Electronic Transitions of CsC_2, CsC_2^-, and CsC_4 in Neon Matrixes[†]

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The anions of CsC_2 and CsC_4 produced by sputtering a graphite surface with Cs^+ were mass-selected and trapped in neon matrixes at 6 K. The electronic absorption spectra of CsC_2 and CsC_4, obtained by photodetachment of electrons from the anions, were measured subsequently and reveal strong absorptions in the visible range, which resemble the known band systems of C_2^- and C_4^-, respectively. The origin band of CsC_2 (500.4 nm) and CsC_4 (442.6 nm) is shifted by ∼1100 or by ∼700 cm^{-1} to the blue from the position of the 0_0^0 band of C_2^- or C_4^-. The observed system of CsC_2 is assigned to the $^2B_2-X\ ^2A_1$ electronic transition of the T-shaped form. The CsC_4 spectrum is consistent with a C_4^- chain slightly perturbed by the Cs atom. The oscillator strength of the observed electronic transition of CsC_2 and CsC_4 is an order of magnitude larger than for the respective carbon anions. CsC_2^- has a weak electronic transition, assigned to $^1B_2-X\ ^1A_1$ in the C_{2v} form, with origin band at 516.5 nm.

Introduction

Metal carbides are materials of technological importance. They also occur in extraterrestrial environments as they have been found in meteorites, are likely constituents of interstellar dust, and occur in hot regions such as the circumstellar envelopes of carbon-rich stars.[1] Though the properties of bulk metal carbides are well-known, their free-gas-phase species are still poorly recognized.

A growing interest in metal carbide molecules is evident in recent years. Alkali metal carbides,[2−5] alkali earth metal carbides,[6−12] AlC_n,[13−16] and transition-metal carbides[17−19] have been studied by theoretical methods. They were also the subject of numerous experimental works.[20−25] Because of the refractory nature of the bulk metal carbides (e.g., ZrC has one of the highest melting points among known materials), laser ablation of solid targets is the most popular way to bring the molecules into the gas phase. Anions of transition-metal carbides,[22−24] lanthanide carbides,[25] and $Al_2C_2^-$[26] produced by laser ablation of the appropriate targets have been studied by photoelectron spectroscopy.

Metal carbides are still exotic objects in spectroscopy. NaC, KC, and CaC have been characterized by microwave methods.[27−29] Only several transition-metal monocarbides have been characterized so far by the electronic spectroscopy in the gas phase[30−32] and MC_2 (M = Li, Na, K, Rb, Cs) in rare gas matrixes.[33] In this paper, the electronic transitions of CsC_4 and CsC_2^- isolated in a neon matrix are reported for the first time and the spectroscopic data on CsC_2 which refine the older results[33] are also given.

Experimental Section

The experimental setup has been described.[34] The CsC_2^- and CsC_4^- anions were generated in the ion source previously used for the production of bare carbon ions.[35] As was demonstrated long ago,[36] bombardment of the graphite surface with Cs^+ with several keV leads not only to the production of C_n^- but also to cesium-substituted carbon anions. The kinetic energy of Cs^+ in the present experiment was about 1 keV. To increase the ion throughput in the electrostatic guiding system, the graphite target was kept at a potential of −50 V. CsC_n^- ($n = 2, 4$) were separated from the other anions generated in the source by means of a quadrupole mass filter and co-deposited with neon during a period of 2 h onto the rhodium-coated sapphire substrate held at 6 K. The resolution of the mass filter was about ±2 amu and CsC_n^- ($n = 2, 4$) was not separated from the C_{13}^- or C_{15}^- anions which differ only by 1 amu. The current of CsC_n^- ($n = 2, 4$) was ∼5 and 1.5 nA, respectively. After growing the matrix to ∼150 μm thickness, the electronic absorption spectra of the species embedded in solid neon were recorded in the 220−1100 nm spectral range by passing monochromatic light through the ∼150 μm thin side of the matrix parallel to the substrate surface. The effective light path was ∼2 cm. To study the mass-selected neutral species, the CsC_n^- anions were irradiated with a medium-pressure mercury lamp resulting in electron detachment.

Results and Discussion

CsC_2. The electronic absorption spectrum recorded after deposition of mass-selected anions ($m/e = 157 \pm 2$ amu) generated from the graphite target in the cesium sputter ion source is shown in Figure 1 (trace a). A new absorption band system with onset at 500.4 nm dominates the spectrum. Weaker bands of smaller ions C_2^- and N_2^+ and the strongest origin band of previously identified C_{13} are also present.[37] New absorptions and the origin band of C_{13} grow in intensity (trace b of Figure 1) after irradiation of the matrix with a medium-pressure mercury lamp equipped with water and cutoff filters ($\lambda > 295$ nm). The bands of C_2^- and N_2^+ vanish under these conditions.

Mass selection of the CsC_2^- anion and the results of the photobleaching experiment point to neutral CsC_2 being respon-

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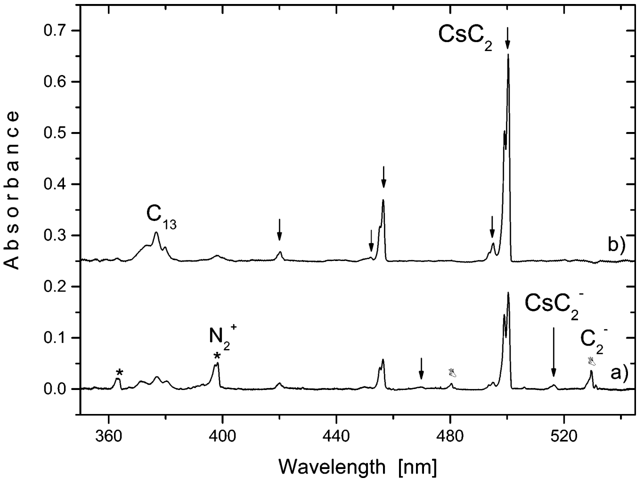

Figure 1. Electronic absorption spectra recorded in a 6 K neon matrix: (a) after mass-selected deposition of CsC_2^- produced from graphite in a cesium sputter ion source and (b) after subsequent UV irradiation of the matrix. Arrows indicate the vibronic bands of the $^2B_2-X\ ^2A_1$ electronic transition of CsC_2 and the $^1B_2-X\ ^1A_1$ transition of CsC_2^- in traces b and a, respectively. The strongest absorption band of C_{13} is seen in the spectrum because the CsC_2^- and C_{13}^- anions, which differ only by 1 amu, were not mass-resolved.

sible for the band system with the onset at 500.4 nm. The detection in the spectrum of C_2^- also substantiates this, because C_2^- appears in the matrix as a result of the fragmentation of deposited CsC_2^- anions. High kinetic energy anions arriving at the matrix also ionize the residual N_2 impurity and form N_2^+. Neutral C_{13} is present following electron detachment from the concomitantly deposited C_{13}^- because of restricted mass resolution.

The absorption band system of CsC_2 shown in Figure 1 is very similar to the spectrum of the Cs^+:C_2^- ion pair, which was measured after VUV photolysis of acetylene isolated in a neon matrix doped with cesium atoms.[33] The present spectrum of CsC_2 is much stronger than that reported[33] and reveals more detail. Besides the previously observed two bands, an additional three vibronic bands of CsC_2 are discernible. Two fundamental modes of frequency 214 and 1922 cm^{-1} are active in the excited electronic state of CsC_2, and they form overtones and combinations. The position of the maxima of the CsC_2 absorption bands and their assignments are collected in Table 1. The latter is based on the results of theoretical calculations of the vibrational frequencies of CsC_2.

Calculations were made using density functional theory (DFT) with the Becke three parameter Lee−Yang−Parr (B3LYP) exchange correlation functional[38,39] and the LANL2DZ basis set.[40] These were carried out with the Gaussian 03 program package. Two isomers of CsC_2, cyclic and linear, were considered. The cyclic structure of C_{2v} symmetry was predicted to be lower in energy by ~21 kJ/mol. The DFT calculations for NaC_2 have also predicted that the cyclic isomer is more stable (by ~50 kJ/mol) than the linear one.[4] The calculated harmonic vibrational frequencies of cyclic CsC_2 in the ground electronic state are $\omega_1 = 1746$ (symmetry a_1), $\omega_2 = 209$ (a_1), and $\omega_3 = 136\ cm^{-1}$ (b_2).

The earlier ESR study of the matrix-isolated Cs^+:C_2^- ion pair revealed that CsC_2 has two equivalent carbon atoms and that Cs is located at the apex of the isosceles triangle. Moreover, the Cs−C bonds have ionic character.[33] The present results confirm these conclusions. The electronic absorption spectrum of CsC_2 shown in Figure 1 is very similar to the $B^2\Sigma_u^+-X^2\Sigma_g^+$ band system of C_2^- isolated in a neon matrix.[41]

TABLE 1: Observed Bands ($\lambda \pm 0.2$ nm, $\tilde{\nu} \pm 5\ cm^{-1}$) in the Electronic Absorption Spectra of CsC_2, CsC_2^-, and CsC_4 in 6 K Neon Matrixes With Suggested Assignment[a]

species	λ [nm]	$\tilde{\nu}$ [cm^{-1}]	δ [cm^{-1}]	assignment	
CsC_2	500.4	19 984	0	0_0^0	$^2B_2-X\ ^2A_1$
	495.1	20 198	214	ν_2	
	456.5	21 906	1922	ν_1	
	452.1	22 119	2135	$\nu_1 + \nu_2$	
	420.2	23 798	3814	$2\nu_1$	
CsC_2^-	516.5	19 361	0	0_0^0	$^1B_2-X\ ^1A_1$
	469.7	21 290	1929	ν_1	
CsC_4	442.6	22 594	0	0_0^0	$^2\Pi-X\ ^2\Pi^b$
	434.2	23 031	437	$2\nu_5^b$	
	428.0	23 364	770	ν_2	
	419.9	23 815	1221	$\nu_2 + 2\nu_5$	
	414.3	24 137	1543	$2\nu_2$	
	410.6	24 355	1761	ν_1	
	406.7	24 588	1994	$2\nu_2 + 2\nu_5$	
	401.6	24 900	2306	$3\nu_2$	
	398.1	25 119	2525	$\nu_1 + \nu_2$	
	389.7	25 661	3067	$4\nu_2$	
	386.2	25 893	3299	$\nu_1 + 2\nu_2$	
	378.0	26 455	0	0_0^0	(2) $^2\Pi-X\ ^2\Pi$
	367.6	27 203	748	$2\nu_5$	
	358.9	27 863	1408	ν_2	
	350.5	28 531	2076	ν_1	
	341.5	29 283	2828	$\nu_1 + 2\nu_5 (2\nu_2)$	
	335.1	29 842	3387	$\nu_1 + \nu_2$	
	331.9	30 130	0	0_0^0	(3) $^2\Pi-X\ ^2\Pi$

[a] The wavelengths correspond to the most prominent site in the spectra. [b] Using the symmetry of the electronic states and the numbering of the normal modes of C_4^- moiety.

The origin band of CsC_2 is shifted ~1100 cm^{-1} to the blue of the C_2^- value. The main progression in the spectrum of CsC_2 is built on the CC stretching mode ν_1, 1922 cm^{-1}, which is close to the frequency (1944 cm^{-1}) determined from the B $^2\Sigma_u^+-X\ ^2\Sigma_g^+$ spectrum of C_2^-. Therefore, one can conclude that the C_2^- moiety is a chromophore which accounts for the appearance of the electronic spectrum of CsC_2. The Cs atom (or more precisely Cs^+) has its own signature in the spectrum of CsC_2, namely, the weak band 214 cm^{-1} above the origin, and its combination band with ν_1, due to the totally symmetric motion of Cs^+ and C_2^- subunit in the direction perpendicular to the C_2 axis. The calculated frequency $\omega_2 = 209\ cm^{-1}$ (a_1) in the $^2A_1$ ground electronic state of cyclic CsC_2 is close to this value. The spectrum depicted in Figure 1 is therefore assigned to the $^2B_2-X\ ^2A_1$ electronic transition of cyclic, or more strictly T-shaped CsC_2, as the molecule is composed from two distinct subunits (C_2^- and Cs^+) separated by the distance of 3.125 Å, which is much larger than the CC bond (1.294 Å).

The most striking feature of the $^2B_2-X\ ^2A_1$ electronic transition of T-shaped CsC_2 is the intensity. If a comparison is made of the ion current (5 nA) of CsC_2^- used during deposition with the high current (~1000 nA) of C_2^- in standard matrix experiments which lead to comparable absorptions, and taking into account that C_{13}^- contributes also to the current, one can conservatively estimate that the oscillator strength of the $^2B_2-X\ ^2A_1$ electronic transition of CsC_2 exceeds by an order of magnitude the value for B $^2\Sigma_u^+-X\ ^2\Sigma_g^+$ of C_2^- (0.04 for the origin band).[42]

CsC_2^-. As one can see in Figure 1, the UV irradiation of the matrix containing anions of m/e ~ 157 amu leads to a substantial growth of the bands of neutral CsC_2 and C_{13}. Therefore, the anions of CsC_2 and C_{13} must be present in the matrix prior to irradiation. The electronic spectrum of C_{13}^- in the gas phase is known,[43] but the concentration of this anion in the matrix was

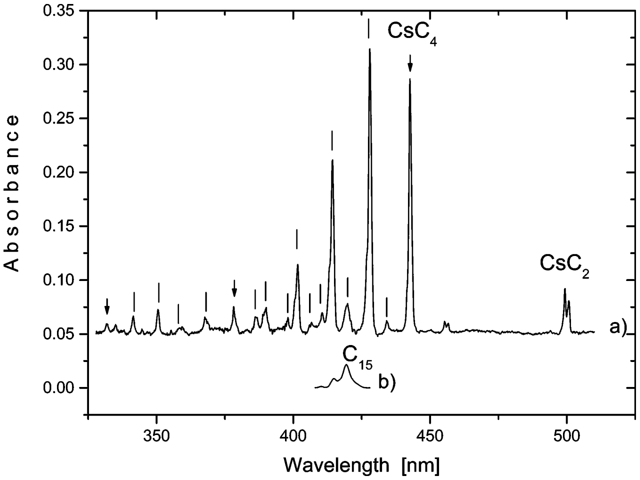

Figure 2. Electronic transition of CsC_4 observed in a 6 K neon matrix after mass-selected deposition of CsC_4^- generated from graphite in a cesium sputter ion source (trace a). The sample was continuously irradiated with UV photons (>295 nm) during growth of the matrix to produce the neutrals from the anions. The absorption bands of CsC_2 are also seen because of fragmentation of deposited anions. Trace b shows the known[37] strongest origin band of C_{15} which was concomitantly deposited with CsC_4.

too low as its absorption was not observed. However, inspection of trace **a** of Figure 1 reveals two weak bands at 516.5 and 469.7 nm which vanish after UV irradiation of the matrix. These peaks are separated from each other by 1929 cm^{-1}. The position of these bands (they lie in the range where absorptions of C_2^- and CsC_2 are observed) and the frequency of 1929 cm^{-1} derived from the spectrum suggest that the C_2^- chromophore is involved in this transition. Therefore, these absorptions are assigned to the origin and a vibronic band of CsC_2^-. From the photoconversion yield, one can estimate that the oscillator strength of the electronic transition of CsC_2^- is at least a factor of 10 less than for CsC_2. It also suggests that CsC_2^- has a T-shaped structure because T-shaped CsC_2 is formed upon electron detachment. Hence, the band system with the origin band at 516.5 nm is assigned to the $^1B_2$−X $^1A_1$ electronic transition of T-shaped CsC_2^-. This is supported by DFT calculations which predict that the $^1A_1$ ground state of cyclic C_{2v} form of CsC_2^- lies ~19 kJ/mol lower in energy than the $^1\Sigma^+$ linear ground state. A similar stability of cyclic NaC_2^- over the linear one (by ~35 kJ/mol) was indicated by the earlier DFT calculations.[4]

CsC_4. Mass-selected trapping of CsC_4^- anions in a neon matrix with concomitant irradiation UV photons ($\lambda > 295$ nm) gave rise to new strong absorptions (trace a of Figure 2). The CsC_4^- ion beam was contaminated with C_{15}^-, which differs only by one amu. These anions were produced simultaneously in the source. During UV irradiation of the matrix, the neutral species are produced from the anions. Thus, after growing of the matrix, only neutral CsC_4 and C_{15} and their fragments are present.

Inspection of the spectrum shown in trace a of Figure 2 reveals two band systems with onsets at 500.4 and 442.6 nm. These differ in their peak shapes and intensities. The first system consists of two weak doublets which are due to the neutral CsC_2, already identified in Figure 1. CsC_2 is present as a result of collisionally induced fragmentation of the CsC_4^- anions. The strong system with the origin band at 442.6 cannot be attributed to C_{15}: its electronic spectrum in a neon matrix is known[37] and the strongest band (origin) lies at 419.5 nm (trace b of Figure 2). Only one weak absorption band (at 419.5 nm) in trace a coincides with a transition of C_{15}. No other smaller fragments which can be formed from C_{15} are seen. Thus, the absorptions which dominate the spectrum shown are due to neutral CsC_4.

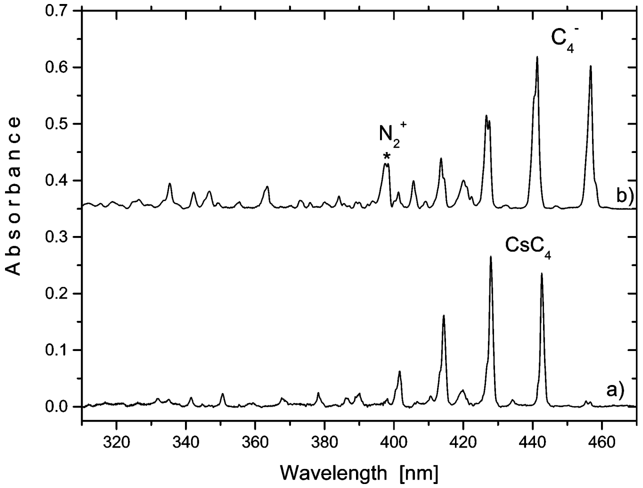

Figure 3. Comparison of the electronic absorption spectrum of CsC_4 (trace a) with the known C $^2\Pi_u$−X $^2\Pi_g$ electronic transition of C_4^- in a neon matrix[44] (trace b). Almost all the bands seen in the spectrum of C_4^- have counterparts in the spectrum of CsC_4 indicating that C_4^- is the chromophore causing the absorption.

The electronic absorption spectrum of CsC_4 resembles the strongest C $^2\Pi_u$−X $^2\Pi_g$ electronic transition of C_4^- anion.[44] For a comparison, these are plotted above each other in Figure 3 after normalization of the strongest band to the same intensity in both spectra. The origin band of CsC_4 (trace a) is shifted ~700 cm^{-1} to the violet from the position in the spectrum of C_4^- (trace b). Almost all the bands seen for CsC_4 have counterparts in the spectrum of C_4^-, together with the weak bands, lying in the 320−400 nm range and which were assigned to the (2) $^2\Pi_u$−X $^2\Pi_g$ and (3) $^2\Pi_u$−X $^2\Pi_g$ transitions of C_4^-.[45] The latter has two further weak electronic transitions in the near-infrared;[45] however, no absorptions of CsC_4 were detected there.

The band system of CsC_4 with the onset at 442.6 nm is based on three fundamental modes of frequency 437, 770, and 1761 cm^{-1}, leading to overtone and combination bands (Table 1). In the analogous transition of C_4^-, only two vibrations, 759 and 2241 cm^{-1} were found, and they were assigned to the ν_2 and ν_1 modes, respectively.[44] However, the vibrational assignment of the C $^2\Pi_u$−X $^2\Pi_g$ transition of C_4^- must be revised in light of the present results for CsC_4 and theoretical calculations.[46] The weak band 483 cm^{-1} to the blue from the origin of C_4^- which was overlooked in ref 44 is genuine, because it forms the combination bands with the mode of frequency 759 cm^{-1} and they have counterparts, 437 cm^{-1} and its combination with 770 cm^{-1} mode, in the spectrum of CsC_4. Also, the frequency of the ν_1 mode (2241 cm^{-1}) of C_4^- inferred in ref 44 is erroneous. Coupled cluster calculations[46] for the C $^2\Pi_u$ state of C_4^- gave the harmonic frequencies 1913 and 777 cm^{-1}. The frequency of ω_1 differs too much from the experimental value of 2241 cm^{-1}. An inspection of the spectrum of C_4^- revealed a weak absorption band located 1801 cm^{-1} above the origin and close to the 1761 cm^{-1} mode derived from the spectrum of CsC_4. This agrees much better with the theoretically predicted energy of ω_1 in the C $^2\Pi_u$ state of C_4^-.

From the similarity of the CsC_4 and C_4^- spectra, one can conclude that both molecules have the same chromophore, the C_4^- moiety, and the Cs−C bond like in the case of CsC_2 which is strongly ionic. Thus, the spectra of CsC_4 and C_4^- can be assigned in a similar way. Namely, the ν_1 vibration of C_4^- with energy of 1801 cm^{-1} corresponds to the $\nu_1 = 1761$ cm^{-1} mode of CsC_4. The second active mode ν_2 in the spectrum of C_4^- with frequency of 759 cm^{-1} has its counterpart in CsC_4, the 770 cm^{-1} vibration. Finally, the weak band with frequency of 483 cm^{-1} in the spectrum of C_4^-, and assigned to the double excitation of the ν_5 mode, corresponds to the 437 cm^{-1} excitation in the case of CsC_4.

The structures and energies of linear and cyclic CsC_4 in their ground electronic states have been determined by the DFT method. Contrary to the case of NaC_4,[4] the linear (open-chain) structure of CsC_4 is slightly less stable (by ∼4 kJ/mol) than the cyclic one. A small deviation from the linearity of the C_4 backbone ($\Theta_{123} = \Theta_{234} = 173°$) of CsC_4 was predicted for the lowest energy cyclic form in which Cs is attached to the two middle carbon atoms with the Cs−C bond length of 3.29 Å (with C_{2v} symmetry). As the energy difference between the linear and cyclic (T-shaped) forms of CsC_4 is small, the DFT calculations cannot answer the question which of the structures was observed in the present experiment.

Substitution of C_4 with Cs preserves all the features of the unsubstituted C_4^- anion. Cs^+ shifts slightly the electronic energy levels of the C_4^- moiety (the origin band of CsC_4 is shifted by 700 cm^{-1} in comparison to the origin of C_4^-) and it modifies but a little the frequency of its modes. The vibration which corresponds to the stretching of the Cs−C bond is not active in this electronic transition. Its frequency is predicted by DFT as 155 cm^{-1} for the linear isomer, and the stretching of the Cs−C bond has a considerable contribution in the two lowest energy symmetric modes (131 and 239 cm^{-1}) of the cyclic form. Because of the similarity to the spectrum of C_4^-, the absorption band system in Figure 2 is attributed to the $^2\Pi - X\ ^2\Pi$ electronic transitions of the C_4^- moiety (Table 1).

The most significant influence of Cs on the spectrum of the C_4^- moiety is a drastic change of the oscillator strength of this electronic transition. By comparison of the ion current and the observed absorption intensities, one can conclude that the oscillator strength of the $^2\Pi - X\ ^2\Pi$ transition of CsC_4 is an order of magnitude larger than for the $C\ ^2\Pi_u - X\ ^2\Pi_g$ transition of C_4^-.

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