geometry, the latter observed in the vibrations in the excited electronic state and the cation ground state. The magnitude of these effects depends on the number, the type, as well as the relative position of the substituents. In particular in the case of the molecular geometry change it is worthwhile to know the involved vibrational modes to understand, e.g. the different behavior of isomers in chemical reactions. As the changes are mostly small (from a few wavenumbers up to a few hundreds of wavenumbers) the investigations require powerful, high-resolution examination methods such as mass analyzed threshold ionization (MATI) or zero kinetic energy (ZEKE) spectroscopy [4–6]. The former method has the advantage of featuring mass resolution which enables the investigation of isotopomers in a mixture. Previous publications presented corresponding results for difluorobenzene [7] and dichlorobenzene [8,9], but similar results for trichlorobenzene are still rarely found in the literature. Weickhardt et al. [10] presented resonance-enhanced multiphoton ionization (REMPI) spectra of the first electronically excited state of the three structural trichlorobenzene isomers (1,2,3-TCB, 1,2,4-TCB and 1,3,5-TCB) and showed that it is possible to differentiate between them as the transition energies as well as the vibrations differ strongly from each other.

Trichlorobenzenes are substances that are in increasing amounts used as intermediate and end products for pharmaceutica and pesticides. The three isomers exhibit different toxicities. While 1,2,3-TCB and 1,2,4-TCB are hazardous to health and environment, 1,3,5-TCB is classified to be only hazardous to health.

In this paper we present two color two photon REMPI spectra of the S_1 states and two color two photon MATI spectra via different S_1 intermediate states of all TCB isomers. The experimental data is compared to theoretical calculations which enables the possibility of assigning the observed vibrational modes.

2. Experimental setup

The experimental setup consists of a homemade time-of-flight mass spectrometer as described in detail elsewhere [11,12]. In short the spectrometer consists of a single stage ion source and a stan-

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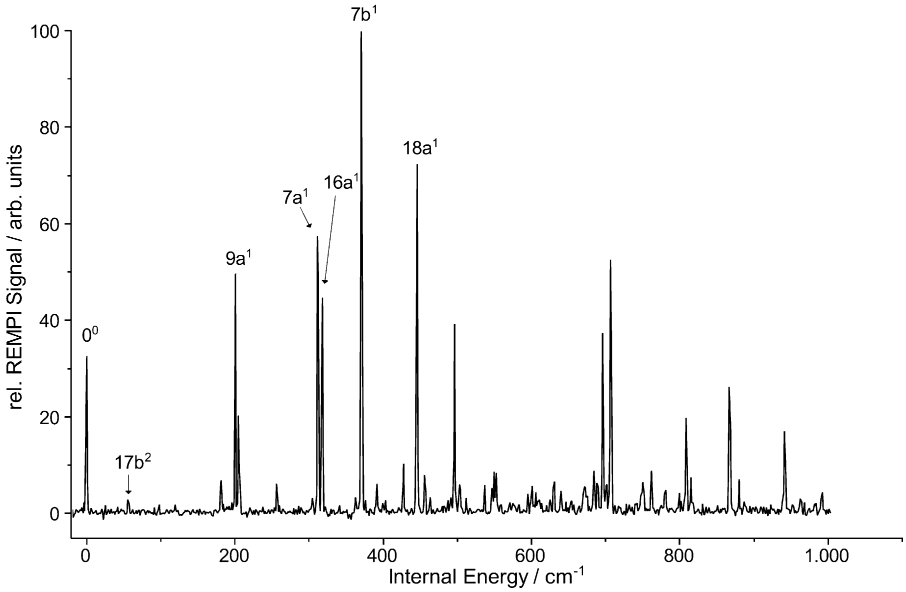

Fig. 1. (1 + 1′)REMPI spectrum of 1,2,3-trichlorobenzene.

dard second order corrected time-of-flight mass spectrometer. The trichlorobenzenes were purchased from Sigma–Aldrich and used without further purification. The sample is seeded in argon with a backing pressure of 2 bar and expanded into the vacuum through the orifice of a pulsed valve. To obtain a sufficient vapor pressure the sample is heated to approximately 80 °C. After skimming the supersonic beam enters the ion source where the multi-photon-absorption takes place. Two different dye lasers, pumped by the same Nd:YAG laser, are used for excitation and ionization of the molecules. This experimental setup guarantees a very low jitter and therefore a stable signal to noise ratio. The output of each dye laser is frequency-doubled by a BBO-I crystal yielding tunable ranges from 250 to 285 nm. Wavelength calibration of both dye lasers is performed by recording an optogalvanic spectrum with a neon hollow cathode lamp yielding an accuracy better than 2 cm^{-1}. The excitation of the molecules by the incident lasers is performed under field-free conditions in all experiments. To observe MATI spectra a small electric field of 1–2 V cm^{-1} is applied after

Table 1
Observed and calculated vibrational frequencies (cm^{-1}) of 1,2,3-TCB.

Mode			S_0		S_1		D_0	
Varsanyi	Herzberg	Symm.	Exp. [a]	DFT	Exp.	TDDFT	Exp.	DFT
9a	11	a_1	212	208	201	171	209	188
7a	10	a_1	352	346	312	392	267	237
2	9	a_1	513	506		518		508
6a	8	a_1	738	743		651		706
12	7	a_1	1050	1050		974		1033
18b	6	a_1	1088	1102		1091		1045
1	5	a_1	1161	1167		1054		1137
19a	4	a_1	1416	1435		1392		1114
8a	3	a_1	1566	1603		1507		1545
13	2	a_1	3072	3187		3125		3131
20a	1	a_1	3072	3211		3147		3150
10a	14	a_2	212	201		166		168
16a	13	a_2	524	536	318	319		519
17a	12	a_2	896	907		1001		911
17b	20	b_1	90	83	30 [b]	22	87	70
10b	19	b_1	242	248		172		230
16b	18	b_1	500	521		400		422
4	17	b_1	697	725		646		642
11	16	b_1	773	790		793		771
5	15	b_1	963	981		964		972
15	30	b_2	212	215		82		201
7b	29	b_2	400	404	371	368	332	376
18a	28	b_2	492	487	446	399	437	443
6b	27	b_2	791	786		764		798
9b	26	b_2		1177		1144		1114
3	25	b_2	1192	1220		1070		1100
14	24	b_2	1261	1292		1352		1331
19b	23	b_2	1436	1462		1369		1392
8b	22	b_2	1566	1597		1462		1425
20b	21	b_2	3072	3206		3132		3139

[a] Taken from Ref. [21].
[b] Half of the observed overtone.

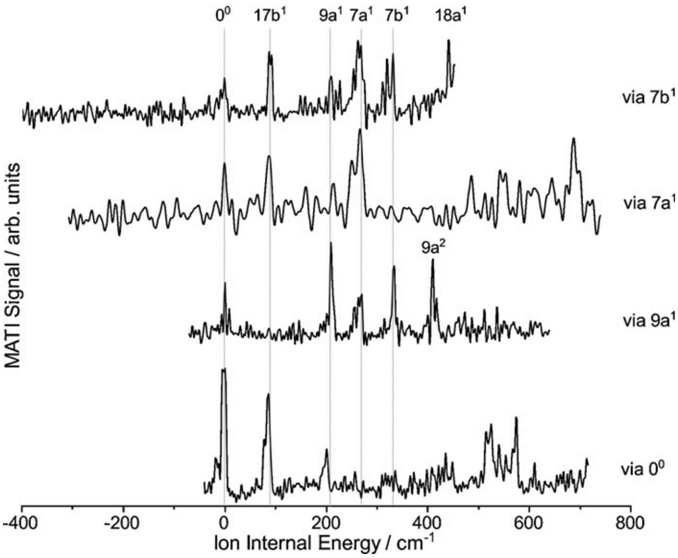

Fig. 2. MATI spectra of 1,2,3-TCB via different intermediate states of the first excited state: via the electronic origin, via $9a^1$, via $7a^1$ and via $7b^1$.

100 ns to separate any prompt ions from the Rydberg molecules. Approximately 5 μs later the Rydberg neutrals are field-ionized by switching an electric field (890 V cm^{-1}) by a Behlke HS56-01 fast thyristor switch. The formed ions are accelerated into the mass spectrometer and detected by a conventional dual micro-channel-plate detector. The signal is measured and visualized by a LeCroy 534M digital oscilloscope as well as transferred to a computer for further investigations.

3. Quantum-chemical calculations

In order to assign the observed vibrational bands and to support the experimental findings quantum-chemical calculations have been performed using the software package Turbomole [13–16]. The ground state calculations for both the neutral and the cation (geometries and harmonic frequencies) were carried out using the density functional theory (DFT) with Becke's three-parameter functional B3LYP [17]. The triple ζ basis set TZVP [18] was used for all calculations. The geometries of the first electronically excited state and the related harmonic frequencies were calculated with the time dependent density functional theory (TDDFT) using the TZVP basis set. As the isomers of trichlorobenzene consist of 12 atoms they have 30 normal modes. According to Varsanyi and Szoke [19] these isomers are classified as heavy-trisubstituated benzene derivatives and the assignment of the vibrations is given in the corresponding nomenclature which is derived from Wilson's notation of the benzene modes [20].

4. Experimental results

Owing to the natural abundance of chlorine the time-of-flight mass spectrum shows four peaks originating from the $^{35}Cl_3$-, $^{35}Cl_2{}^{37}Cl$-, $^{35}Cl^{37}Cl_2$- and $^{37}Cl_3$-isotopomers with a ratio of intensity of 33 : 31 : 10 : 1. We recorded the spectra of the two main isotopomers. While the REMPI spectra of the 1,2,3-isomer exhibit a quite good S/N ratio the MATI spectra of this isomer are not so good. For this isomer we recorded MATI spectra via the total symmetric vibrations $9a^1$ and $7a^1$ as well as the b_2 symmetric mode $7b^1$. In the case of the 1,2,4-isomer it was possible to record MATI spectra via the total symmetric modes 15^1, $6b^1$, $7b^1$, 3^1, $17b^2$ and via the vibrations $10b^1$ and $16a^1$ with a$''$ symmetry. The 1,3,5-isomer belongs to the symmetry point group D_{3h}. Here we recorded MATI spectra via the degenerated vibrations 6^1 and 7^1. A complete presentation of the vibrations observed by MATI spectroscopy is given in Tables 1, 3 and 5.

4.1. 1,2,3-Trichlorobenzene

4.1.1. REMPI spectrum

The electronic excitation into the S_1 state is a $S_1(^1B_2) \leftarrow S_0(^1A_1)$ transition; the molecule belongs to the C_{2v} symmetry point group. According to the Franck Condon principle only total symmetric vibrational modes should be allowed in the S_1 state. However, the REMPI spectrum shown in Fig. 1 is dominated by the b_2 symmetric modes $7b^1$ and $18a^1$. These vibrations are allowed due to Herzberg Teller coupling. The electronic origin was found at 35558 ± 2 cm^{-1} which is in good accordance with the value of 35540 cm^{-1} from previous REMPI measurements [10].

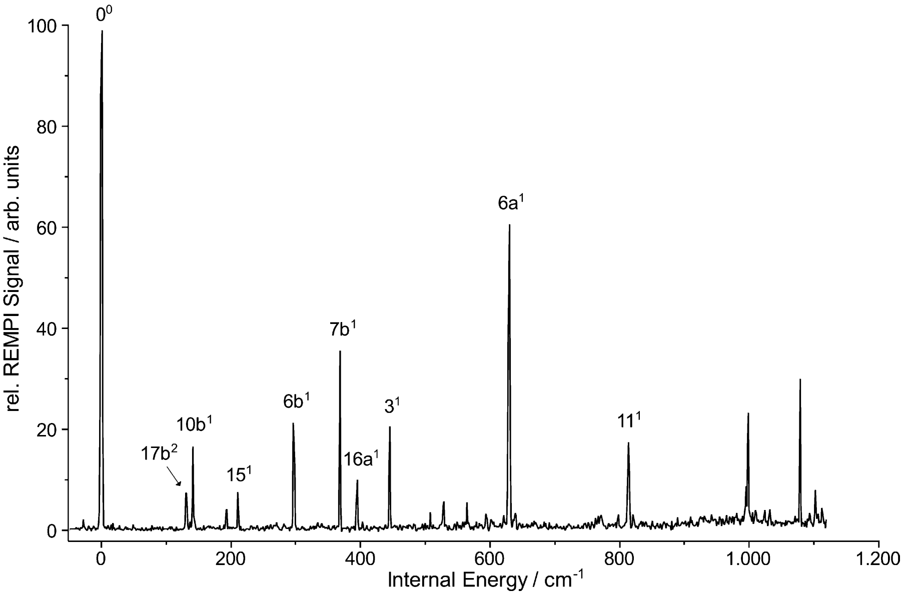

Fig. 3. (1 + 1′)REMPI spectrum of 1,2,4-trichlorobenzene.

4.1.2. MATI spectra

Fig. 2 shows the MATI spectra via the S_1 intermediate states 0^0, $9a^1$, $7a^1$ and $7b^1$. All spectra show a comparatively poor S/N ratio. This is probably due to an intense geometry change during the ionization, so there seems to be no good Franck Condon overlap between the electronic states. Another possible reason for a weak MATI signal could be a predissociation of the intermediate neutrals.

At excitation via the electronic origin and via the total symmetric modes $9a^1$ and $7a^1$ (lower three spectra in Fig. 2) the "$\Delta\nu = 0$" propensity rule [22,23] is retained. The most prominent peaks are via 0^0 the electronic origin of the D_0 state at 74289 ± 6 cm^{-1} and 209 cm^{-1} and 267 cm^{-1} via $9a^1$ and $7a^1$, respectively. These measured frequencies are in good agreement with the calculated values in the cation ground state with 188 cm^{-1} for the $9a^1$ and 237 cm^{-1} for the $7a^1$. The electronic origin designates the adiabatic ionization energy and the determined value of 74289 ± 6 cm^{-1} is in good accordance to the previously by photo electron spectroscopy measured value of 74040 ± 240 cm^{-1}[24].

In the spectrum via the $9a^1$ appears the first overtone $9a^2$ comparatively intense at 409 cm^{-1}. Additionally both $7a^1$ and $7b^1$ are excited when excitation via the $9a^1$ takes place. This can be traced back to the fact that the vibrational modes 7a, 7b and 9a become rather similar due to a coupling of the vibrational movement of the heavy chlorines to the aromatic ring movement [25]. The appearance of the overtone $9a^2$ gives rise to the assumption that the 9a vibration is somehow involved in a geometry change during the ionization.

When the excitation via $7b^1$ takes place the propensity rule is broken (Fig. 2 upper spectrum). Here the $7a^1$ is the most prominent peak at 269 cm^{-1}. The $7b^1$ itself at 332 cm^{-1} has a significantly lower intensity. So the geometry of the molecule should also be changed along the 7b vibration during the ionization. Moreover noteworthy here is the appearance of the $18a^1$ vibration at 442 cm^{-1}. This mode does not appear in any other measured MATI spectrum.

Furthermore the occurrence of the 17b vibration in the spectra is remarkable. This vibration with b_1 symmetry is symmetry forbidden in the S_1 state and appears in the REMPI spectrum only as overtone $17b^2$ at 57 cm^{-1} with weak intensity. In the MATI spectra via 0^0, $7a^1$ and $7b^1$ the $17b^1$ is detected at 87 cm^{-1}. This is in good agreement with the calculated value of 70 cm^{-1} for the cationic ground state. In addition this vibration undergoes a strong frequency decrease from the neutral ground state to the first excited state. From IR measurements the $17b^1$ in the S_0 state could be determined to 90 cm^{-1}[21]. On the contrary in the S_1 state the frequency can be estimated to ca. 30 cm^{-1} which is in excellent agreement to the calculated value of 22 cm^{-1}. The strong occurrence of the $17b^1$ in the MATI spectra could indicate that this mode is also involved in a geometry change during the ionization. In this case 1,2,3-TCB would undergo a symmetry lowering from C_{2v} to C_s. Up to now this situation could not be resolved sufficiently (Table 2).

Table 2
Summary of all observed MATI peaks of 1,2,3-TCB.

Mode	S_1 Intermediate state				
	0^0	$9a^1$	$7a^1$	$7b^1$	$18a^1$
0^0	0	0	0	0	
$17b^1$	86		87	87	88[a]
$9a^1$	203	209		201	
$7a^1$		270	267	269	
$7b^1$		333		332	
$9a^2$		409			
$18a^1$				442	437 [a]

[a] Value from PIE measurement.

Table 3
Observed and calculated vibrational frequencies (cm^{-1}) of 1,2,4-TCB.

Mode			S_0		S_1		D_0	
Varsanyi	Herzberg	Symm.	Exp. [a]	DFT	Exp.	TDDFT	Exp.	DFT
9b	21	a'	197	187		59		199
15	20	a'	211	202	210	176	221	215
6b	19	a'	328	318	297	322	313	311
7b	18	a'	396	387	368	358	390	387
3	17	a'	456	447	445	256	463	452
13	16	a'	576	554		547		580
6a	15	a'	679	667	630	586	659	653
7a	14	a'	817	792		751		823
12	13	a'	1036	1011		982		1016
18a	12	a'	1096	1078		1048		1073
18b	11	a'	1132	1131		1131		1152
1	10	a'	1156	1116		1055		1115
9a	9	a'	1245	1230		1223		1215
14	8	a'	1267	1307		1313		1303
19b	7	a'	1377	1361		1345		1380
19a	6	a'	1461	1438		1441		1417
8b	5	a'	1562	1547		1417		1427
8a	4	a'	1571	1557		1555		1541
20b	3	a'	3072	3130		3126		3139
20a	2	a'	3072	3145		3145		3147
2	1	a'	3094	3149		3149		3149
17b	30	a''	117	91	66[b]	38	75 [b]	71
10a	29	a''	183	162		85		123
10b	28	a''	305	289	142	306	292	243
16b	27	a''	435	424				404
16a	26	a''	551	522	395	519	536	538
4	25	a''	688	573		737		454
11	24	a''	811	779	813	817	850	783
5	23	a''	869	813		1021		826
17a	22	a''	942	886		942		912

[a] Taken from Ref. [21].
[b] Half of the observed overtone.

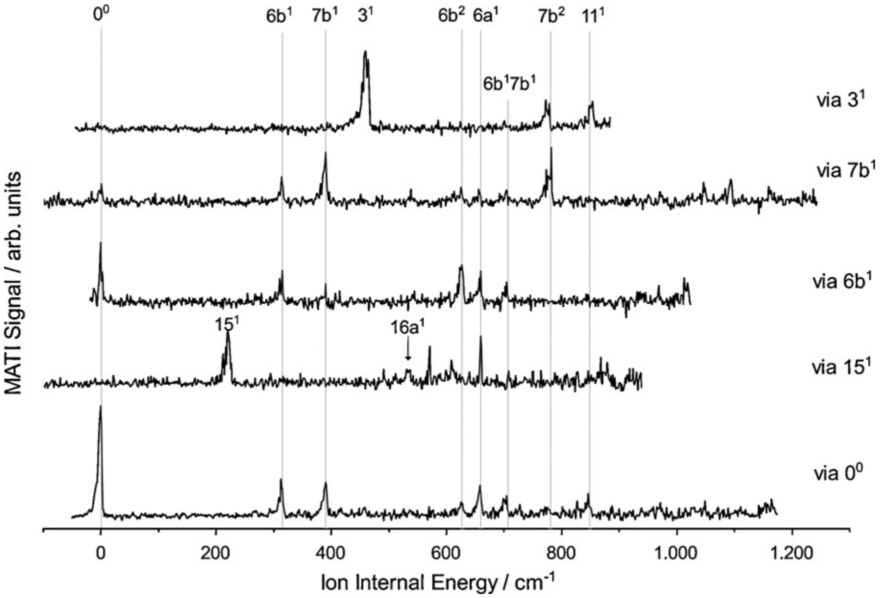

Fig. 4. MATI spectra of 1,2,4-TCB via different intermediate states of the first excited state: via the electronic origin, via 15^1, via $6b^1$, via $7b^1$ and via 3^1.

4.2. 1,2,4-Trichlorobenzene

4.2.1. REMPI spectrum

The electronic excitation of 1,2,4-TCB (C_s symmetry) into the S_1 state is a $S_1(^1A') \leftarrow S_0(^1A')$ transition. This means that according to the Franck Condon principle only vibrations of a' symmetry should appear in the spectrum. But due to Herzberg-Teller coupling there are also a'' symmetric modes allowed. Therefore vibrations of both symmetries appear in the spectrum.

The strongest band in the spectrum shown in Fig. 3 is the electronic origin which was found at $35111 \pm 2\,\text{cm}^{-1}$. From previous REMPI measurements a value of $35092\,\text{cm}^{-1}$ is known [10] which fits the here determined value very well. Most of the assigned bands are total symmetric vibrations: $17b^2$, 15^1, $6b^1$, $7b^1$, 3^1, $6a^1$ and 11^1. The modes $10b^1$ and $16a^1$ have a'' symmetry (Tables 3 and 4).

4.2.2. MATI spectra via the electronic origin and via the vibrations 15^1, $6b^1$, $7b^1$ and 3^1

The MATI spectra via the S_1 intermediate states 0^0, 15^1, $6b^1$, $7b^1$ and 3^1 are shown in Fig. 4. At excitation via the electronic origin and the vibrations 15^1 and 3^1 the propensity rule is retained. The most prominent peaks in the spectra are the electronic origin of the D_0 state at $72779 \pm 6\,\text{cm}^{-1}$ via 0^0 and $221\,\text{cm}^{-1}$ and $463\,\text{cm}^{-1}$ via 15^1 and 3^1, respectively. The measured values are in excellent agreement to the calculated values for the cationic ground state of $215\,\text{cm}^{-1}$ and $452\,\text{cm}^{-1}$. The adiabatic ionization energy of $72779 \pm 6\,\text{cm}^{-1}$ fits excellently the previously by photoelectron spectroscopy determined value of $72910 \pm 240\,\text{cm}^{-1}$[24].

A first hint for a geometry change of the molecule is already found in the MATI spectrum via the electronic origin. Among the dominating 0^0 transition the vibrations $6b^1$ ($313\,\text{cm}^{-1}$), $6b^2$ ($626\,\text{cm}^{-1}$), $7b^1$ ($390\,\text{cm}^{-1}$), $6a^1$ ($658\,\text{cm}^{-1}$), 11^1 ($845\,\text{cm}^{-1}$) and even the combination band $6b^17b^1$ ($702\,\text{cm}^{-1}$) are active. The strong occurrence of the 6b mode suggests a geometry change during the ionization along this vibration.

This is confirmed by the MATI spectrum via the $6b^1$ vibration itself. Here the propensity rule is broken: the most prominent peaks are the electronic origin of the D_0 state and the overtone $6b^2$. Furthermore the spectrum is rather similar to the spectrum recorded via 0^0. The combination band $6b^17b^1$ is found here, too.

The MATI spectrum via the $7b^1$ vibration also shows a breakdown of the propensity rule, as there is the overtone $7b^2$ the most intensive peak at $778\,\text{cm}^{-1}$. Here also the $6b^1$ and the electronic origin are active.

As it is the case for 1,2,3-TCB the 7b vibration exhibits a coupling of the heavy chlorines' movement to the aromatic ring movement. This leads to a kind of similarity of the vibrational movements of the 7b and 6b modes which explains the appearance of the combination band $6b^17b^1$ in the spectra.

All measured frequencies are in very good accordance with the results of the theoretical calculations for the D_0 state (cf. Table 3).

4.2.3. MATI spectra via the vibrations $17b^2$, $10b^1$, and $16a^1$

The vibrational bands $10b^1$ and $16a^1$ are symmetry forbidden in the $S_1 \leftarrow S_0$ transition. The assignment of these two bands with a'' symmetry in the S_1 state could be verified by recording MATI spectra via these states (Fig. 5, upper two spectra).

The most prominent peaks under observance of the propensity rule are located at $292\,\text{cm}^{-1}$ and $536\,\text{cm}^{-1}$. These measured values are in good agreement with the calculated values in the cation ground state with $243\,\text{cm}^{-1}$ for the $10b^1$ and $538\,\text{cm}^{-1}$ for the $16a^1$,

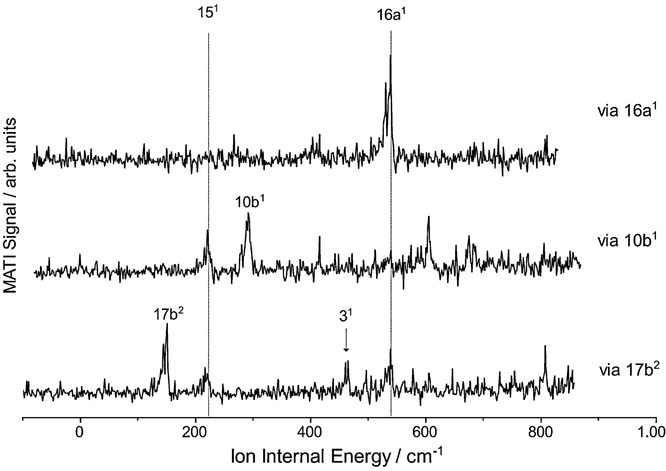

Fig. 5. MATI spectra of 1,2,4-TCB via different intermediate states of the first excited state: via $17b^2$, via $10b^1$ and via $16a^1$.

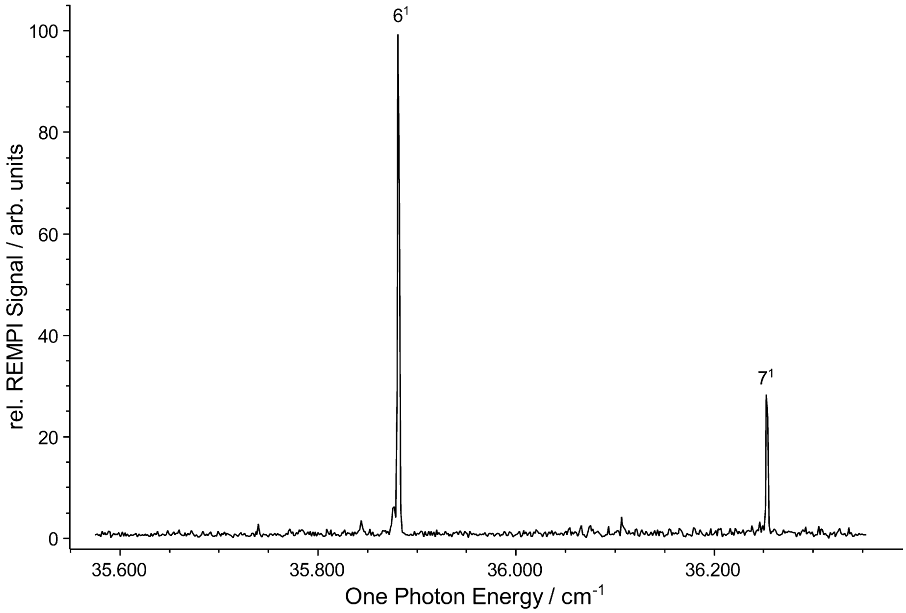

Fig. 6. (1 + 1′)REMPI spectrum of 1,3,5-trichlorobenzene.

respectively. The strong frequency changes of both vibrations during excitation and ionization are remarkable. The 16a vibration is found at 395 cm^{-1} in the first excited state. During the ionization the frequency then increases to 536 cm^{-1} which is nearby the value for the neutral ground state of 551 cm^{-1}[21].

The 10b vibration is found at 305 cm^{-1} in the S_0 state [21] and decreases to 142 cm^{-1} in the S_1 state. After the ionization it is found nearly at the same value as it is in the S_0 state: 292 cm^{-1}. This strong frequency change is not predicted by the TDDFT calculation. On the contrary the calculation predicts a strong frequency decrease for the 17b mode from the neutral ground state to the first excited state. This is in good agreement with the measured values of 117 cm^{-1} in the S_0 state [21] and 66 cm^{-1} in the S_1 state. In the cation ground state the frequency increases to 76 cm^{-1} (cf. Fig. 5 lower spectrum) which fits the calculated value of 71 cm^{-1} very well. The lower spectrum in Fig. 5 shows the spectrum recorded via the 17b^2 in the S_1 state. The 17b^1 mode is symmetry forbidden in the $S_1 \leftarrow S_0$ excitation but the overtone 17b^2 is totally symmetric and therefore allowed. In this spectrum the propensity rule is also retained and the vertical transition into the 17b^2 vibration is the most intense peak at 150 cm^{-1}.

4.3. 1,3,5-Trichlorobenzene

4.3.1. REMPI spectrum

The $S_1(^1A_2') \leftarrow S_0(^1A_1')$ electronic excitation of 1,2,3-TCB (D_{3h} symmetry) is symmetry forbidden which is the same case in benzene. So the structure of the spectrum shown in Fig. 6 is comparatively simple: there are only two intensive peaks. As the 0^0 transition is symmetry forbidden the first intensive peak at 35881 cm^{-1} cannot be this transition. In dependence on benzene this vibration is assigned as 6^1. This peak was also observed by Weickhardt et al. at 35862 cm^{-1}[10] which is in good agreement. The second intensive peak at 36253 cm^{-1} is assigned as the 7^1 vibration. These two vibrations with e′ symmetry can be observed due to Herzberg Teller coupling.

The substitution of one ^{35}Cl atom by a ^{37}Cl atom leads to a symmetry reduction from D_{3h} to C_{2v}. Therefore the degenerated e′ vibrations 6^1 and 7^1 split in each case in two vibrations of a_1 and b_1 symmetry. This effect was recorded for both vibrations with higher resolution and is shown in Fig. 7 for the splitting of the 6^1 band into 6a^1 and 6b^1; the splitting of the 7^1 band into 7a^1 and 7b^1 is shown in Fig. 8. In each case the splitting amounts to 5 cm^{-1}.

Table 4
Summary of all observed MATI peaks of 1,2,4-TCB.

Mode	S_1 intermediate state									
	0^0	17b^2	10b^1	15^1	6b^1	7b^1	16a^1	3^1	6a^1	11^1
0^0	0				0	0				
17b^2		150								
15^1		219	221	221						
10b^1			292							
6b^1	313				313	314				
7b^1	390				390	390				
3^1		463						463		
16a^1		538		534			536			
6b^2	626				626					
6a^1	658			659	658				659	
6b^1 7b^1	702				702					
7b^2						778		778		
11^1	845							848		845

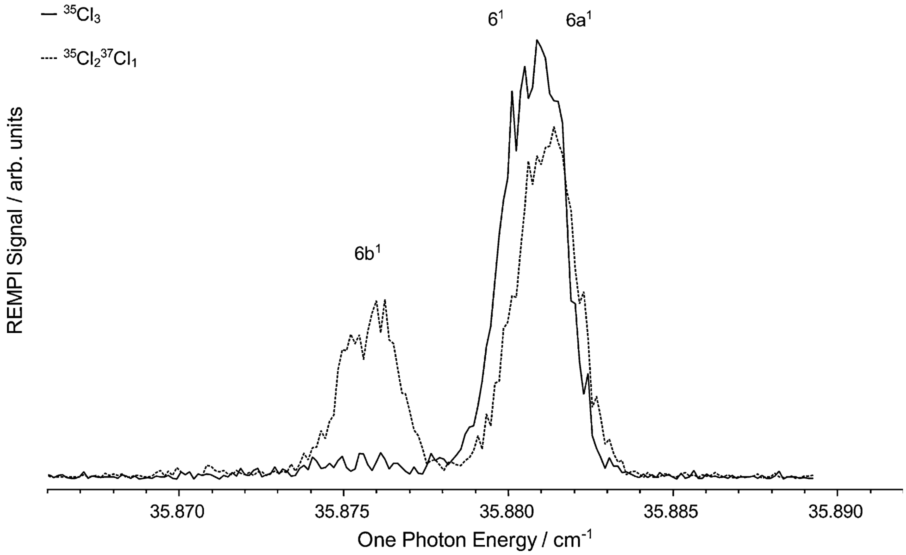

Fig. 7. (1 + 1′)REMPI spectrum of 1,3,5-trichlorobenzene: splitting of the 6^1 mode in $6a^1$ and $6b^1$ due to symmetry reduction of the molecule.

4.3.2. The Jahn–Teller effect in the cation ground state

The excitation into the cation ground state is a $D_0(^2E'') \leftarrow S_1(^1A_2')$ transition. Due to the electronical degeneracy of the D_0 state a Jahn–Teller splitting into two electronic states of A_2 and B_1 symmetry is expected: the D_{3h} symmetry of the molecule is lowered to C_{2v}. So a Jahn–Teller active degenerated vibration splits into two states with different vibronic angular momentum $j = \pm 3/2$ and $j = \pm 1/2$. Due to the quadratic portion of the coupling the state with $j = \pm 3/2$ then splits again into two states with $j = +3/2$ and $j = -3/2$ [27–29].

In a molecule with D_{3h} symmetry the e′ symmetric modes 6 and 7 should therefore split into states with a_1'', a_2'' and e″ symmetry.

This effect in the cation ground state was already examined for benzene [30] and 1,3,5-trifluorobenzene [31].

For examination of this effect in 1,3,5-TCB it seems likely to compare the MATI spectra obtained via the Jahn–Teller active vibrations 6^1 and 7^1 of the $^{35}Cl_3$ isotopomer with the ones obtained via the vibrations $6a^1$, $6b^1$, $7a^1$ and $7b^1$ of the $^{35}Cl_2{}^{37}Cl$ isotopomer which posesses C_{2v} symmetry and therefore exhibits no Jahn–Teller effect. Due to signal weakness it was not possible here to obtain MATI spectra via the modes $7a^1$ and $7b^1$ of the latter isotopomer. The other recorded spectra are presented in Fig. 9. The upper two spectra were obtained via the vibrations 6^1 and 7^1 of the $^{35}Cl_3$ isotopomer; the lower two spectra were obtained via the vibrations $6a^1$ and $6b^1$ of the $^{35}Cl_2{}^{37}Cl$ isotopomer.

It is noteworthy that all the spectra are very similar especially those via the modes 6^1, $6a^1$ and $6b^1$. Due to this similarity we presume that the $^{35}Cl_3$ isotopomer posesses C_{2v} symmetry in the D_0 state as it is the case for the $^{35}Cl_2{}^{37}Cl$ isotopomer. Furthermore we deduce that the Jahn–Teller effect is so small that it cannot be detected here with MATI spectroscopy. From the FWHM of the MATI peaks the Jahn–Teller splitting is estimated to be less than 10 cm⁻¹.

4.3.3. Assignment of the vibrations observed in the cation ground state

The first strong transition via the 6^1 vibration (isotopomer with three ^{35}Cl, second spectrum from above in Fig. 9) appears at 75289 cm⁻¹. This peak also appears in the other three recorded

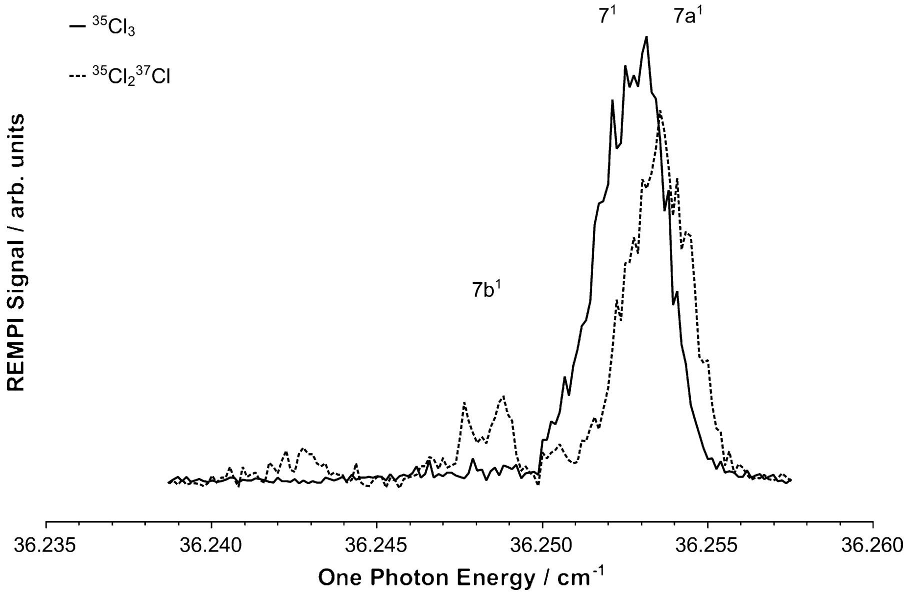

Fig. 8. (1 + 1′)REMPI spectrum of 1,3,5-trichlorobenzene: splitting of the 7^1 mode in $7a^1$ and $7b^1$ due to symmetry reduction of the molecule.

Table 5
Observed and calculated vibrational frequencies (cm^{-1}) of 1,3,5-TCB; the assignment of the normal modes is not secure, thus the frequencies are italicized.

Mode			S_0		S_1		D_0	
Varsanyi	Herzberg	Symm.	Exp. [a]	DFT	Exp.	TDDFT	Exp.	DFT
13	4	a_1'	376	370		371		367
12	3	a_1'	997	1016		986	*1062*	1015
1	2	a_1'	1148	1151		1138	*1214*	1143
2	1	a_1'	3083	3227		3249		3225
3	7	a_2'		446		443		469
15	6	a_2'		1265		1271		1288
14	5	a_2'		1320		1466		1361
11	10	a_2''	142	131		105		132
4	9	a_2''	660	614		477		558
5	8	a_2''	853	834		687		820
9a	24	e'	190	187		186		207
9b	23	e'	190	187		186		207
6a	22	e'	426	429	*430*	373	*429*	429
6b	21	e'	426	429	*430*	373	*429*	429
7a	20	e'	817	802	*802*	790	*820*	799
7b	19	e'	817	802	*802*	790	*820*	799
18a	18	e'	1103	1121		1058		1132
18b	17	e'	1103	1121		1058		1132
19a	16	e'	1422	1442		1360		1459
19b	15	e'	1422	1442		1360		1459
8a	14	e'	1569	1601		1494		1621
8b	13	e'	1569	1601		1494		1621
20a	12	e'	3078	3226		3242		3225
20b	11	e'	3078	3226		3242		3225
17a	30	e''	221	203		105		201
17b	29	e''	221	203		105		201
16a	28	e''	530	532		335		510
16b	27	e''	530	532		335		510
10a	26	e''	945	889		659	*930*	885
10b	25	e''	945	889		659	*930*	885

[a] Taken from Ref. [26].

spectra. The spectra show further peaks at 75466 cm^{-1} and 75534 cm^{-1}. The latter one is observed in all four spectra; the first one is only clearly visible in the spectra via 6^1 and 7^1 and can hardly be recognized in the other two spectra. Additional transitions that can be observed in all spectra are at 75680 cm^{-1} and 75790 cm^{-1}. Moreover there are two peaks at 75922 cm^{-1} and 76074 cm^{-1}. The first one appears clearly in the spectra via the modes 6^1 and $6b^1$; in the spectrum via $6a^1$ this transition is hardly recognizable. The latter one at 76074 cm^{-1} is present in all spectra (via 6^1, $6a^1$ and $6b^1$).

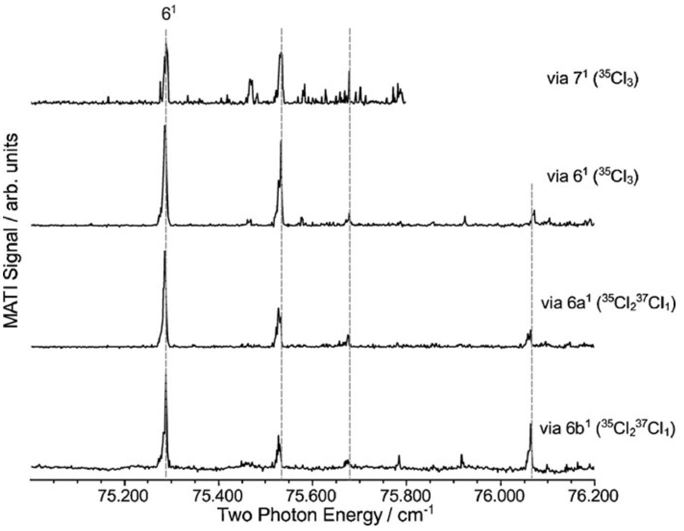

Fig. 9. MATI spectra of 1,3,5-TCB via different intermediate states of the first excited state (different isotopomers): via 6^1 and 7^1 (isotopomer with three 35Cl), via $6a^1$ and $6b^1$ (isotopomer with two 35Cl and one 37Cl).

The assignment of the vibrations is difficult because all recorded spectra exhibit nearly the same structure independend of the chosen S_1 intermediate state. Provided that the propensity rule is valid at least for the excitation via the modes 6^1, $6a^1$ and $6b^1$ we assign the MATI peak at 75289 cm^{-1} as 6^1, $6a^1$ and $6b^1$ vibration for the isotopomers with three ^{35}Cl and two ^{35}Cl, respectively. This seems reasonable because in the cation ground state a splitting between the modes $6a^1$ and $6b^1$ of the nearly the same order of magnitude is expected as it is the case for the first excited state (5 cm^{-1}). So the MATI peak at 75289 cm^{-1} in the spectra of the isotopomer with one ^{37}Cl via $6a^1$ and $6b^1$ includes both the vibrations 6a and 6b and the splitting cannot be observed due to a FWHM of 10 cm^{-1}. With a calculated frequency of 429 cm^{-1} for the 6^1 normal mode in the cation ground state the adiabatic ionization energy can be estimated to 74900 ± 100 cm^{-1}. The error stems from generously estimated deviations of the calculated frequencies from the measured ones. In spite of the uncertainty this value is in good accordance to previously measured values for the ionization energy of 75110 ± 240 cm^{-1} obtained by photo electron spectroscopy [24].

Table 6
Summary of all observed MATI peaks of 1,3,5-TCB, values given in italics are hardly visible in the spectra.

Mode	S_1 intermediate state			
	6^1 $^{35}Cl_3$	$6a^1$ $^{35}Cl_2$$^{37}Cl$	$6b^1$ $^{35}Cl_2$$^{37}Cl$	7^1 $^{35}Cl_3$
				75165
$6a^1/6b^1$	75289	75289	75289	75289
	75466			75470
	75534	75534	75534	75535
	75578			75584
$7a^1/7b^1$	75680	75680	75680	75678
$10a^1/10b^1$	*75790*	*75790*	75790	75789
12^1	75922	*75922*	75922	
1^1	76074	76074	76074	

When the molecule is excited via the 7^1 vibration the propensity rule is broken. Here also the 6^1 mode is the most prominent peak in the spectrum. This is a hint for a geometry change along the 7 vibration during the ionization of 1,3,5-TCB.

With the assigned 6 vibrations as point of reference and with the theoretical calculation of the D_0 state a further assignment is feasible. A possible assignment is given in Tables 5 and 6.

5. Conclusions

MATI spectra of the three structural isomers of trichlorobenzene were recorded by ionization via various intermediate levels of their corresponding S_1 state. The activity, the appearance and the frequency of the observed modes change dramatically between the three isomers. From breakdowns of the "$\Delta\nu = 0$" propensity rule hints for a geometry change of the molecules upon the $D_0 \leftarrow S_1$ excitation were found. So all isomers change their geometry upon ionization along the $7b^1$ mode (7^1 in the case of 1,3,5-TCB). Furthermore 1,2,4-TCB changes its geometry along the vibrational mode $6b^1$. In 1,2,3-TCB the geometry is additionally changed along the $9a^1$ mode and the unusual strong occurrence of the symmetry forbidden $17b^1$ mode in the MATI spectra might give rise to the assumption that 1,2,3-TCB lowers its symmetry in the S_1 state from C_{2v} to C_s.

For 1,3,5-TCB a Jahn–Teller distorsion in the cation ground state is predicted due to the degenerated electronic state of E'' symmetry. The Jahn–Teller effect could be verified by comparison of the MATI spectra of the isotopomer with D_{3h} symmetry (three ^{35}Cl) with the ones of the isotopomer with C_{2v} symmetry (one ^{35}Cl substituted by a ^{37}Cl). Due to the similarity of these spectra a Jahn–Teller splitting within the full width half maximum of the MATI peaks of 10 cm^{-1} is deduced.

The obtained results concerning the changes of the molecular geometry of the three isomers during the $D_0 \leftarrow S_1$ excitation differ slightly from those obtained for the dichlorobenzenes [8,9]. All dichlorobenzenes retain their symmetry when excited into the cation ground state and a geometry change arises for all isomers along the 7a vibrational mode. This vibration does not play a decisive role in the case of the trichlorobenzenes where the 7b mode is the prominent one. In general, the trichlorobenzenes show a considerably more heterogeneous vibrational structure as it is the case for the dichlorobenzenes. The reason for this is the different electronic distribution of the molecules due to other substitution patterns arising from the substitution of one more hydrogen by another chlorine.

The adiabatic ionization energies of 1,2,3-TCB and 1,2,4-TCB could be determined very precicely to 74289 ± 6 cm^{-1} and $72779 \pm$ cm^{-1}, respectively. The adiabatic ionization energy of 1,3,5-TCB can only be estimated to 74900 ± 100 cm^{-1} because the 0^0 transition is symmetry forbidden. All values are in good accordance with previously determined values that were measured with photo electron spectroscopy. The values obtained in this publication are the most precise data for these molecules.

The two color two photon $(1+1')$ REMPI spectra of the three structural isomers of trichlorobenzene differ in their vibrational structure due to the different molecular symmetries of the isomers. All three isomers exhibit the appearance of symmetry forbidden vibrations in the first excited state which can be explained by a benzene-like Herzberg–Teller coupling. The excitation energies of the isomers could be determined very precicely to 35558 ± 2 cm^{-1}, 35111 ± 2 cm^{-1} and 35881 ± 2 cm^{-1} for 1,2,3-, 1,2,4- and 1,3,5-TCB, respectively. In the case of 1,3,5-TCB a splitting of the degenerated e' vibrational modes 6^1 and 7^1 into $6a^1$, $6b^1$, $7a^1$ and $7b^1$ is expected for the $^{35}Cl_2{}^{37}Cl$ isotopomer with C_{2v} symmetry. This splitting was determined to 5 cm^{-1}.

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