Resonance-enhanced multiphoton ionization (REMPI) spectroscopy of *p*-chlorofluorobenzene

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Abstract

The $S_1 \leftarrow S_0$ ($\tilde{A}\,^1B_2 \leftarrow \tilde{X}\,^1A_1$) electronic transition of *para*-chlorofluorobenzene has been investigated using resonance-enhanced multiphoton ionization (REMPI) spectroscopy. Assignment of the vibrational structure has been achieved by comparison with corresponding spectra of related molecules, via quantum chemical calculations, and via shifts in bands between the spectra of the ^{35}Cl and ^{37}Cl isotopologues. In addition, we have also partially reassigned a previously-published spectrum of *para*-dichlorobenzene.

1. Introduction

In recent work from our group we have focused on the recording and assignment of vibrations of substituted benzenes in the S_1 state, with a particular interest in identifying common activity across related species. Thus, we have recorded resonance-enhanced multiphoton ionization (REMPI) spectra of the three monohalobenzenes, fluorobenzene (FBz), chlorobenzene (ClBz) and bromobenzene (BrBz) [1],[2],[3], toluene (Tol) [4],[5], *para*-fluorotoluene (*p*FT) [6], [7] and *para*-xylene (*p*Xyl) [8], [9]. Central to establishing the common activity, is the use of consistent labelling schemes, which we have described for the monosubstituted benzenes [10] and the *para*-disubstituted benzenes [11]. We shall use the latter scheme in the present work to compare the activity in the titular molecule and other related ones. In contrast to the work on Tol, *p*FT and *p*Xyl cited above, we shall not report zero-kinetic-energy (ZEKE) photoelectron spectra via intermediate S_1 vibrational levels as a means of establishing the assignments, but instead rely on quantum chemical calculations of the vibrational wavenumbers, including shifts between *p*DFB and *p*ClFB, shifts between the spectra reported herein for p^{35}ClFB and p^{37}ClFB, and further comparison to the corresponding spectrum of *p*FT.

There appears to be very little work on *p*ClFB, with the available S_0 vibrational wavenumbers having been discussed in depth in Ref. 11, to which the reader is referred, and a recommended “best set” put forward; many of these were taken from the gas-phase work of Narasimham et al. [12] and the liquid-phase values of Green [13]. With regards to the S_1 state, there also appears to be only a handful of studies. The origin transition was analysed via UV absorption spectroscopy by Cvitaš and Hollas [14], but the most pertinent is a resonance-enhanced multiphoton ionization (REMPI) study from Numata et al. [15] to which we shall refer to further in the below; however, we note that only band position wavenumbers were given, but no assignments. There has also been a REMPI study of the *p*ClFB…methanol complex by Riehn et al. [16], but that of the monomer was not presented.

2. **Experimental**

The vapour above room temperature *para*-chlorofluorotoluene (98% purity, Aldrich) was seeded in ~1.5 bar of Ar and the gaseous mixture passed through a General Valve pulsed nozzle (750 μm, 10 Hz, opening time of 180–210 μs) to create the free jet expansion. The laser was a dye laser (Sirah Cobra-Stretch) operating with either C503 or C540A and was pumped with the third harmonic (355 nm) of a Surelite Nd:YAG laser, and the fundamental output was frequency doubled using a BBO crystal. The spectra recorded are REMPI spectra, recorded in the parent mass channel, with separate spectra recorded for the ^{35}Cl and ^{37}Cl isotopologues. The region below 1400 cm^{-1} was recorded as a two-colour spectrum, with the ionizing photon being 37990 cm^{-1}, while the remainder of the spectrum was recorded as a one-colour spectrum. This was necessary as it is not possible to ionize via the $S_1 \leftarrow S_0$ transition in a (1+1) REMPI process in the first ~ 350 cm^{-1} as the ionization energy is too high[15] (for convenience we continued with the two-colour scheme for the range of the C540A dye employed). Calibration has been achieved by setting the origin band position to that of Cvitaš and Hollas [14], with the uncertainty estimated from the width of the rotational profile.

3. **Calculational Details**

We have shown in the studies cited in the Introduction, that the time-dependent B3LYP (TD-B3LYP) method generally appear to work well, with caveats, for calculating vibrational wavenumbers for the S_1 states of substituted benzenes, and we use that level of theory here. The basis sets employed are aug-cc-pVTZ, which we have also used in previous work and we employed the Gaussian package [17]. We note that the calculated wavenumbers have been scaled by 0.97 to correct both for anharmonicity and other weaknesses in the method; additionally, as we have commented on previously [3], [6], [8] the lowest wavenumber a_2 vibration (D_{14} here) does not appear to be described well for substituted benzenes and we do not report values for this vibration, instead relying on the appearance of the spectrum to assign transitions involving this vibration. Further comments on the calculations will be made below.

4. **Results and Assignment**

We present the calculated wavenumbers for p^{35}ClFB and p^{37}ClFB in Table 1. It should be noted that the wavenumber ordering of the D_i modes in *p*ClFB is not the same as in *p*DFB and again highlights a weakness in the use of Mulliken labels, even for very closely-related molecules. Additionally, we present the calculated and available experimental values for *p*DFB (from previous work [7],[18]) to which we shall compare.

In Figure 1 we show an overview of the REMPI spectra of p^{35}ClFB together with the corresponding spectra of *p*FT and *p*DFB for comparison – regions of the latter two spectra have been presented in previous work [6], [7], [8]. The origin of the $S_1 \leftarrow S_0$ transition is measured as 36275±2 cm^{-1}, and is the same for both isotopologues, within 1 cm^{-1} as judged from the position and band profiles.

To assign the *p*ClFB spectrum, we compare the activity across the three spectra, and also with the calculated wavenumbers presented in Table 1, particularly the *p*DFB/*p*ClFB shifts, but also the p^{35}ClFB/p^{37}ClFB isotopic shifts; the latter were very useful in assigning some bands in ClBz [2]. As is usual, we expect activity from a_1 symmetry vibrations from the Franck-Condon (FC) principle, and b_2 vibrations from Herzberg-Teller (HT) vibronic coupling, noting also that the intensity of a_1 vibrations can also be affected by HT coupling. We give detailed assignments for the region below 1000 cm^{-1}, which are shown in Figure 2 for both the p^{35}ClFB and p^{37}ClFB isotopologues, with assignment of the main features also indicated up to 1400 cm^{-1}. We can see that both spectra are very similar with many bands showing no discernible shift, but that there are small but significant shifts in some of the bands to lower wavenumber for the heavier isotopologue. These can be compared to the calculated ^{35}Cl–^{37}Cl shifts, also presented in Table 1, and prove a useful tool in confirming the assignments.

Assignment of the spectrum generally turns out to be relatively straightforward with experience gained from our work on similar molecules. For example, the most intense bands are the expected a_1 fundamentals, but with the caveat that we know that Fermi resonance (FR) can give occasional unexpected activity, while others are HT-allowed b_2 vibrations. We briefly outline the assignments indicated in Figure 2, noting our rationale when the situation is less clear. Band positions given in the text refer to the ^{35} Cl isotopologue, with the values for both isotopologues being given in Table 2.

At first sight, assignment of the bands at 344 cm^{-1}, 623 cm^{-1} and 962 cm^{-1} to the 11^1, 10^1 and 8^1 FC-allowed fundamental transitions, respectively, appears straightforward, but we shall come back to the 344 cm^{-1} band again. We expect the 9^1 transition close to 795 cm^{-1}, but we see that there are two intense bands here. Knowledge of the $9^1 \ldots 29^2$ FR in *p*FT [7] prompted us to consider whether the same situation could hold here, and indeed since we can confidently identify the 29^1 transition at 397 cm^{-1}, then the 29^2 transition is indeed expected to be close in wavenumber to 9^1. Without further information from time-resolved, coherent-excitation spectroscopies, or zero-kinetic-energy (ZEKE) photoelectron spectroscopy, we cannot comment in much detail on the interaction, but simply represent the transitions by $[9^1 \ldots 29^2]$, with the ordering being unclear. Further comparison to the *p*FT and *p*DFB spectra, suggest we should expect the 28^1 transition, which can be identified at 546 cm^{-1}, and the 30^1 transition, which we observe at 265 cm^{-1}. The above assignments (barring the 344 cm^{-1} band – see below) are in very good agreement with the calculated values – See Table 1.

From our [7] and other's [18] previous work, we also expect to observe overtones of various b_1 vibrations, and it is straightforward to identify the 20^2 transition at 187 cm^{-1}, the 19^2 transition at 488 cm^{-1} and the 18^2 transition at 861 cm^{-1}. Reaching these latter assignments is more problematic since the calculated b_1, and a_2, vibrational wavenumbers are known to be in rather poorer agreement with experiment than are the a_1 ones [7]. To get a better estimate, we compared the calculated versus experimental wavenumbers for *p*DFB and applied the same scaling to the *p*ClFB calculated values for the out-of-plane modes (referred to as "*p*DFB-scaled" values) – this led to a viable assignment for all of the main bands. Assigning the rest of the bands is achieved by using estimations of the fundamentals from the assigned overtones and then looking for FC-allowed ($b_1 \times b_1$) or ($a_2 \times a_2$) combinations and then also ($b_1 \times a_2$) HT-allowed combinations. In this way we were able to achieve reasonably confident assignments for most features under 1000 cm^{-1} with the exceptions being for some very weak bands. We also note that the two bands visible to the red of the main origin band for *p*ClFB in Figure 2 at -31 cm^{-1} and -88 cm^{-1} can be assigned to the 20^1_1 and 19^1_1 vibrational hot bands. (It is also possible that there is some minor contribution to the -31 cm^{-1} band from the *p*ClFB-Ar complex – a typical shift for such complexes.[6])

One feature that we wish to discuss in more detail is the one with a peak at ~344 cm^{-1}. It may be seen that this band has more than one contribution when recorded in the p^{35}ClFB mass channel, but is apparently a single band in the p^{37}ClFB mass channel (see Figure 2). For p^{35}ClFB, the two bands are at 344 cm^{-1} and 347 cm^{-1}, while in p^{37}ClFB the single band is at 342 cm^{-1}. Based upon the other spectra, we expect to see two transitions at about this wavenumber: 11^1 and 14^2; the 11^1 transition is calculated to shift ~ 5 cm^{-1} between the two Cl isotopologues (see Table 1), while the 14^2 transition is not expected to move significantly. The intensity of the 11^1 transition in the $S_1 \leftarrow S_0$ transition of substituted benzenes appears to be affected by HT-coupling (see, for example, Ref. [8]) and so it is difficult to be sure of its expected intensity, and similar comments could be made about 14^2. However, the observed isotopic shifting of the bands suggests the higher wavenumber, weaker contribution at ~347

cm^{-1} is the 11^1 transition for p^{35}ClFB, and the lower one, whose maximum is uncertain because of the overlap, is due to 14^2. Of course, there is the possibility that D_{11} and $2D_{14}$ are interacting, but evidence from other studies suggests that this is weak [4],[6],[8]. Since the D_{11} vibration shifts, while the D_{14} overtone is not expected to, it seem that in p^{37}ClFB these two transitions are now coincident (and the fact that they are also supports the very weak interaction suggested.) Additionally, the fact that the intensity of the band in the p^{37}ClFB channel is greater than 1/3 of that in the p^{35}ClFB mass channel is consistent with there being overlapped features.

A summary of the assignments is presented in Table 2 and these are satisfactorily internally self-consistent. In this way we have obtained values for two of the a_2 fundamentals and all six b_1 fundamentals, which are summarized in Table 1. The activity and the wavenumbers are very much in line with activity seen in corresponding spectra of other molecules; in particular, we refer to our recent paper on *p*FT where we able to assign all of the b_1 and a_2 modes with the aid of ZEKE spectroscopy [7].

We now move onto a more cursory description of the higher wavenumber regions of the spectrum – see Figure 3. We can straightforwardly identify the 6^1, 5^1 and 3^1 transitions at 1064 cm^{-1}, 1231 cm^{-1} and 1489 cm^{-1}; these assignments are based on the expected activity together with the good agreement expected between the experimental and calculated wavenumbers. Note that although we did not expect to see either a 4^1 or 7^1 transition, since these are not seen for other molecules. In Figure 3, we have indicated the assignments of the most intense bands moving up to higher wavenumber, and these involve expected progressions in the D_{11} and D_9 coordinates. We note that the overtone of the latter is complicated by interaction with the $2D_{29}$ and so, for example we can see a complicated feature at ~1590 cm^{-1} which will involve the overtones and combination transitions: 9^2, $9^1 29^2$ and 29^4, as well as others that coincidentally fall in this narrow region. Various other complicated features appear throughout the spectrum and if desired assignments can be put forward, but clearly the increasing complexity of bands means that near-coincidences will make firm assignments hard to establish, together with the issues of anharmonicity and associated coupling between like-symmetry levels.

Finally, we have also re-examined the published $S_1 \leftarrow S_0$ spectrum of *para*-dichlorobenzene (*p*DClB), which has been presented in Refs [19], [20] and [21], with an LIF spectrum presented in Ref. [22]. No assignments were presented in Ref. [19], while those given in Ref. [21] are in terms of Wilson notation and are not wholly consistent with those of other related molecules, including *p*DFB [7],[18] and others given herein, in contrast, the assignments in Refs. [21] and [22] are in terms of Mulliken notation (but based on D_{2h} *p*DFB). As a consequence, we recalculated the vibrational wavenumbers using the B3LYP/aug-cc-pVTZ approach and present the findings in Table 1. Notably, optimizing a planar D_{2h} structure gave an out-of-plane imaginary wavenumber – along the D_{14} coordinate – and so we reoptimized a D_2 symmetry non-planar structure, which led to all-real wavenumbers. (We also then reoptimized the structures of *p*DFB and *p*ClFB, commencing at non-planar structures, but these reverted to the planar structure in both cases.) As we have discussed in Ref. [6], the literature has various comments on the planarity or otherwise of the S_1 state of various substituted benzenes, with conflicting conclusions from both experiment and theory, but the source of this is not well-established and at present, the conclusions from quantum chemical calculations must be treated with caution for the out-of plane modes. In Table 1, we present the calculated wavenumbers for the D_2 symmetry structure, but keep the same D_i vibrational labels, this lowering in symmetry removes the centre of symmetry and can cause mixing of the D_i vibrations (see below). (The symmetry classes of the D_{2h} and D_2 point groups are related by a removal of the u/g labels for the D_2 point group.)

In Table 3 we also present the reassignments of the main bands of the *p*DClB REMPI spectrum. We take the values reported in ref. [20], as well as estimates for some weaker features seen in their spectrum. As may be seen, there is generally good agreement with the calculated wavenumbers for the a_1 and b_2 symmetry modes and those arising from the assignments, which are now consistent with those of the other related molecules. For the b_1 and a_2 modes, for the assigned values (except for D_{14} – see above), the agreement with the "*p*DFB-scaled" values is remarkably good, as noted above for *p*ClFB. (There are a number of weak features that are not consistent between the different published spectra – it is possible that these may relate to impurities or complexes.) Of note is that in the REMPI spectrum of Ref. [20], some reasonably intense features appear in the range 800–900 cm^{-1}, but these are evident to differing degrees in the REMPI spectrum of Ref. [21] and the LIF spectrum of Ref. [22], with the latter suffering from contributions from the three main isotopologues.

Of particular interest is a band that appears at 1094 cm^{-1}, for which the only reasonable assignment is 10^2. (The fundamental is commented on below as being one of the vibrations this is symmetry-allowed in the C_{2v} asymmetric species, but not in the symmetric D_{2h} ones.) The assignment of the overtone appears to be clear as it is observed to undergo a significant isotopic shift in the REMPI and LIF studies by the expected amount. The interest lies in the fact that it does not appear to be active to any significant level in other related species, and so its intense appearance is unusual. One rationale may be related to the calculated non-planarity of the S_1 state of *p*DClB – the D_{10} and D_{13} modes are quite close in wavenumber and both become b_1 symmetry under D_2 symmetry. These may thus form linear combinations which contain both in-plane and out-of-plane character; thus, the "D_{10}" could gain some FC-activity via this route, since the 13^2 vibration is thought to be active in *p*DFB [18] and we believe in *p*FT (work in progress). Additionally, an unassigned band at 1139 cm^{-1} in the LIF spectrum of *p*DClB [22] looks plausibly assignable to 13^2. These assignments yield vibrational wavenumbers that are in only reasonable agreement with the calculated wavenumbers, but not out of line with those of other related molecules. Further, the large shift in wavenumber upon isotopic substitution is a strong piece of evidence for the 10^2 assignment.

A summary of the deduced assignments is given in Table 3, and the derived fundamental wavenumbers are given in Table 1.

5. Concluding Remarks

In the present work, we have assigned the vibrational structure in the $S_1 \leftarrow S_0$ ($\tilde{A}\,^1B_2 \leftarrow \tilde{X}\,^1A_1$) transition of the *p*ClFB molecule for the first time. A number of bands below 1100 cm^{-1} were observed by Numata et al. [15], but no assignments were given therein; these were also seen in the present work, and many more, and are now assigned. We have presented a detailed assignment of the bands below 1000 cm^{-1}, allowing the wavenumber two of the three a_2 and all six of the b_1 symmetry vibrations to be established. The values are consistent with those in *p*DFB, and so support the assignment, despite limitations in the ability of TD-B3LYP to describe these out-of-plane vibrations. We also establish values for the lowest three b_2 symmetry modes, and those of seven a_1 modes. The assignments may be seen to be consistent across the spectra of the three molecules presented in Figure 1, with the exception being the low-wavenumber torsional and vibtor transitions in *p*FT, described in depth in Ref. [6]. There is also good comparison to *p*Xyl – see ref. [8], with the torsions having been discussed in depth in Ref. [9].

As previously noted in our work on the effectively C_{2v} molecule, *p*FT [7], it is interesting to note that the 10^1 and 30^1 transitions are observed, but not in the D_{2h} *p*DFB molecule. This is rationalized in terms of symmetry – with the former being FC-allowed and the latter being HT-allowed; neither meet the symmetry criteria to be allowed in *p*DFB. It will be noted that in the present work, with the symmetry of *p*ClFB being lowered to C_{2v}, then both of these transitions are now observed, as in *p*FT. We also highlight here the same arguments apply to 6^1, which is an intense band in the REMPI spectra of *p*FT and *p*ClFB, but is absent in that of *p*DFB – see Figure 1; additionally, there is no 6^1 band in the *p*DClB spectrum (see Ref. [21] and Table 3). However, in all of the spectra there is a 5^1 FC-allowed transition. In Ref. [11] we have discussed the evolution of the D_5 and D_6 vibrations on moving from the $D_{2\mathrm{h}}$ *p*DFB molecule to the C_{2v} asymmetric *p*-dihalobenzenes and other asymmetric *para*-disubstituted species. Briefly, these evolve from vibrations that contain in-phase (D_5) and out-of-phase (D_6) C-F stretches into more local mode C-X and C-Y stretches, where X and Y are the two different *para* substituents. The change in electronic structure during the $S_1 \leftarrow S_0$ transition causes symmetric changes in the C-F bond lengths in *p*DFB, and so we only see the 5^1 transition; the same arguments also hold for *p*DClB. This geometric argument follows the symmetry arguments where the D_5 vibration is totally symmetric (a_g) in $D_{2\mathrm{h}}$, while the D_6 vibration is of $b_{1\mathrm{u}}$ symmetry (see Table 1). For the asymmetric cases of *p*FT and *p*ClFB the corresponding bond lengths can change independently and so both 5^1 and 6^1 transitions are active.

We have outlined assignments for the higher wavenumber region of the spectrum, where clear progressions can be identified for totally-symmetric vibrations that correspond to elongation of the benzene ring, in common with the $S_1 \leftarrow S_0$ transition in many substituted benzenes. The level structure becomes increasingly more complicated as the number of levels builds up; as a consequence, the likelihood of vibrational interactions increases and definitive assignment in terms of single combinations/overtones becomes ever less meaningful.

Finally, we have drawn analogies with the published spectra of *p*DClB, noting a large degree of consistency with the other spectra discussed herein; we have also commented on the apparent anomaly of the intensity of the 10^2 band.

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Figure Captions

Figure 1: Comparison of the first 1380 cm^{-1} of the REMPI spectra of (a) *p*FT; (b) *p*DFB; and (c) *p*ClFB. The *p*FT bands marked with an asterisk consist of a number of assignments and will be the subject of future publications.

Figure 2: Assignments of the first 1380 cm^{-1} of the REMPI spectrum of *p*ClFB, showing both the p^{35}ClFB and p^{37}ClFB isotopologues. Assignments are given for the ^{35}Cl isotopologue and are discussed in the text; those for the ^{37}Cl isotopologue are deduced to be very close or coincident – see text and Table 2.

Figure 3: Overview showing the main progressions of the first ~3200 cm^{-1} of the REMPI spectrum of *p*ClFB – see text. Progressions are indicated with a comb, and we use $[9^1\ldots29^2]$ to indicate a pair of transitions that are thought to be in Fermi resonance (see text), and $[9^1\ldots29^2]^n$ to indicate overtones and combinations of the components. The dashed lines indicate the intensity of the frequency-doubled dyes employed, over the indicated ranges.

Table 1: Calculated and experimental vibrational wavenumbers (cm^{-1}) for the S_1 states of *p*ClFB, *p*FT and *p*DClB

D_i[a]	Mulliken (D_{2h})[b]	*p*^{35}ClFB		*p*^{37}ClFB			*p*DFB		*p*D^{35}ClB	
		Calc[c]	Expt	Calc[c]	Expt[d]	Δ_{calc}[c]	Calc[c]	Expt[e]	Calc[c]	Expt[f]
a_1										
D_1	$1(a_g)$	3143		3143		0	3143		3118	
D_2	$10(b_{1u})$	3130		3130		0	3131		3114	
D_3	$2(a_g)$	1491	1489	1491	1489	0	1519		1456	
D_4	$11(b_{1u})$	1411		1411		0	1422	1335	1395	
D_5	$3(a_g)/4(a_g)$[g]	1211	1231	1211	1232	0	1235	1251	1012	1054
D_6	$12(b_{1u})$	1037	1064	1036	1063	-1	1198	1015	1009	
D_7	$4(a_g)/3(a_g)$[g]	1112		1112		0	1099	[1116]	1124	1139
D_8	$13(b_{1u})$	963	962	963	961	0	951	937	972	
D_9	$5(a_g)$	796	793	796	793	0	820	818	727	726
D_{10}	$14(b_{1u})$	617	623	614	620	-3	710	[666]	503	547
D_{11}	$6(a_g)$	348	347	343	342	-5	414	410	302	298
a_2										
D_{12}	$7(a_u)$	532 (619)		532		0	501	583	610 (710)	714
D_{13}	$9(b_{1g})$	482 (534)	538	482	539	0	429	475	531 (588)	570
D_{14}	$8(a_u)$	-[h]	172	-[h]	171	-[h]	-[h]	175	-[h]	166
b_1										
D_{15}	$15(b_{2g})$	696 (669)	676	696	676	0	697	670	723 (695)	
D_{16}	$28(b_{3u})$	653 (606)	611	652	611	-1	667	619	658 (611)	613
D_{17}	$16(b_{2g})$	558 (520)	519	558	519	0	567	528	556 (518)	
D_{18}	$29(b_{3u})$	486 (437)	431	486	430	0	487	438	481 (433)	436
D_{19}	$17(b_{2g})$	254 (249)	244	254	244	0	279	274	213 (209)	208
D_{20}	$30(b_{3u})$	99 (96)	94	99	93	0	124	120	70 (68)	75
b_2										
D_{21}	$18(b_{2u})$	3138		3138		0	3139		3120	
D_{22}	$23(b_{3g})$	3125		3125		0	3126		3109	
D_{23}	$24(b_{3g})$	1366		1366		0	1407	[1516]	1357	
D_{24}	$19(b_{2u})/ 20(b_{2u})$[g]	1303		1303		0	1397		1305	
D_{25}	$20(b_{2u})/19(b_{2u})$[g]	1408		1408		0	1317	[1591]	1388	
D_{26}	$25(b_{3g})$	1225		1225		0	1232		1216	
D_{27}	$21(b_{2u})$	1018		1018		0	1022	1100	1028	
D_{28}	$26(b_{3g})$	542	546	542	546	0	553	558	544	536
D_{29}	$27(b_{3g})$	394	397	394	397	0	396	403	336	337
D_{30}	$22(b_{2u})$	263	265	261	263	-2	347	352	226	226

[a] See Ref. [11].

[b] Numbers from standard Mulliken numbering in the D_{2h} point group.

[c] TD-B3LYP/aug-cc-pVTZ calculated values. Values in parentheses are "*p*DFB-scaled" values based on the calculated/experimental ratio for *p*DFB – see text. Δ_{calc} represents the calculated isotopic shift between the ^{35}Cl and ^{37}Cl isotopologues.

[d] Present work.

[e] See Refs. [7] and [18]. Values in square brackets are uncertain. Note that the value for D_{13} was concluded in Ref. [7] to be the second offered value in Ref. [18].

[f] Wavenumber values taken from Refs. [20] and [21]; assignments are from the present work – see text.

[g] For the indicated vibrations, the energetic ordering changes between *p*DFB and *p*DClB, and hence the "standard" Mulliken label ordering would switch. The first label refers to *p*DFB and the second to *p*DClB.

[h] The D_{14} calculated values are known to be unreliable – see text.

Table 2: Assignments of the REMPI bands of *p*^{35}ClFB and *p*^{37}ClFB [a]

Position / cm^{-1}		**Assignment**	**Position / cm^{-1}**		**Assignment**
^{35}Cl	**^{37}Cl**		**^{35}Cl**	**^{37}Cl**	
-88	-88	19^1_1	1130-1143	1135-1147	$[9^1\ldots29^2]+14^2$, $[9^1\ldots29^2]+11^1$,
-31	-30	20^1_1	1231[d]	1232[d]	5^1
0	0	0^0	1245	1241	10^2
187	186	20^2	1489	1489	3^1
265	263	$30^1/14^1 20^1$	1591[e]	1590[e]	$[9^1\ldots29^2]^2$ [c]
316			1855[d]	1854[d]	$[9^1\ldots29^2]+6^1$
337	336	$19^1 20^1$	1860[d]	1858[d]	$[9^1\ldots29^2]+6^1$
344	342[b]	14^2	2025	2025	$5^1 9^1$
347	342[b]	11^1	2038	2033	$9^1 10^2$
397	397	29^1	2124	2121	6^2
458		$14^1 20^3/20^2 30^1$	2293	2293	$5^1 6^1$
488	488	19^2	2306	2300	$6^1 10^2$
502			2382[e]	2382[e]	$[9^1\ldots29^2]^3$ [c]
517		$18^1 20^1$	2455[d]	2453[d]	5^2
546	546	28^1	2469	2463	$6^2 11^1$
593			2477	[d]	$5^1 10^2$
612	612	$17^1 20^1$	2491	[d]	10^4
623	620	10^1	2651[e]	2650[e]	$[9^1\ldots29^2]^2 + 6^1$ [c]
689	683	$11^2/11^1 14^2$	2818[d,e]	2817[d,e]	$[9^1\ldots29^2]^2 +5^1$ [b]
705	704	$16^1 20^1$	2831[d,e]	2826[d,e]	$[9^1\ldots29^2]^2 +10^2$ [c]
710	710	$13^1 14^1$	2911-2919[d]	2909-2917[d]	$[9^1\ldots29^2]+6^2$ [c]
732	731		3083-3088[d]	3080-3086[d]	$[9^1\ldots29^2] + 5^1 6^1$ [c]
740	738	$11^1 29^1$	3096-3102[d]	[d]	$[9^1\ldots29^2] + 6^1 10^2$ [b]
762	762	$17^1 19^1$	3178[e]		$[9^1\ldots29^2]^4$ [c]
769	769	$15^1 20^1$			
793	793	$[9^1\ldots29^2]$[c]			
798	798	$[9^1\ldots29^2]$[c]			
808	808				
813	811	$10^1 20^2/28^1 30^1$			
861	860	18^2			
872	866	$11^2 20^2$			
887	887[c]	$19^2 29^1/14^2 28^1$			
893	887[c]	$11^1 28^1$			
936	936				
945	944	$17^1 18^1/28^1 29^1$			
962	961	8^1			
975	975	$9^1 20^2$			
982	981	$29^2 20^2$			
1064	1063	6^1			

[a] Line positions are relative to the origin at 36275±2 cm^{-1} (same for both isotopologues). The lower state is the zero point level in S_0, unless noted otherwise. Detailed assignments are given in the range -100 – 1000 cm^{-1}, with selected assignments given for the higher wavenumber bands. See Figures 2 and 3 for the spectra. Below 1000 cm^{-1}, if an assignment is not given, no reasonable assignment could be found – such bands are generally very weak. If two transitions are given separated by a solidus, then these are thought to be overlapping transitions. Some

bands were too weak to be definitively identified for the ^{37}Cl isotopologue and the Position entry is left blank for these.

[b] Bands are coincident.

[c] Bands involving the 9^1 and 29^2 transitions, and combinations and overtones thereof, arise from eigenstates that are linear combinations of D_9 and $2D_{29}$, but the precise make-up is unknown. Such bands are indicated by square brackets for the most intense feature of a group, but this is usually part of a more complicated feature, whose eigenstates will be mixtures of the indicated S_1 levels that are involved in the transition. No inference should be made from the ordering of the transitions given as to the relative magnitudes of the contributing states.

[d] Overlapped feature. Indicated position or range, if given, is a best estimate.

[e] Band position taken from the maximum of a clump of bands, which are thought to arise from transitions to levels that comprise various combinations of the indicated transitions.

Table 3: Assignments of the REMPI/LIF bands of *p*D^{35}ClB

Position[a]	**Assignment** D_i [b]	**Previous Assignment** **Mulliken –D_{2h}/Wilson** [c]
0		
150	20^2	30^2 (11^1)
245	$14^1 20^1$	-
301	11^1	6^1 ($7a^1$)
334	14^2	8^2 ($16a^2$)
339	29^1	27^1 ($9b^1$)
416	19^2	
451	30^2 ($+11^1 20^2$)[d]	17^2 ($10b^2$)
538	28^1	26^1 ($6b^1$)
588	$14^1 18^1$	29^2 ($16b^2$)
602	11^2	
636	$11^1 14^2$	
641	$11^1 29^1$	$6^1 27^1$ ($7a^1 6b^1$)
672	$14^2 29^1$	$8^2 27^1$ ($16a^2 9b^1$)
680	29^2	
688	$16^1 20^1$	
708	Ar[e]	
716	Ar[e]	
727	9^1 ($+17^1 19^1$)[d]	5^1 ($6a^1$)
831	19^4	16^2 (4^2)
838/841[f]	$11^1 28^1$	$6^1 26^1$ ($7a^1 6b^1$)
870	18^2	
877	$12^1 14^1$	
1027	$9^1 11^1$	$5^1 6^1$ ($7a^1 6a^1$)
1053	5^1	4^1 (1^1)
1059	$9^1 14^2$	
1065	$9^1 29^1$	$27^1 5^1$ ($9b^1 6a^1$)
1079	28^2	
1094	10^2	14^2 ($20a^2$)
1139	13^2	3^1 ($9a^1$)

[a] From Ref. [20] and [21] unless otherwise stated; italicized values have been estimated from the spectra presented in those studies.

[b] This work – see text.

[c] Assignments from Ref. [20], also carried over into Refs. [21] and [22]; note that the D_{2h} Mulliken labels are termed "Herzberg" labels in Ref. [21]. An empty entry means an assignment was not given in previous work.

[d] Possible coincident band with minor contribution in parentheses.

[e] These appear to be bands arising from complexes of *p*DClB with Ar, from the work of Ref. [21].

[f] From Ref. [22].

Figure 1

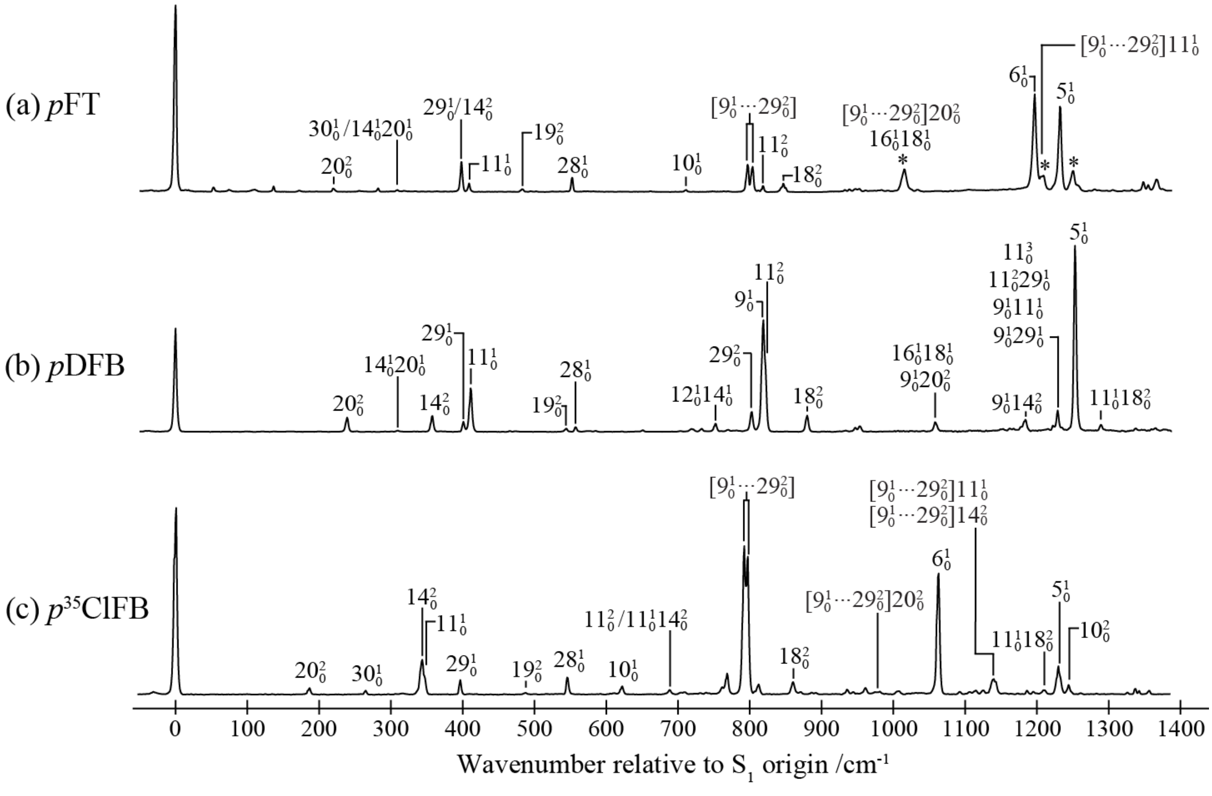

(a) *p*FT
$30^1_0/14^1_0 20^1_0$
20^2_0
$29^1_0/14^2_0$
11^1_0
19^2_0
28^1_0
10^1_0
$[9^1_0 \cdots 29^2_0]$
11^2_0
18^2_0
$[9^1_0 \cdots 29^2_0]20^2_0$
$16^1_0 18^1_0$
*
6^1_0
$[9^1_0 \cdots 29^2_0]11^1_0$
5^1_0
*
*
(b) *p*DFB
20^2_0
$14^1_0 20^1_0$
14^2_0
29^1_0
11^1_0
19^2_0
28^1_0
$12^1_0 14^1_0$
29^2_0
9^1_0
11^2_0
18^2_0
$16^1_0 18^1_0$
$9^1_0 20^2_0$
$9^1_0 14^2_0$
11^3_0
$11^2_0 29^1_0$
$9^1_0 11^1_0$
$9^1_0 29^1_0$
5^1_0
$11^1_0 18^2_0$
(c) p^{35}ClFB
20^2_0
30^1_0
14^2_0
11^1_0
29^1_0
19^2_0
28^1_0
10^1_0
$11^2_0/11^1_0 14^2_0$
$[9^1_0 \cdots 29^2_0]$
18^2_0
$[9^1_0 \cdots 29^2_0]20^2_0$
$[9^1_0 \cdots 29^2_0]11^1_0$
$[9^1_0 \cdots 29^2_0]14^2_0$
6^1_0
$11^1_0 18^2_0$
5^1_0
10^2_0
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
Wavenumber relative to S_1 origin /cm^{-1}

Figure 2

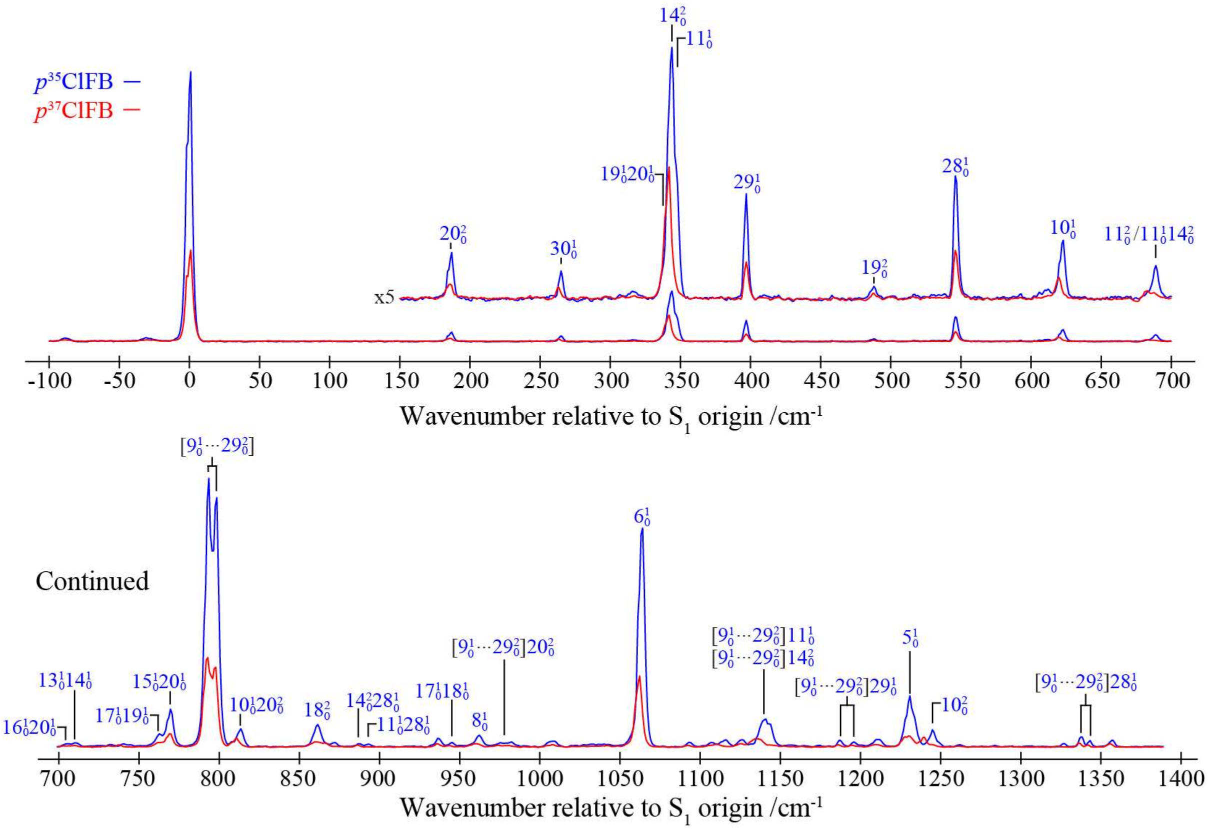
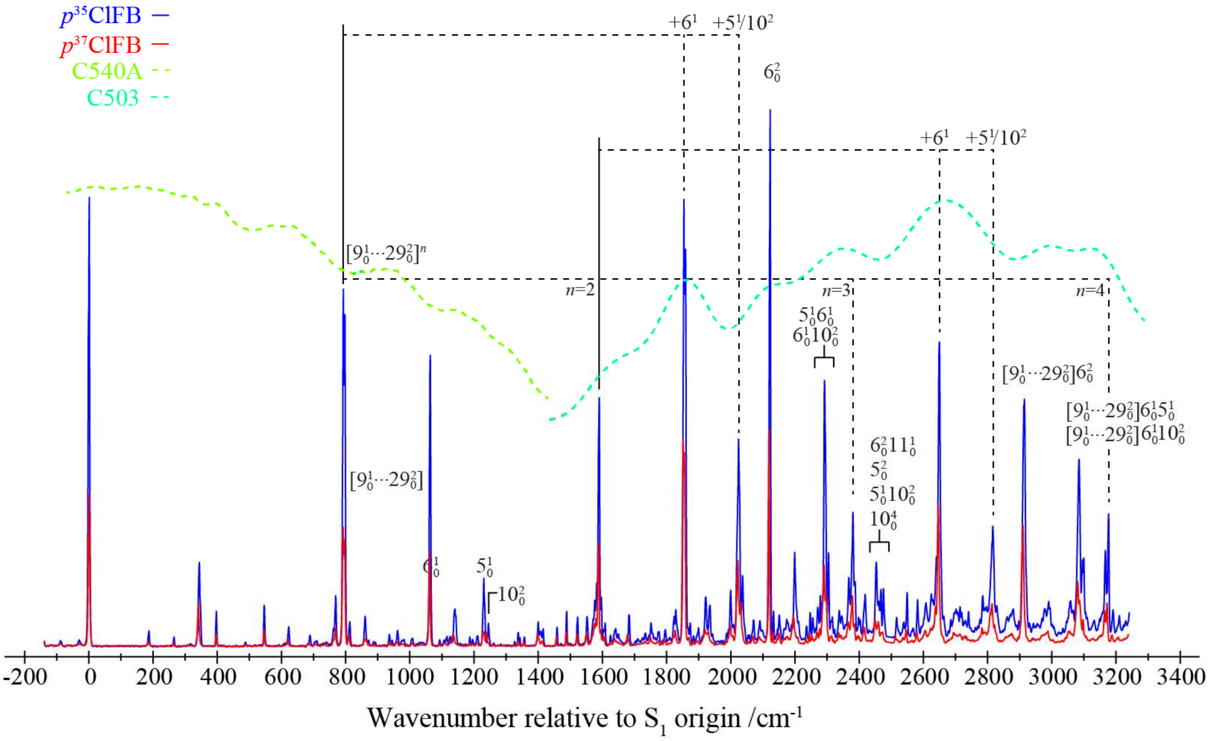

p^{35}ClFB —
p^{37}ClFB —
x5
14^{2}_{0}
11^{1}_{0}
$19^{1}_{0}20^{1}_{0}$
29^{1}_{0}
28^{1}_{0}
20^{2}_{0}
30^{1}_{0}
19^{2}_{0}
10^{1}_{0}
$11^{2}_{0}/11^{1}_{0}14^{2}_{0}$
-100
-50
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
Wavenumber relative to S_1 origin /cm^{-1}
$[9^{1}_{0}\cdots29^{2}_{0}]$
Continued
6^{1}_{0}
$[9^{1}_{0}\cdots29^{2}_{0}]11^{1}_{0}$
$[9^{1}_{0}\cdots29^{2}_{0}]14^{2}_{0}$
5^{1}_{0}
$[9^{1}_{0}\cdots29^{2}_{0}]20^{2}_{0}$
$13^{1}_{0}14^{1}_{0}$
$15^{1}_{0}20^{1}_{0}$
$17^{1}_{0}18^{1}_{0}$
$[9^{1}_{0}\cdots29^{2}_{0}]29^{1}_{0}$
$[9^{1}_{0}\cdots29^{2}_{0}]28^{1}_{0}$
$14^{2}_{0}28^{1}_{0}$
$10^{1}_{0}20^{2}_{0}$
18^{2}_{0}
$17^{1}_{0}19^{1}_{0}$
$11^{1}_{0}28^{1}_{0}$
8^{1}_{0}
10^{2}_{0}
$16^{1}_{0}20^{1}_{0}$
700
750
800
850
900
950
1000
1050
1100
1150
1200
1250
1300
1350
1400
Wavenumber relative to S_1 origin /cm^{-1}

Figure 3


p^{35}ClFB
p^{37}ClFB
C540A
C503
$+6^1$
$+5^1/10^2$
6^2_0
$+6^1$
$+5^1/10^2$
$[9^1_0\cdots29^2_0]^n$
n=2
n=3
n=4
$5^1_06^1_0$
$6^1_010^2_0$
$[9^1_0\cdots29^2_0]6^2_0$
$[9^1_0\cdots29^2_0]6^1_05^1_0$
$[9^1_0\cdots29^2_0]6^1_010^2_0$
$[9^1_0\cdots29^2_0]$
$6^2_011^1_0$
5^2_0
$5^1_010^2_0$
10^4_0
6^1_0
5^1_0
10^2_0
-200
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
3400
Wavenumber relative to S_1 origin /cm^{-1}

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