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

Jennifer van Wijngaarden,[†] Anton Batalov,[†] Ivan Shnitko,[†] Jan Fulara,[†,‡] and John P. Maier*,[†]

Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland, and Instytut Fizyki Polskiej Akademii Nauk, Al. Lotników 32-46, 02-668 Warsaw, Poland

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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.[1] 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.[2]

Chlorine-terminated carbon chains are also candidates for astronomical detection, although to date, the only chlorine-containing molecules to be observed are (HCl)[3] and a small number of metal chlorides (AlCl, NaCl, and KCl)[4] 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.[5,6] It has been proposed, on the basis of an ab initio study,[7] 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.[8] 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,[9] infrared,[10−12] and ultraviolet regions.[13−15] Emission spectra of the CCl^+ cation have also been reported[16] and rotationally analyzed.[17] The triatomic radical C_2Cl was recently investigated by using a combination of microwave spectroscopy and ab initio calculations.[18] 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.[19,20]

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).[21,22] 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.[23] 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 polyynic 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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* Corresponding author. E-mail: j.p.maier@unibas.ch. Phone: +41 61 267 38 26. Fax: +41 61 267 38 55.

[†] University of Basel.

[‡] Instytut Fizyki Polskiej Akademii Nauk.

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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.[21] The spectral assignments are further verified through comparison with the bands reported earlier for the isoelectronic C_nS and C_nS^- species ($n = 5, 6$).[24]

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.[25] 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.[26] 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 (∼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 netralize 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.

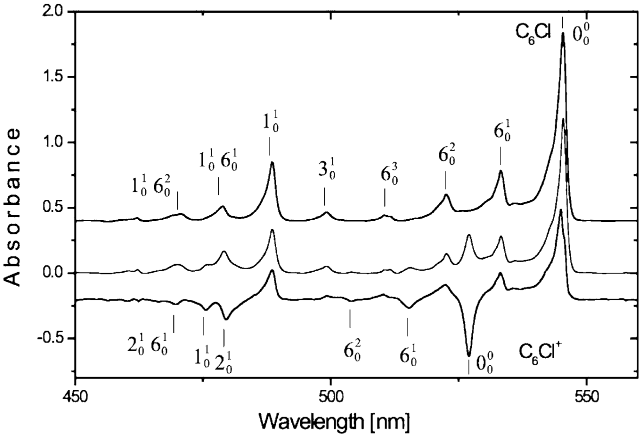

Figure 1. Electronic absorption spectra of the B $^2\Pi \leftarrow$ X $^2\Pi$ electronic transition of C_6Cl and the $^3\Sigma^- \leftarrow$ X $^3\Sigma^-$ electronic transition of C_6Cl^+ recorded in a 6 K neon matrix. The upper trace shows the bands which remain after UV irradiation of the sample which 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 (±0.2 cm^{-1}) Observed for the B $^2\Pi \leftarrow$ X $^2\Pi$ Electronic Transition of C_6Cl in a 6 K Neon Matrix

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

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 5π 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 5π 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 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.[24] This result is reasonable because these electronic transitions predominantly involve electronic excitation within the π-bonding systems of the carbon chains. The terminal chlorine and sulfur atoms make small contributions to the π-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.[27]

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 (ν_1, ν_3) and to the C−Cl stretch (ν_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 (±0.2 cm^{-1}) Observed for the $^3\Sigma^- \leftarrow X\ ^3\Sigma^-$ Electronic Transition of C_6Cl^+ in a 6 K Neon Matrix

λ/nm	$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}$/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[21] ($\nu_1 = 2194$, $\nu_3 = 1917$, and $\nu_6 = 441$ 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 isolectronic 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.[24] 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 π donation from chlorine to the chain produces a small positive charge on the terminal chlorine atom.[21] 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[21] ($\nu_1 = 2153$, $\nu_2 = 2139$ and $\nu_6 = 488$ 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 $\nu_6 = 452$ cm^{-1})[24] 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 ν_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).[21] The vibrational frequencies extracted from the present experiment seem to support a similar phenomenon in the excited electronic state and the observed larger ν_6 vibrational frequency for C_6Cl^+ can be attributed to a greater degree of electron donation from chlorine to the carbon π 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 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.

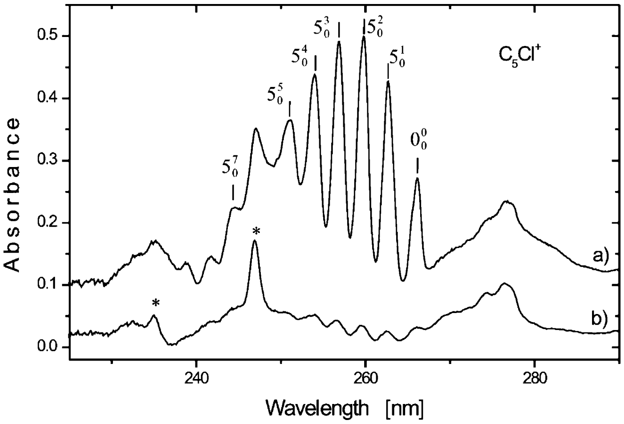

Figure 2. Electronic absorption spectra of the $^1\Sigma^+ \leftarrow X\ ^1\Sigma^+$ electronic transition of C_5Cl^+ recorded in a 6 K neon matrix. The traces show the observed absorptions both (a) before and (b) after UV irradiation of the sample. The bands marked by asterisks are tentatively assigned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

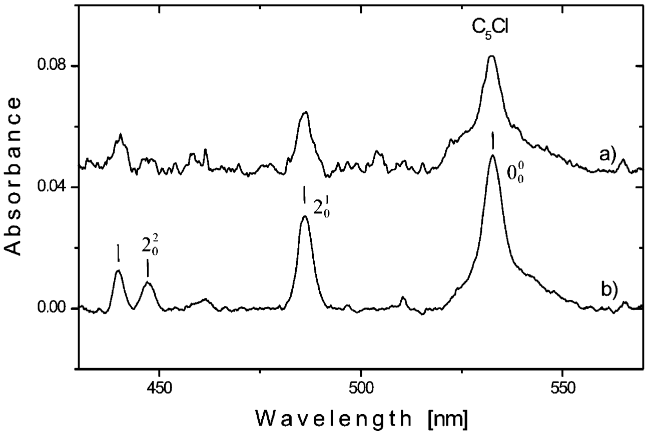

Figure 3. Electronic absorption spectra of the $\Sigma^+ \leftarrow X\ ^2\Pi$ electronic transition of C_5Cl recorded after mass selected deposition of C_5Cl^+ in a 6 K neon matrix. The traces show the observed absorptions in the visible region both (a) before and (b) after UV irradiation of the sample. 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.

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.[24]

The rich vibrational structure observed for C_5Cl^+ consists of several bands which are approximately evenly spaced. These are assigned to the ν_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 cm^{-1}, is in good agreement with the calculated value for the $^1\Sigma^+$ ground electronic state, $\nu_5 = 514$ cm^{-1}, and is greater than the C−Cl stretching

TABLE 3: Positions of the Band Maxima (±0.2 cm^{-1}) Observed for the $^1\Sigma^+ \leftarrow X\ ^1\Sigma^+$ Electronic Transition of C_5Cl^+ in a 6 K Neon Matrix

λ/nm	$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}$/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 (±0.2 cm^{-1}) Observed for Two Electronic Transitions of C_5Cl in a 6 K Neon Matrix

λ/nm	$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}$/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	$2_0^2\ 5_0^1$
			$B\ ^2\Pi \leftarrow X\ ^2\Pi$
247.1	40469		0_0^0
235.3	42499	2030	1_0^1

frequencies of C_6Cl and C_6Cl^+ as predicted for a shorter chain.[21] 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 ν_5 mode in the excited state of C_5Cl^+ are the most intense. This is anomalous in comparison to the vibronic progressions observed for C_6Cl and C_6Cl^+ in which the predominant bands correspond to single excitation of the ν_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 C_5Cl^+.

The ground-state electronic configuration of linear C_5Cl corresponds to a doublet $X\ ^2\Pi ...5\pi^1$, and like C_5Cl^+, one possible electronic excitation involves electron promotion to a π^* antibonding orbital as was suggested for the isoelectronic C_5S^- anion. This transition was predicted to lie in the UV region for C_5S^- but could not be observed due to lack of an accessible bound state.[24] For C_5Cl, 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 C_5Cl^+. 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 cm^{-1}. This is a reasonable value for excitation of the ν_1 mode in the excited electronic state of C_5Cl as it is smaller than the value predicted for the ground electronic state, 2108 cm^{-1}.[21] Furthermore, the magnitude of the ν_1 mode is comparable to that observed for C_6Cl (2128 cm^{-1}) in this work, which was also slightly smaller than the predicted ground-state vibrational frequency (2194 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 C_5Cl neutral. Since the promotion of an electron to a π^* 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 5π 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 C_nH (n = even) species, $\pi-\pi$ transitions have been observed in the visible region[28] whereas for the C_nH (n = odd) chains, $\sigma-\pi$ transitions have been recorded in this range.[27] As there are no calculations available for the excited-state configurations of C_5Cl, 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 C_4O^-, 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.[29]

The vibrational assignment of the bands observed for C_5Cl in Figure 3 is given in Table 4. The transition closest to the origin band is blue shifted by 1794 cm^{-1}, which is consistent with the excitation of the ν_2 vibrational mode in the excited electronic state based on the ab initio calculations of the ground electronic state which predict $\nu_2 = 1959$ cm^{-1}.[21] A comparable difference has been observed for the ν_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 C_6Cl^+, C_6S, and C_5S, the experimentally determined excited state ν_2 stretching frequencies are 1872, 1863, and 1734 cm^{-1}, while the predicted ground-state values of these modes are 2139, 2025, and 2013 cm^{-1}, respectively.[30] The transition appearing at 439.9 nm in Figure 3 is blue shifted from the nearest band by only 401 cm^{-1}. This value is considerably smaller than the ν_5 vibrational frequency predicted for the ground electronic state, 501 cm^{-1},[21] and that determined for the $^1\Sigma^+$ excited state of C_5Cl^+, 486 cm^{-1}, in this work. The observed blue shift of this band in the spectrum of C_5Cl is, however, comparable to the experimentally determined ν_6 frequencies for the excited states of C_6Cl and C_6Cl^+, 415 and 430 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 ν_5 vibrational modes in the excited electronic state of C_5Cl 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 C_6Cl, C_6Cl^+, C_5Cl ,and C_5Cl^+ have been recorded in 6 K neon matrices. The transitions observed are $B\ ^2\Pi \leftarrow X\ ^2\Pi$ for C_6Cl, $^3\Sigma^- \leftarrow X\ ^3\Sigma^-$ for C_6Cl^+, $^2\Pi \leftarrow X\ ^2\Pi$ and $\Sigma^+ \leftarrow X\ ^2\Pi$ for C_5Cl, and $^1\Sigma^+ \leftarrow X\ ^1\Sigma^+$ for C_5Cl^+. 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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