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# Electronic Absorption Spectra of $C_nCl$ Radicals ( $n = 5, 6$ ) and Their Cations in Neon Matrices

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Electronic absorption spectra of  $C_6Cl$ ,  $C_6Cl^+$ ,  $C_5Cl$ , and  $C_5Cl^+$  have been recorded in 6 K neon matrices. The bands observed are assigned to the  $B\ ^2\Pi \leftarrow X\ ^2\Pi$  electronic transition of  $C_6Cl$ ,  $^3\Sigma^- \leftarrow X\ ^3\Sigma^-$  of  $C_6Cl^+$ , and  $^1\Sigma^+ \leftarrow X\ ^1\Sigma^+$  of  $C_5Cl^+$  with band origins at 545.8, 527.4, and 226.1 nm, respectively. Two electronic band systems are apparent for  $C_5Cl$  and these are tentatively assigned to a  $^2\Pi \leftarrow X\ ^2\Pi$  transition with a band origin at 247.1 nm and to  $\Sigma^+ \leftarrow X\ ^2\Pi$  at 532.3 nm. For each of the four molecules, several transitions due to the excitation of vibrational modes in the excited electronic states are observed. The spectral assignments in each case are based upon the observation of clear, vibronic progressions with appropriate spacing for C–C and C–Cl stretching modes and by comparison with the absorption spectra of the isoelectronic sulfur-terminated carbon chains.

## Introduction

A number of neutral and ionic carbon chain molecules have been studied by experimentalists and theoreticians due to their proposed roles as intermediates in various terrestrial chemical reactions and their established presence in circumstellar and interstellar bodies.<sup>1</sup> Laboratory-based rotational spectra have proved integral to the identification of these molecules and their electronic spectra may finally lead to the assignment of the carriers of the diffuse interstellar bands. In recent years, carbon chains terminated by second row elements, such as Si, P, and S, have received increasing attention since several short chains of this type have been positively identified in space.<sup>2</sup>

Chlorine-terminated carbon chains are also candidates for astronomical detection, although to date, the only chlorine-containing molecules to be observed are (HCl)<sup>3</sup> and a small number of metal chlorides (AlCl, NaCl, and KCl)<sup>4</sup> in interstellar and circumstellar environments, respectively. The formation of C–Cl bonds under interstellar conditions is thought to be feasible by reaction of HCl with  $C^+$  or by reaction of  $H_2Cl^+$  with C to produce  $CCl^+$  in both cases.<sup>5,6</sup> It has been proposed, on the basis of an ab initio study,<sup>7</sup> that the product of the latter reaction is actually  $HCCl^+$ , which is a precursor of the CCl dimer. More recently, ab initio calculations have predicted the formation of the triatomic chain  $C_2Cl$  by dissociative recombination of  $HC_2Cl^+$  formed via the reaction of  $C_2H^+$  and HCl.<sup>8</sup> As a result of these studies, it is expected that these molecules, along with longer  $C_nCl$  chains and their corresponding ions, are promising candidates for interstellar observation.

To date, the CCl radical is the most extensively studied of these species in the laboratory and spectra have been reported in the microwave,<sup>9</sup> infrared,<sup>10–12</sup> and ultraviolet regions.<sup>13–15</sup> Emission spectra of the  $CCl^+$  cation have also been reported<sup>16</sup> and rotationally analyzed.<sup>17</sup> The triatomic radical  $C_2Cl$  was

recently investigated by using a combination of microwave spectroscopy and ab initio calculations.<sup>18</sup> The results of this study support the presence of strong vibronic coupling between the ground ( $^2\Sigma^+$ ) and first excited ( $^2\Pi$ ) electronic states resulting in a bent molecular geometry. Earlier ab initio calculations similarly predicted a small energy separation for the two lowest states but had their ordering reversed.<sup>19,20</sup>

Recently, ground-state electronic structures and vibrational frequencies have been estimated for the  $C_nCl$ ,  $C_nCl^+$ , and  $C_nCl^-$  ( $n = 1–7$ ) series, using DFT (B3LYP).<sup>21,22</sup> For all but  $C_3Cl$ , the lowest energy structures are predicted to be linear or quasilinear chains terminated on one end by the chlorine atom. In the case of  $C_3Cl$ , geometry optimization calculations suggest that the ground-state structure is a cyclic triatomic carbon ring with an exocyclic chlorine ( $^2B_2$ ) although quasilinear ( $^2A'$ ) and linear ( $^2\Pi$ ) structures lie approximately 12 kJ/mol higher in energy.<sup>23</sup> For the larger species, the calculated C–C bond distances suggest that the most important valence structures are cumulenic although the observation of bond length alternation suggests that polyyenic ones also contribute. For each of the  $C_nCl$  neutral species, the ground state corresponds to a doublet state electronic configuration and the lowest lying quartet state is more than 150 kJ/mol higher in energy. The  $n$ -even  $C_nCl^+$  cations have triplet ground states while the  $n$ -odd clusters are singlets. The  $C_nCl^-$  anions are characterized by singlet ground states for all values of  $n$  (with the exception of CCl which is  $^3\Sigma$ ) although the  $n$ -odd species also possess low-lying triplet states. Furthermore, a pattern of alternating stability of the molecules was reported depending on the parity of  $n$ . For the  $C_nCl^+$  cations, the  $n$ -odd chains are predicted to be more stable than the  $n$ -even ones, while for the neutral and anionic counterparts, the trend is reversed. These results can be rationalized in terms of the corresponding electronic configurations (orbital occupancies). Spectroscopic investigations of chlorine-terminated carbon molecules thus provide a useful test of these theoretical predictions, and furthermore, a comparison with known spectra of carbon chains with other second row

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elements at the end may establish interesting periodic trends in their molecular properties.

In this paper, we report the first spectroscopic study of  $C_5Cl$  and  $C_6Cl$  and their cations,  $C_5Cl^+$  and  $C_6Cl^+$ , using mass-selective neon matrix isolation spectroscopy. The band assignments of each molecule are based upon the observation of clear vibronic progressions of C–C and C–Cl excited state stretching modes which are slightly smaller than those predicted for the ground state from ab initio calculations as expected.<sup>21</sup> The spectral assignments are further verified through comparison with the bands reported earlier for the isoelectronic  $C_nS$  and  $C_nS^-$  species ( $n = 5, 6$ ).<sup>24</sup>

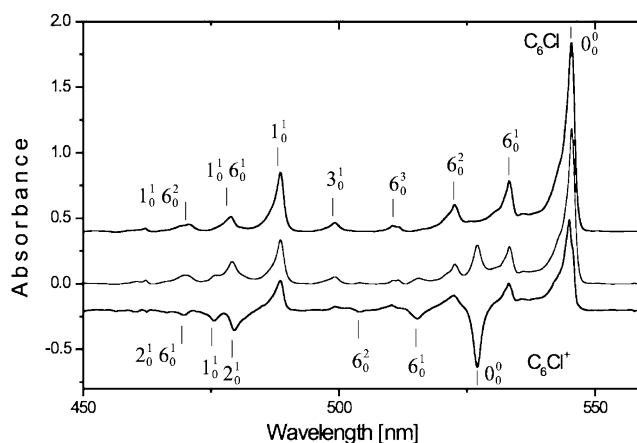
## Experimental Section

The electronic absorption spectra of the  $C_nCl$  and  $C_nCl^+$  ( $n = 5, 6$ ) species were recorded following mass-selective deposition in neon matrices.<sup>25</sup> A gas mixture containing the appropriate precursor was prepared by passing helium over a heated sample of solid  $C_6Cl_6$  or liquid  $C_5Cl_6$ . From these respective mixtures, a series of  $C_6Cl_m^+$  and  $C_5Cl_m^+$  cations were produced, along with the corresponding neutral and anionic species, using a hot cathode discharge source, and the cation beam was focused and directed into a quadrupole mass filter by using a series of electrostatic lenses.<sup>26</sup> The singly chlorinated carbon cations were mass-selected and ion currents of 25 and 18 nA were obtained for  $C_6Cl^+$  and  $C_5Cl^+$ , respectively. The cations were deposited simultaneously with neon on a rhodium-coated sapphire substrate over a period of 3 h to produce a 6 K matrix. The sample was irradiated with monochromatic light from halogen and xenon arc lamps with beams running parallel to the substrate surface. The absorption spectra of the trapped species were recorded between 220 and 1100 nm, using photomultiplier and silicon diode detectors. Following exposure to UV light ( $\sim 5.4$  eV) from a medium-pressure mercury lamp, the same spectral region was rescanned to identify the absorptions of the corresponding neutral species,  $C_6Cl$  and  $C_5Cl$ . During co-deposition of neon and the mass-selected cations, positive charge is quickly built up in the matrix and subsequent cations are repelled. These cations collide with nearby metals surfaces and liberate electrons which are electrostatically attracted toward the positively charged neon matrix and recombine with the cations to form neutral molecules. These electrons also form weakly bound anions with impurity molecules in the matrix. After UV irradiation, the electrons are photodetached from these weakly bound anions and neutralize the remaining cations.

## Results and Discussion

**(a)  $C_6Cl$  and  $C_6Cl^+$ .** After mass selection,  $C_6Cl^+$  was co-deposited with an excess of neon to form a 6 K matrix and the electronic absorption spectrum of this sample was subsequently recorded. As shown in Figure 1, two clear vibronic band systems are observed in the visible spectral range between 470 and 570 nm. The higher energy band system disappeared after irradiation with UV light and is consequently attributed to the  $C_6Cl^+$  cation. The remaining band system is assigned to the  $C_6Cl$  neutral.

For linear  $C_6Cl$ , the ground-state electronic configuration is doublet  $X^2\Pi...5\pi^3$  and electronic excitation to the first excited state involves promotion of an electron from a lower energy orbital to the  $5\pi$  orbital. In the case of the linear  $C_6Cl^+$  cation, the ground state is described by a triplet  $X^3\Sigma^-...5\pi^2$  electronic configuration and the first excited state is likewise expected to involve excitation to the  $5\pi$  orbital. The electronic absorption spectra corresponding to the lowest energy transitions of both  $C_6Cl$  and  $C_6Cl^+$  are therefore expected to arise from electronic



**Figure 1.** Electronic absorption spectra of the  $B^2\Pi \leftarrow X^2\Pi$  electronic transition of  $C_6Cl$  and the  $^3\Sigma^- \leftarrow X^3\Sigma^-$  electronic transition of  $C_6Cl^+$  recorded in a 6 K neon matrix. The upper trace shows the bands which remain after UV irradiation of the sample which are assigned to the  $C_6Cl$  neutral radical. The middle trace is the spectrum of the same sample before UV irradiation and contains absorptions due to both the neutral and cationic species. The lower trace is the difference between the first two traces multiplied by a factor of 2 for better visualization. The peaks which point downward are those that vanish after UV exposure and are thus attributed to  $C_6Cl^+$ .

**TABLE 1: Positions of the Band Maxima ( $\pm 0.2$  cm<sup>-1</sup>) Observed for the  $B^2\Pi \leftarrow X^2\Pi$  Electronic Transition of  $C_6Cl$  in a 6 K Neon Matrix**

$\lambda$ /nm	$\tilde{\nu}$ /cm <sup>-1</sup>	$\Delta\tilde{\nu}$ /cm <sup>-1</sup>	assignment
545.8	18322		$0_0^0$
533.7	18737	415	$6_0^1$
523.0	19120	798	$6_0^2$
510.9	19573	1251	$6_0^3$
499.7	20012	1690	$3_0^1$
489.0	20450	2128	$1_0^1$
479.3	20864	2542	$1_0^1 6_0^1$
471.3	21218	2896	$1_0^1 6_0^2$

excitation within the bonding manifold and the band origins of these two species are anticipated to be similar in energy. This is supported by the observation of two band systems in Figure 1 within 18 nm of each other in the visible region, one of which disappears after UV irradiation.

The band centered at 545.8 nm in Figure 1 corresponds to the band origin of the  $B^2\Pi \leftarrow X^2\Pi$  electronic transition of  $C_6Cl$ . The position of the observed band maximum of  $C_6Cl$  is comparable to that attributed to the analogous transition of the isoelectronic  $C_6S^-$  anion at 608 nm in a neon matrix.<sup>24</sup> This result is reasonable because these electronic transitions predominantly involve electronic excitation within the  $\pi$ -bonding systems of the carbon chains. The terminal chlorine and sulfur atoms make small contributions to the  $\pi$ -systems via donation of some electron density to the carbon chains, and thus it is not surprising that the band origins differ by 62 nm. It is also interesting to note that the position of the band origin of  $C_6Cl$  is only 16 nm higher than that observed for the  $B^2\Pi \leftarrow X^2\Pi$  transition of  $C_6H$  in a neon matrix, which was reported at 530 nm.<sup>27</sup>

Analysis of the vibrational structure of the  $B^2\Pi \leftarrow X^2\Pi$  electronic transition of  $C_6Cl$  reveals the excitation of three vibrational modes as indicated by the list of the observed band positions in Table 1. These modes essentially correspond to stretching motions of the C–C bonds ( $\nu_1, \nu_3$ ) and to the C–Cl stretch ( $\nu_6$ ) in the excited electronic state of  $C_6Cl$  as well as to several overtone and combination bands. The experimentally

**TABLE 2: Positions of the Band Maxima ( $\pm 0.2\text{ cm}^{-1}$ ) Observed for the  ${}^3\Sigma^- \leftarrow X\ {}^3\Sigma^-$  Electronic Transition of  $C_6Cl^+$  in a 6 K Neon Matrix**

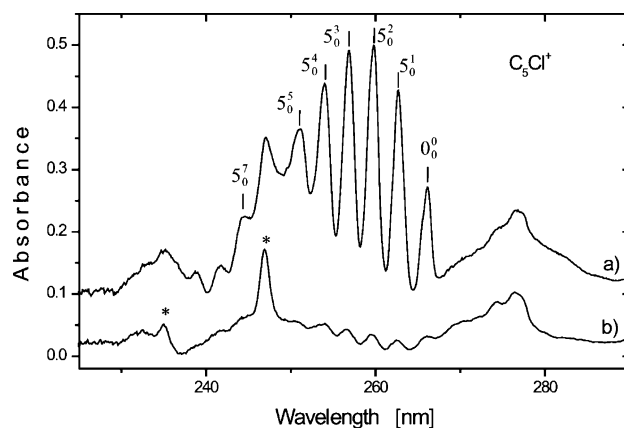
$\lambda/\text{nm}$	$\tilde{\nu}/\text{cm}^{-1}$	$\Delta\tilde{\nu}/\text{cm}^{-1}$	assignment
527.4	18961		$0_0^0$
515.7	19391	430	$6_0^1$
504.3	19829	868	$6_0^2$
480.0	20833	1872	$2_0^1$
476.1	21004	2043	$1_0^1$
470.1	21272	2311	$2_0^1\ 6_0^1$

determined vibrational frequencies are lower in energy than the calculated values for the ground electronic state<sup>21</sup> ( $\nu_1 = 2194$ ,  $\nu_3 = 1917$ , and  $\nu_6 = 441\text{ cm}^{-1}$ ) as expected since the electronic transition in question corresponds to promotion of an electron to an orbital with a greater number of nodes.

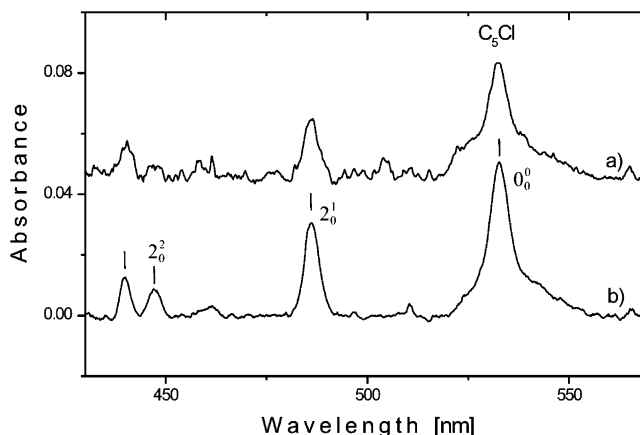
The peak centered at 527.4 nm in Figure 1 is assigned to the band origin of the  ${}^3\Sigma^- \leftarrow X\ {}^3\Sigma^-$  electronic transition of the linear  $C_6Cl^+$  cation. For the isoelectronic  $C_6S$  molecule, the observed band origin in a neon matrix for the analogous transition lies 47 nm to the red at 574.2 nm.<sup>24</sup> The blue shift of the chlorinated species relative to the isoelectronic sulfur-containing species is slightly smaller for the  $C_6Cl^+$  cation (47 nm) than for the  $C_6Cl$  neutral (62 nm), suggesting that the former has more energetically similar electronic states to  $C_6S$  than the latter has to  $C_6S^-$ . Ab initio calculations involving population analysis of the  $C_nCl^+$  cations suggest that the positive charge is mainly carried by the carbon chain in these species but that a certain degree of  $\pi$  donation from chlorine to the chain produces a small positive charge on the terminal chlorine atom.<sup>21</sup> In effect, the positive charge is, to some extent, spread over the entire molecule resulting in electronic states with energies comparable to those of the neutral  $C_6S$  molecule.

The vibrational structure of the  $C_6Cl^+$  cation is similar to that observed for the neutral molecule and the positions of the band maxima of the assigned modes are listed in Table 2. As with  $C_6Cl$ , the experimentally observed frequencies are lower than the calculated ground-state values<sup>21</sup> ( $\nu_1 = 2153$ ,  $\nu_2 = 2139$  and  $\nu_6 = 488\text{ cm}^{-1}$ ) as expected for such a  $\pi-\pi$  transition. A comparison of the observed spectrum with the vibrational modes reported for the isoelectronic  $C_6S$  species ( $\nu_1 = 2081$ ,  $\nu_2 = 1863$ , and  $\nu_6 = 452\text{ cm}^{-1}$ )<sup>24</sup> shows agreement within tens of wavenumbers for each of the observed modes. Furthermore, the vibrational frequencies of  $C_6Cl^+$  are similar to those of  $C_6Cl$ , which suggests that there is little difference in their excited-state geometries upon electronic excitation to these particular states. Ab initio predictions suggest that for the ground electronic states of these molecules, the  $\nu_6$  mode (essentially the C–Cl stretch) is slightly larger for  $C_6Cl^+$  than for  $C_6Cl$  and the optimized geometry of the ground state of the cation predicts a shorter C–Cl bond distance (1.583 Å) compared to that of the neutral (1.626 Å).<sup>21</sup> The vibrational frequencies extracted from the present experiment seem to support a similar phenomenon in the excited electronic state and the observed larger  $\nu_6$  vibrational frequency for  $C_6Cl^+$  can be attributed to a greater degree of electron donation from chlorine to the carbon  $\pi$  backbone in the cationic species.

**(b)  $C_5Cl$  and  $C_5Cl^+$ .** An analogous experiment was performed by co-depositing mass-selected  $C_5Cl^+$  with neon to form a 6 K matrix. The electronic absorption spectra of this sample revealed one clear band system in the UV range between 240 and 270 nm and a second system in the visible region between 430 and 550 nm as shown in Figures 2 and 3, respectively. The band system originating at 532.3 nm is assigned to the  $C_5Cl$  neutral since the spectral lines became more intense after



**Figure 2.** Electronic absorption spectra of the  ${}^1\Sigma^+ \leftarrow X\ {}^1\Sigma^+$  electronic transition of  $C_5Cl^+$  recorded in a 6 K neon matrix. The traces show the observed absorptions both (a) before and (b) after UV irradiation of the sample. The bands marked by asterisks are tentatively assigned to a higher excited electronic transition of  $C_5Cl$  ( ${}^2\Pi \leftarrow X\ {}^2\Pi$ ) as described in the text.



**Figure 3.** Electronic absorption spectra of the  $\Sigma^+ \leftarrow X\ {}^2\Pi$  electronic transition of  $C_5Cl$  recorded after mass selected deposition of  $C_5Cl^+$  in a 6 K neon matrix. The traces show the observed absorptions in the visible region both (a) before and (b) after UV irradiation of the sample. The intensity increases after irradiation due to an increase in the concentration of  $C_5Cl$  in the matrix upon neutralization of some  $C_5Cl^+$  cations.

UV irradiation. The band system in the UV range has its origin at 266.1 nm and disappeared after irradiation with UV light. These transitions are thus assigned to the  $C_5Cl^+$  cation.

For the linear  $C_5Cl^+$  cation, the ground state is described by a singlet  $X\ {}^1\Sigma^+...4\pi^4$  electronic configuration and the lowest excited electronic state involves promotion of an electron to the  $5\pi^*$  antibonding orbital. The vibronic band system originating at 266.1 nm in Figure 2 is assigned to the  ${}^1\Sigma^+ \leftarrow X\ {}^1\Sigma^+$  electronic transition of  $C_5Cl^+$  and it is not surprising that this is found at UV wavelengths because the ground state of the cation is energetically stabilized as a consequence of its closed shell electronic configuration. The band origin reported for the  ${}^1\Sigma^+ \leftarrow X\ {}^1\Sigma^+$  transition of the isoelectronic  $C_5S$  molecule in a neon matrix lies only 18 nm to the red at 284.3 nm.<sup>24</sup>

The rich vibrational structure observed for  $C_5Cl^+$  consists of several bands which are approximately evenly spaced. These are assigned to the  $\nu_5$  vibrational mode (essentially the C–Cl stretch) and to overtones of this mode and the positions of the band maxima are listed in Table 3. The experimentally determined vibrational frequency,  $486\text{ cm}^{-1}$ , is in good agreement with the calculated value for the  ${}^1\Sigma^+$  ground electronic state,  $\nu_5 = 514\text{ cm}^{-1}$ , and is greater than the C–Cl stretching



**TABLE 3: Positions of the Band Maxima ( $\pm 0.2 \text{ cm}^{-1}$ ) Observed for the  ${}^1\Sigma^+ \leftarrow X {}^1\Sigma^+$  Electronic Transition of  $\text{C}_5\text{Cl}^+$  in a 6 K Neon Matrix**

$\lambda/\text{nm}$	$\tilde{\nu}/\text{cm}^{-1}$	$\Delta\tilde{\nu}/\text{cm}^{-1}$	assignment
266.1	37580		$0_0^0$
262.7	38066	486	$5_0^1$
259.8	38491	911	$5_0^2$
257.0	38911	1331	$5_0^3$
254.0	39370	1790	$5_0^4$
251.2	39809	2229	$5_0^5$
244.5	40900	3320	

**TABLE 4: Positions of the Band Maxima ( $\pm 0.2 \text{ cm}^{-1}$ ) Observed for Two Electronic Transitions of  $\text{C}_5\text{Cl}$  in a 6 K Neon Matrix**

$\lambda/\text{nm}$	$\tilde{\nu}/\text{cm}^{-1}$	$\Delta\tilde{\nu}/\text{cm}^{-1}$	assignment
			$\Sigma^+ \leftarrow X {}^2\Pi$
532.3	18786		$0_0^0$
485.9	20580	1794	$2_0^1$
447.0	22331	3545	$2_0^2$
439.9	22732	3946	$2_0^3$
			$B {}^2\Pi \leftarrow X {}^2\Pi$
247.1	40469		$0_0^0$
235.3	42499	2030	$1_0^1$

frequencies of  $\text{C}_6\text{Cl}$  and  $\text{C}_6\text{Cl}^+$  as predicted for a shorter chain.<sup>21</sup> On the basis of the assignment given in Table 3, the higher order overtones corresponding to the excitation of two or three quanta of the  $\nu_5$  mode in the excited state of  $\text{C}_5\text{Cl}^+$  are the most intense. This is anomalous in comparison to the vibronic progressions observed for  $\text{C}_6\text{Cl}$  and  $\text{C}_6\text{Cl}^+$  in which the predominant bands correspond to single excitation of the  $\nu_6$  mode. This difference may be attributed to a comparatively larger geometry change upon promotion of an electron to the  $5\pi^*$  antibonding orbital in  $\text{C}_5\text{Cl}^+$ .

The ground-state electronic configuration of linear  $\text{C}_5\text{Cl}$  corresponds to a doublet  $X {}^2\Pi \dots 5\pi^1$ , and like  $\text{C}_5\text{Cl}^+$ , one possible electronic excitation involves electron promotion to a  $\pi^*$  antibonding orbital as was suggested for the isoelectronic  $\text{C}_5\text{S}^-$  anion. This transition was predicted to lie in the UV region for  $\text{C}_5\text{S}^-$  but could not be observed due to lack of an accessible bound state.<sup>24</sup> For  $\text{C}_5\text{Cl}$ , this transition is also expected to fall in the UV range and its origin should be similar to that of the  ${}^1\Sigma^+ \leftarrow X {}^1\Sigma^+$  electronic transition of  $\text{C}_5\text{Cl}^+$ . In Figure 2, the weak bands marked by asterisks were observed to remain after UV irradiation and are therefore attributed to some neutral species in the matrix sample. If the sharp band observed at 247.1 nm is the band origin of this  $\pi-\pi^*$  transition, then the next observed band is blue shifted by  $2030 \text{ cm}^{-1}$ . This is a reasonable value for excitation of the  $\nu_1$  mode in the excited electronic state of  $\text{C}_5\text{Cl}$  as it is smaller than the value predicted for the ground electronic state,  $2108 \text{ cm}^{-1}$ .<sup>21</sup> Furthermore, the magnitude of the  $\nu_1$  mode is comparable to that observed for  $\text{C}_6\text{Cl}$  ( $2128 \text{ cm}^{-1}$ ) in this work, which was also slightly smaller than the predicted ground-state vibrational frequency ( $2194 \text{ cm}^{-1}$ ). The assignment of this electronic transition, as shown in Table 4, is offered only tentatively and would be more convincing if these bands increased in intensity after exposure to UV light.

Figure 3 shows the electronic absorption spectra recorded for this same matrix sample in the visible range. Four bands are observed and each increases in intensity after UV irradiation, which suggests that these bands arise from electronic excitation of the  $\text{C}_5\text{Cl}$  neutral. Since the promotion of an electron to a  $\pi^*$  orbital is expected to lie in the UV region, the band centered at 532.3 nm must therefore correspond to the band origin of a

lower energy transition involving electron promotion from a fully occupied molecular orbital to the  $5\pi$  partially occupied valence orbital. Strong transitions of this type have been reported for other carbon chain molecules with  $X {}^2\Pi$  ground electronic states. In the case of the  $\text{C}_n\text{H}$  ( $n = \text{even}$ ) species,  $\pi-\pi$  transitions have been observed in the visible region<sup>28</sup> whereas for the  $\text{C}_n\text{H}$  ( $n = \text{odd}$ ) chains,  $\sigma-\pi$  transitions have been recorded in this range.<sup>27</sup> As there are no calculations available for the excited-state configurations of  $\text{C}_5\text{Cl}$ , it is not possible to definitively assign the upper state involved in the transition with origin at 532.3 nm. The low intensity of the band system suggests that the transition is likely of the type  $\Sigma^+ \leftarrow X {}^2\Pi$  because its absorbance is an order of magnitude less than for other  $\pi-\pi$  transitions (see Figures 1 and 3). In the case of  $\text{C}_4\text{O}^-$ , for example, the  $A {}^2\Sigma^+ \leftarrow X {}^2\Pi$  transition was also observed to have considerably lower intensity than the  $B {}^2\Pi \leftarrow X {}^2\Pi$  band in a neon matrix.<sup>29</sup>

The vibrational assignment of the bands observed for  $\text{C}_5\text{Cl}$  in Figure 3 is given in Table 4. The transition closest to the origin band is blue shifted by  $1794 \text{ cm}^{-1}$ , which is consistent with the excitation of the  $\nu_2$  vibrational mode in the excited electronic state based on the ab initio calculations of the ground electronic state which predict  $\nu_2 = 1959 \text{ cm}^{-1}$ .<sup>21</sup> A comparable difference has been observed for the  $\nu_2$  modes of related molecules when the experimental excited-state vibrational frequencies and the ground-state theoretical values are considered. For example, in the case of  $\text{C}_6\text{Cl}^+$ ,  $\text{C}_6\text{S}$ , and  $\text{C}_5\text{S}$ , the experimentally determined excited state  $\nu_2$  stretching frequencies are 1872, 1863, and  $1734 \text{ cm}^{-1}$ , while the predicted ground-state values of these modes are 2139, 2025, and  $2013 \text{ cm}^{-1}$ , respectively.<sup>30</sup> The transition appearing at 439.9 nm in Figure 3 is blue shifted from the nearest band by only  $401 \text{ cm}^{-1}$ . This value is considerably smaller than the  $\nu_5$  vibrational frequency predicted for the ground electronic state,  $501 \text{ cm}^{-1}$ ,<sup>21</sup> and that determined for the  ${}^1\Sigma^+$  excited state of  $\text{C}_5\text{Cl}^+$ ,  $486 \text{ cm}^{-1}$ , in this work. The observed blue shift of this band in the spectrum of  $\text{C}_5\text{Cl}$  is, however, comparable to the experimentally determined  $\nu_6$  frequencies for the excited states of  $\text{C}_6\text{Cl}$  and  $\text{C}_6\text{Cl}^+$ , 415 and  $430 \text{ cm}^{-1}$ , respectively. Consequently, the band centered at 439.9 nm in Figure 3 may be tentatively assigned to the excitation of a vibronic transition involving the coupling of the  $2\nu_2$  and  $\nu_5$  vibrational modes in the excited electronic state of  $\text{C}_5\text{Cl}$  as listed in Table 4 although the band in question may alternatively be due to excitation of a higher energy electronic state.

## Conclusion

In this work, electronic absorption spectra of the chlorine-terminated carbon chains  $\text{C}_6\text{Cl}$ ,  $\text{C}_6\text{Cl}^+$ ,  $\text{C}_5\text{Cl}$ , and  $\text{C}_5\text{Cl}^+$  have been recorded in 6 K neon matrices. The transitions observed are  $B {}^2\Pi \leftarrow X {}^2\Pi$  for  $\text{C}_6\text{Cl}$ ,  ${}^3\Sigma^- \leftarrow X {}^3\Sigma^-$  for  $\text{C}_6\text{Cl}^+$ ,  ${}^2\Pi \leftarrow X {}^2\Pi$  and  $\Sigma^+ \leftarrow X {}^2\Pi$  for  $\text{C}_5\text{Cl}$ , and  ${}^1\Sigma^+ \leftarrow X {}^1\Sigma^+$  for  $\text{C}_5\text{Cl}^+$ . These studies provide the basis for gas-phase spectroscopic measurements which are necessary for determining whether these or related species play a role in the chemistry of the interstellar medium via electronic spectroscopy.

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## References and Notes

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