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Spectroscopy of excited states of carbon anions above the photodetachment threshold

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Electronic transitions of C_3^- and C_5^- to states lying above the electron affinity of the neutral (EA) have been recorded in the gas phase by laser photodetachment spectroscopy. The excited states are identified by comparison with absorption spectra for the mass-selected ions deposited in neon matrices and with *ab initio* calculations. The $C\,^2\Sigma_u^+ - X\,^2\Pi_g$ transition and two higher energy band systems are observed for C_3^-, corresponding to excitation energies more than 1.5 eV above the EA. In the case of C_5^- the strongest features, at about 0.6 eV above the EA, are attributed to close lying $^2\Delta_g - X\,^2\Pi_u$ and $^2\Sigma_g^- - X\,^2\Pi_u$ transitions. The dominant configurations in these states identify them as long-lived Feshbach resonances. Lifetimes for these resonances in C_3^- are estimated to be between 200 fs and 3 ps from the band widths.

Bound excited electronic states of negative ions were long believed to be uncommon and play a minor role in their chemistry and spectroscopy.[1–3] Dipole-bound excited anion states, formed when a neutral possesses a sufficiently high dipole moment (*e.g.*, CH_2CN,[1] l-C_3H_2[3]), appeared an exception to this rule but excited valence states of negative ions were considered unusual. This picture changed considerably with the observation of a number of bound excited valence states for carbon anions,[4–11] which demonstrated that these states are important for molecules with high electron affinities (EAs).

In the case of C_2^-[12] and C_6^-[8] it has been shown that the lowest excited electronic states lie below the photodetachment threshold and their accompanying vibrational levels undergo autodetachment. Transitions to states above the threshold in C_3^- have recently been observed by photodetachment spectroscopy.[13] Anion states at excitation energies greater than the EA are well known from electron scattering experiments; they can be classified as Feshbach or shape resonances depending on whether their energy is above or below the corresponding parent neutral state.[14,15] The states observed for C_3^- are identified as Feshbach resonances on the basis of theoretical calculations. The spectrum is rotationally resolved for one transition, more than 1 eV above the EA, and a lifetime of 3–5 ps is deduced from the linewidths. The observation of such relatively long-lived Feshbach states is particularly difficult in electron scattering experiments because of the limited resolution of electron monochromators (~ 20 meV[16]) and the low cross-sections for concerted two electron processes.

This is an exciting discovery as it indicates that the number of electronic excitations in carbon anions which are optically accessible is much higher than previously considered. A systematic study of these highly excited anion states is important because of its implications for the chemistry of combustion as well that of the interstellar medium (ISM). In addition, the description of these

states is a considerable challenge to current theoretical methods. This paper addresses this issue by presenting experimental observations for transitions to states above the photodetachment threshold in C_5^- and further data on C_3^-. Assignments of the transitions are made by comparison with measurements on the mass-selected ions in neon matrices and with quantum chemical calculations.

The spectroscopy of carbon clusters has been the subject of two extensive reviews.[17,18] Low resolution UV photoelectron spectroscopy for C_n^- ($n = 2$–29)[19,20] reveals the high EAs of the neutral clusters. As a result, with the exception of C_3^-,[13] all of the carbon cluster anions studied possess a number of bound excited electronic states. Higher resolution photoelectron studies were carried out on mass-selected C_n^-;[21,22] the spectra are dominated by the vertical transitions, suggesting that the electron detachment mainly resulted in a molecule of similar geometry to the parent ion. The EA of C_5 was accurately determined in a threshold photodetachment study giving a value of 2.853 ± 0.001 eV.[23] A doublet structure on bands of the $X\,^1\Sigma_g^+$–$X\,^2\Pi_u$ transition was interpreted as the spin–orbit splitting in the anion ground state, yielding the constant $A'' \approx 22$ cm^{-1}. Hot band structure in the spectrum gave 200 ± 50 cm^{-1} for the ν_7 antisymmetric bending wavenumber in the ground state. The $A\,^2\Pi_g$–$X\,^2\Pi_u$ electronic transition of C_5^- in the gas phase was detected using resonance enhanced multiphoton electron detachment (REMPED) spectroscopy. The bound excited electronic state was assigned on the basis of *ab initio* calculations.[9] This transition was vibrationally resolved by a two-colour REMPED study, yielding frequencies for the ν_1 and ν_2 symmetric stretching modes (1649, 729 cm^{-1}, respectively) and for the ν_7 bending mode (165 cm^{-1}).[7]

A major advance in the study of the electronic spectroscopy of the anions came with the measurement of UV–VIS absorption spectra for mass-selected species in neon matrices.[24] IR measurements for these ions isolated in neon and argon matrices were also performed.[25,26] Several homologous series of electronic transitions were identified and assigned as $^2\Pi$–$X\,^2\Pi$ excitations. These series included transitions to states lying above the gas phase photodetachment threshold. In particular for C_5^-, in addition to the $A\,^2\Pi_g$–$X\,^2\Pi_u$ system already recorded in the gas phase,[7,9] a more intense band system, originating around 359 nm, was observed. The observation of electronic states above the photodetachment threshold was thought to arise because of the stabilizing influence of the rare gas matrix. The measurement of dipole-allowed transitions to resonant states of C_3^- in the gas phase using photodetachment spectroscopy[13] suggests, however, that the states observed in the neon matrix above the detachment threshold for larger carbon chains may have a similar origin.

Experimental

The experimental set-up used for laser excited photodetachment spectroscopy with detection of the neutral products has been described elsewhere.[7] Briefly, carbon anions are generated in a pulsed discharge ($\sim$3 µs, 400–600 V, 30 Hz) ignited in a 0.5% mixture of acetylene and argon at a backing pressure of 10 bar. The expansion is shaped by a skimmer before entering a time-of-flight mass spectrometer. This produces mass-selected ion bunches which are then intersected perpendicularly by the pulsed radiation from either an excimer-pumped dye laser or the frequency doubled output of a Nd : YAG-pumped dye laser. A multichannel plate detector collects a portion of the neutrals resulting from the laser-induced photodetachment and the remaining ions are deflected onto a second detector, mounted at right angles to the beam, which allows the spectra to be normalized for source fluctuations. The experimental detection limits observations to those anions with lifetimes shorter than $\sim$1 µs in the excited state. The dye laser has a bandwidth of $\sim$0.15 cm^{-1} and pulsewidth of 15–20 ns. The output power is maintained below $\sim$30 mJ cm^{-2} to minimize power saturation and the intensity of the laser is monitored using a photodiode for normalization purposes.

Results and comparison with neon matrix spectra

C_3^-

In the previous study the $A\,^2\Delta_u$–$X\,^2\Pi_g$ and $B\,^2\Sigma_u^-$–$X\,^2\Pi_g$ transitions in the photodetachment spectrum of C_3^- were assigned on the basis of their rotational structure.[13] These assignments
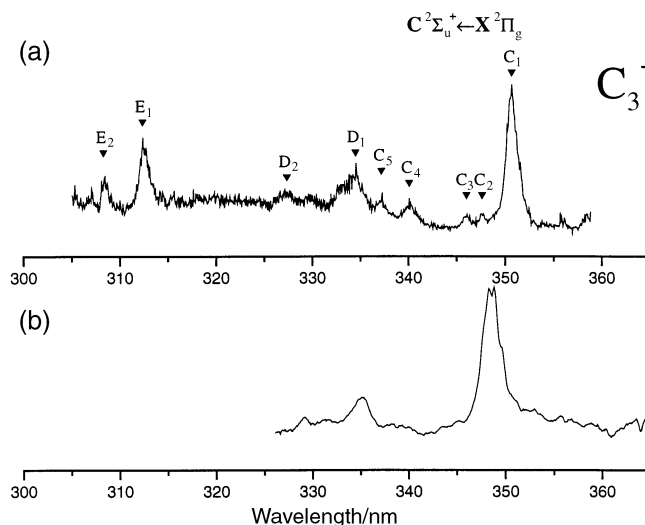
Fig. 1 (a) Photodetachment spectrum of C_3^- in the gas phase and (b) absorption spectrum of C_3^- in a neon matrix at 5 K.[13] Reproduced with permission from *J. Chem. Phys.*

were supported by *ab initio* calculations which suggested that a third strong, unresolved feature at around 350 nm is most likely the origin of the $C\,^2\Sigma_u^+$–$X\,^2\Pi_g$ system. Fig. 1 shows an improved spectrum for this feature (a) compared to the corresponding absorption spectrum for these anions in a neon matrix at 5 K (b). The photodetachment measurement has been extended down to 305 nm to reveal further bands. The maxima of the band positions in both sets of spectra, matrix shifts and suggested assignments are listed in Table 1.

The first four bands to the blue of the origin band (C_1) are much weaker and have relative positions similar to those associated with the A–X and B–X systems. These bands are therefore given corresponding assignments: two very weak features (C_2, C_3) are attributed to sequence band structure produced by the Renner–Teller effect in the ground state and the other two (C_4, C_5) to vibrational progressions. The vibrational wavenumbers for the C state are compared with those determined for the other states of the ion in Table 2. The matrix shift for C_1 is positive and of a similar magnitude to those for the A–X and B–X origin bands, suggesting that the three excited states have similar electronic structures. Two broad bands (D_1, D_2) are observed which

Table 1 Band positions (maxima, ± 3 cm^{-1}) in the photodetachment spectrum of C_3^- in the gas phase and in the absorption spectrum of ions isolated in a neon matrix (maxima, ± 20 cm^{-1})

| Band | λ/nm | | ν_0/cm^{-1} | $\Delta\nu_0$/cm^{-1} | Assignment |
	Matrix	Gas	Gas		
C_1	348.6	350.7	28 506	$+180$	0_0^0
C_2	a	347.7	28 756	a	$2_1^1\ ^2\Pi_g{-}^2\Delta_u$
C_3	a	346.0	28 890	a	$2_1^1\ ^2\Pi_g{-}^2\Sigma_u^-$
C_4	a	340.1	29 396	a	2_0^2
C_5	a	337.2	29 647	a	1_0^1
D_1	335.2	334.5	29 885	-60	
D_2	329.2	327.4	30 540	-170	
E_1	a	312.4	32 003	a	
E_2	a	308.3	32 428	a	

^{a} Not discernible in neon matrix spectrum. The matrix–gas shifts, $\Delta\nu_0 = \nu_0^{\text{matrix}} - \nu_0^{\text{gas}}$, are also listed.

Table 2 Vibrational wavenumbers (cm^{-1}) determined for C_3^- in the ground and excited electronic states (estimated uncertainties are given in parentheses)

State	v_1	v_2
X $^2\Pi_g$	$1722(20)^a$, 1684^b	303^b, 430^b
A $^2\Sigma_u^-$	$1140(6)^b$, $1110(14)^b$	$410(6)^c$
B $^2\Delta_u$	$1072(6)^c$, $1062(14)^d$	$410(6)^c$
C $^2\Sigma_u^+$	$1140(6)^e$, $1180(14)^d$	$445(6)^e$

[a] Argon matrix, ref. 25. [b] Calculated value after scaling, ref. 25. [c] Gas phase, ref. 13. [d] Neon matrix, ref. 13. [e] Gas phase, this work.

have large negative shifts, indicating that they probably arise from a different electronic excitation. In addition, two bands (E_1, E_2) are observed at around 310 nm. The separations and relative intensities of the bands in these two new groupings do not resemble those in the other three band systems.

C_5^-

Fig. 2 compares the gas phase photodetachment spectrum of C_5^- (a) with the absorption spectrum for mass-selected ions in a neon matrix (b). The band maxima, matrix shifts and suggested assignments are listed in Table 3. The bands observed in the photodetachment spectrum can be divided into two series on the basis of their positions and intensities. A series of bands, B_1–B_{10}, can be identified between 370 and 410 nm and a much stronger band system, C_1–C_5, occurs between 335 and 370 nm. All of the bands in this system are broad and show no discernible structure.

The corresponding absorption bands for matrix-isolated C_5^- are overlapped by strong features due to C_3 and N_2^+, produced by fragmentation processes during the deposition. As a result, the weaker B series of bands was not recognized when the spectrum in neon was first recorded.[24]
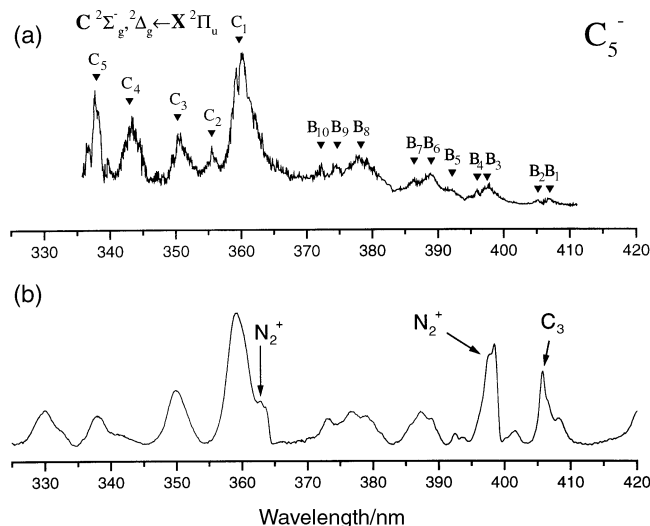

Fig. 2 (a) Photodetachment spectrum of C_5^- in the gas phase and (b) absorption spectrum of C_5^- in a neon matrix at 5 K.[24] Reproduced with permission from *J. Phys. Chem. A.*

Table 3 Band positions (maxima, ± 3 cm^{-1}) in the photodetachment spectrum of C_5^- in the gas phase and in the absorption spectrum of ions isolated in a neon matrix (maxima, ± 20 cm^{-1})

Band	λ/nm Matrix	Gas	v_0/cm^{-1} Gas	Δv_0/cm^{-1}	Assignment
B_1	407.5	407.0	24 563	−30	
B_2	[a]	405.2	24 672	[a]	
B_3	397.8	397.5	25 150	−20	
B_4	396.3	396.0	25 245	−20	
B_5	392.5	392.2	25 490	−20	
B_6	389.1	389.0	25 700	−10	
B_7	387.0	386.4	25 873	−40	
B_8	378.8	378.3	26 427	−40	
B_9	376.7	374.7	26 680	−140	
B_{10}	372.9	372.2	26 860	−50	
C_1	359.1	359.8	27 785	+50	0_0^0
C_2	[a]	355.5	28 121	[a]	7_0^2
C_3	350.0	350.3	28 539	+20	2_0^1
C_4	342.5	343.0	29 146	+40	2_0^2
C_5	337.8	338.0	29 577	+20	1_0^1

[a] Not discernible in the neon matrix spectrum.

Re-examination of the spectrum enables the majority of these bands to be identified: B_1 and B_2 are overlapped but can be recognized as shoulders, whilst the other bands are in reasonable correspondence with the relative positions of bands in the gas phase spectrum. The much stronger C bands were previously identified in the matrix spectrum and attributed to vibrational transitions accompanying the $B\,^2\Pi_g$–$X\,^2\Pi_u$ electronic excitation.[24] In the matrix, band C_1 is overlapped by an N_2^+ absorption; the weaker C_2 band is not observed and C_3 is apparent only as a shoulder on C_4.

The separation of the bands into B and C systems is supported by the matrix shifts: the B bands have negative Δv_0 (i.e., they lie to the red in the neon matrix spectra) which, with the exception of B_5 and B_9, range from −20 to −40 cm^{-1} whilst the C bands have $\Delta v_0 \sim +20$–60 cm^{-1}. The difference in the signs suggests that the two systems correspond to different electronic transitions.

The vibrational structure within the C system is similar to that observed in the gas and neon matrix spectra of the $A\,^2\Pi_g$–$X\,^2\Pi_u$ system.[7,24] In the matrix C_1, C_3 and C_4 have intensities and positions consistent with their assignment to a progression in the v_2 symmetric stretch. In the gas phase the C_4 band has a higher relative intensity perhaps caused by overlap with a weaker band discernible to the red in the matrix spectrum. The weak C_2 band is assigned to a two quantum excitation of the v_7 antisymmetric bend by comparison with the A–X system. The C_5 band is tentatively assigned to excitation of the v_1 symmetric stretch, although the band is somewhat

Table 4 Vibrational wavenumbers (cm^{-1}) determined for C_5^- in the ground and excited electronic states (estimated uncertainties are given in parentheses)

State	v_1	v_2	v_7
$X\,^2\Pi_u$	1832(20)[a], 1822(14)[b]		200(50)[c]
$A\,^2\Pi_g$	1679(20)[d], 1649(2)[e]	737(20)[d], 729(2)[e]	165(2)[e]
C	1756(20)[d], 1792(6)[f]	724(20)[d], 754(6)[f]	168(6)[f]

[a] Argon matrix, ref. 25. [b] Neon matrix, ref. 26. [c] Gas phase, ref. 23. [d] Neon matrix, ref. 24. [e] Gas phase, ref. 7. [f] Gas phase, this work.

narrower than the other C bands in the gas phase spectrum. Table 4 compares the vibrational frequencies inferred for the C state with those determined for the X and A states.

The vibrational structure in the B system is quite different: the clearest pattern is of groups of closely spaced bands (B_1–B_2, B_3–B_4, B_6–B_7, B_8–B_9) suggesting a progression with a separation of ~ 550–600 cm^{-1}. The intensities of the bands do not decay as rapidly with increasing vibrational excitation as occurs in the other two electronic systems. Two bands, separated by ~ 100 cm^{-1}, appear as a repeating unit in the first two groups but thereafter the number of bands and their separations increase. The vibrational structure is not similar to that seen in the other band systems, where the origin carries most of the total intensity. Due to the irregularity of the system no vibrational assignments are made.

Theoretical calculations

Assignments for the observed band systems in C_3^- and C_5^- are made based upon quantum chemical calculations. Feshbach resonant states above the photodetachment threshold in C_3^- have previously been calculated using the CASPT2, ACPF[13] and MRCI[27] methods, and new MRCI calculations for these states in C_5^- are presented here. The application of these bound state electronic structure methods to anion resonances can be unreliable because of the possibility for variational collapse to a 'neutral molecule plus free electron' (NMFE) state. Furthermore, attempts to overcome this in H_2^-, through the avoidance of particular diffuse functions, have been shown to produce superpositions of resonant and NMFE states from which it is difficult to extract the resonance information.[28] As a safeguard against such problems, the resonances calculated for C_5^- have been subject to the following tests: (a) careful examination of their relative energy dependencies on basis set size and the addition of more diffuse orbitals; (b) comparison of their potential energy curves with those for neutral C_5.

C_3^-

The previous CASPT2 and ACPF calculations for C_3^- supported the assignment of the $A\,^2\Delta_u$–$X\,^2\Pi_g$ and $B\,^2\Sigma_u^-$–$X\,^2\Pi_g$ transitions which had been made on the basis of their rotational structure.[13] These states were identified as closed channel Feshbach states produced by the promotion of an electron $1\pi_g \leftarrow 3\sigma_u$ from the ground state of the anion ($X\,^2\Pi_g, \ldots 1\pi_u^4\, 3\sigma_u^2\, 4\sigma_g^2\, 1\pi_g^1$). The strong band at around 350 nm was assigned as the origin of the $C\,^2\Sigma_u^+$–$X\,^2\Pi_g$ system, also produced by this promotion, because of its intensity and good agreement with the calculated vertical excitation energy. In contrast to the $B\,^2\Sigma_u^-$–$X\,^2\Pi_g$ system, rotational structure is not resolved in the C_1 band. The calculations indicate that the equilibrium bond length for this state differ little from those for the $A\,^2\Delta_u$ state. Simulations of the band profile using the rotational constants and temperature (50 K) derived from the $A\,^2\Delta_u$–$X\,^2\Pi_g$ origin band indicate that a linewidth of 20–25 cm^{-1} is required to reproduce the observed profile. This corresponds to a lower limit for the lifetime of the $C\,^2\Sigma_u^+$ state of ~ 200–250 fs, providing that the transition is not significantly saturated. This is in agreement with the expectation of larger matrix elements coupling the $^2\Sigma_u^+$ state to the continuum state, $\sigma^2 k$, *via* a two-electron concerted process, than for the $^2\Delta_u$ and $^2\Sigma_u^-$ states.[13]

The only state calculated to higher energy accessible by dipole selection rules is the $D\,^2\Pi_u$, produced by the electron promotion $1\pi_g \leftarrow 1\pi_u$, for which the oscillator strength is an order of magnitude smaller than for the first three excited electronic states. For this reason, coupled with the good agreement between the observed position and calculated excitation energy, the weak D bands are tentatively assigned to this excitation. No obvious assignments can be made for the E bands based on the calculations. This system is in reasonable agreement with the position expected for the $C\,^2\Sigma_u^+$–$X\,^2\Pi_g\,3_0^2$ where $\nu_3(\sigma_u)$ is the antisymmetric stretching mode (Table 2). The E_1 band would, however, be much more intense than expected based on the similar equilibrium bond lengths calculated for these states. Alternatively these bands are close to the excitation energy calculated for the $^2\Delta_g$ state, which might be observed through vibrational coupling with either $\nu_3(\sigma_u)$ or $\nu_2(\pi_u)$. The latter mode, being of lower frequency, would produce better agreement in the calculated and observed positions. Alternatively, it is noticed that the separation of the bands (E_1–$E_2 \approx 425$ cm^{-1}) is in accord with the ground state ν_2 vibrational frequency (Table 2).

Table 5 Calculated relative energies and the most significant configurations in the CI expansion, along with their weights, c_i^2, for several excited states of C_5^-

| State | Configuration | | | | | | Rel. energies/eV | | |
	c_i^2	$1\pi_u$	$6\sigma_g$	$5\sigma_u$	$1\pi_g$	$2\pi_u$	MRCI	MRCI + Q	f
X $^2\Pi_u$	0.77	4	2	2	4	1	0^a	0^b	
	0.05	4	2	2	2	3			
$^4\Pi_g$	0.80	4	2	2	3	2	2.32	2.37	
	0.03	3	2	2	3	3			
A $^2\Pi_g$	0.80	4	2	2	3	2	2.67	2.67	0.003
	0.03	3	2	2	3	3			
$^4\Sigma_u^-$	0.66	4	2	1	3	3	3.00	2.76	
	0.15	4	1	2	3	3			
$^2\Phi_g$	0.79	4	2	2	3	2	3.01	3.05	
	0.04	3	2	2	3	3			
$^4\Sigma_g^-$	0.61	4	2	1	3	3	3.08	2.85	
	0.22	3	1	2	4	3			
$^1\Sigma_g^+(C_5)$	0.84	4	2	2	4	0	3.13	3.07	
$^2\Pi_g$	0.78	4	2	2	3	2	3.44	3.36	0.0004
	0.04	3	2	2	3	3			
$^2\Sigma_u^-$	0.63	4	1	2	4	2	3.67	3.48	
	0.18	4	1	2	3	3			
$^2\Delta_u$	0.66	4	2	1	4	2	3.75	3.51	
	0.15	4	1	2	3	3			
$^2\Sigma_g^-$	0.62	4	1	2	4	2	3.77	3.59	0.01
	0.19	4	2	1	3	3			
$^2\Delta_g$	0.65	4	1	2	4	2	3.84	3.61	0.01
	0.16	4	2	2	3	3			
$^2\Sigma_u^+$	0.65	4	2	1	4	2	4.11	3.85	
	0.14	4	1	2	3	3			
$^2\Sigma_g^+$	0.65	4	1	2	4	2	4.20	3.95	0.02
	0.16	4	2	2	3	3			

^{a} Absolute energy $-189.7546\ E_h$. ^{b} Absolute energy $-189.8639\ E_h$. The oscillator strengths, f, for dipole-allowed transitions from the ground state are also listed.

Excitation of this bending mode would be consistent with a transition to an excited state of bent geometry. Further computation and experimental work is needed to better elucidate the origin of these bands.

C_5^-

Previous theoretical studies of C_5^- are limited. The geometry of the ground electronic state (X $^2\Pi_u$, ... $1\pi_u^4\ 6\sigma_g^2\ 5\sigma_u^2\ 1\pi_g^4\ 2\pi_u^1$) has been optimized at several levels (MBPT(2),[29] SDCI[17]) and comparison with the neutral carbon chains suggests the most accurate results are those at the RCCSD(T) level: $R_e^o = 1.293$ Å, $R_e^i = 1.307$ Å[30] (o = outer, i = inner C–C bond). The only previous attempt to calculate states above the photodetachment threshold in C_5^- made use of the first-order correlation orbital method to define the virtual space for coupled cluster calculations employing the spin-unrestricted Hartree–Fock reference wavefunction.[29] This method underestimated the experimental value for the electron affinity (2.9 eV[23]) by ~ 0.3 eV. The calculation considered only $\pi \leftarrow \sigma$ promotions and gave the following states (energies in eV): $^4\Sigma_u^-$ (2.50), $^4\Sigma_g^-$ (2.61), $^2\Sigma_u^-$ (2.95), $^2\Sigma_g^-$ (3.08), $^2\Delta_u$ (3.68) and $^2\Delta_g$ (3.80). Later calculations using the SDCI method with the Davidson correction (SDCI + Q) gave vertical values for the excitation energy of the bound A $^2\Pi_g$ state and the EA of C_5 within ~ 0.1 eV of the experimental values.[9]

The present calculations are performed using the MOLPRO96 program package.[31] The ground state geometry is initially optimized at the RCCSD(T)/aug-cc-pVQZ level giving bond lengths which differ insignificantly from those obtained previously.[30] This geometry is used in internally contracted MRCI calculations based on a CASSCF reference wavefunction. In both the CASSCF and MRCI calculations the active space is composed of the $6\sigma_g$, $5\sigma_u$, $1\pi_u$, $1\pi_g$ and $2\pi_u$ orbitals.

As a first test vertical excitation energies for the doublet states of C_5^- located within 5 eV of the ground state are calculated using s, p and d functions from the basis sets aug-cc-pVXZ X = P, T, Q with optimized general contraction schemes.[32] The relative energies of the states are all found to shift by almost equal amounts to lower energy as the size of the basis set increases. The exponents of the diffuse s, p and d orbitals decrease as the size of the basis set increases. The use of additional diffuse s and p orbitals (with the exponents 0.0155 and 0.103, respectively[32]) changes the relative energies by less than 20 cm^{-1} in all cases. It is expected that an NMFE state will be more significantly stabilized by increases in the diffuseness of the basis set than a resonance, in contrast to the similar dependencies on basis set for all of the calculated states.

Table 5 lists the vertical excitation energies (MRCI, MRCI + Q) for the doublet and quartet states of C_5^-, along with the most important configurations contributing to the CI expansion. The table contains the oscillator strengths, f, computed from the CASSCF wavefunctions. In addition the energy of the ground state of neutral C_5 for this geometry is listed. No other neutral states of this geometry are located in the energy range. This is in agreement with previous MRCI calculations which found a manifold of triplet states at excitation energies in the range 2.5–2.7 eV and excited singlet states starting at energies above ~ 2.8 eV.[33] The calculated energies are judged to be accurate to ~ 0.2–0.3 eV on the basis of the agreement between the vertical electron detachment energy and the experimental value, as well between the A–X excitation energy and the observed origin band position.

The same state energies are then calculated for the range of linear geometries obtained with both the inner and outer bond lengths varied at increments of 0.05 Å over the interval $1.2 \leqslant R \leqslant 1.4$ Å. Fig. 3 shows cuts through the 2D potential energy functions for (a) $R^o = 1.3$ Å and (b) $R^i = 1.3$ Å which pass close to the energy minima for all states considered. It is apparent from this figure that none of the cuts for calculated anion resonances run parallel to those for the ground state of the neutral molecule. This provides further evidence that the calculated energies are those of resonances rather than NMFE states. Fig. 3 and Table 5 indicate that the excited states of lowest energy ($^4\Pi_g$, $^2\Phi_g$ and the two $^2\Pi_g$) correspond to the promotion of an electron from $\pi_u \leftarrow \pi_g$ and the higher energy states to $\pi \leftarrow \sigma$ promotions ($^2\Sigma_u^-$, $^2\Sigma_g^-$, $^2\Delta_u$, $^2\Delta_g$, $^2\Sigma_u^+$, $^2\Sigma_g^+$). These states can all be classified as closed-channel Feshbach resonances on the basis of their dominant configurations. The removal an electron produces a parent neutral state which lies
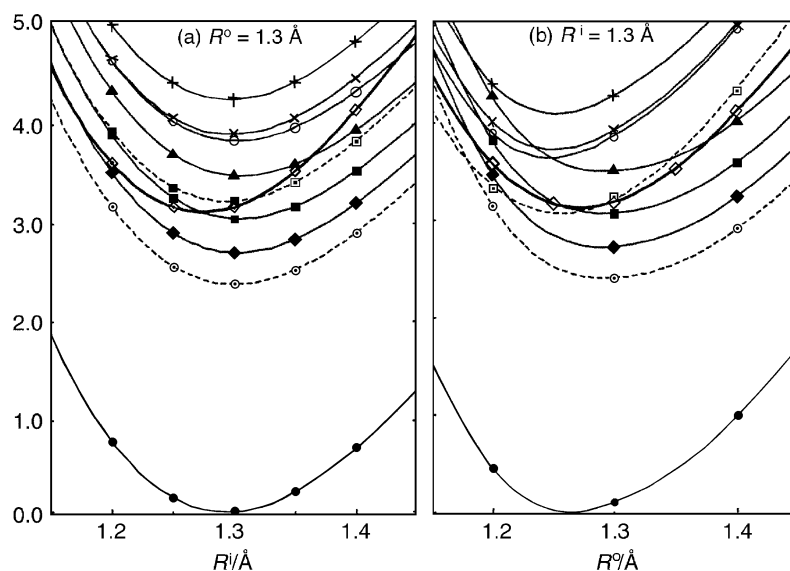

Fig. 3 Radial cuts through the ground and excited state potential energy functions for linear geometries: (a) dependence on R^i, $R^o = 1.3$ Å and (b) dependence on R^o, $R^i = 1.3$ Å. Key: ● X $^2\Pi_u$, ◆ A $^2\Pi_g$, ■ B $^2\Pi_g$, ▲ $^2\Phi_g$, ○ $^2\Sigma_g^-$, × $^2\Delta_g$, + $^2\Sigma_g^+$, ? $^4\Pi_g$, □ · $^4\Sigma_g^-$, ◇ $^1\Sigma_g^+$ (C_5). Thin solid and thin dashed lines are doublet and quartet states of C_5^-, respectively, and the thick solid line is the ground state of C_5.

higher in energy and the ground state of the neutral can only be reached by the concerted removal of one electron and transfer of another to a lower energy orbital.

Compared to the previous calculation for the $\pi \leftarrow \sigma$ states,[29] the vertical excitation energies of the $^2\Delta_u$ and $^2\Delta_g$ states are in good agreement but the present calculation give energies ~ 0.5–0.6 eV higher for the lower states. Compared to C_3^- the optically accessible $^2\Sigma^-$ and $^2\Delta$ states are much closer in energy and their order is reversed. Assuming identical orbitals the relative energies of the states arising from the $\sigma\pi^2$ configurations can be described by two exchange intervals $K_{\sigma\pi}$ and $K_{\pi\pi}$: $^2\Sigma^+$ lies $2K_{\pi\pi}$ above $^2\Delta$ and $^2\Delta$ lies $2K_{\sigma\pi}-2K_{\pi\pi}$ below $^2\Sigma^-$.[13] In contrast to C_3^- the exchange integrals in C_5^- are such that $K_{\sigma\pi} \lesssim K_{\pi\pi}$.

The most likely assignment of the strong C system of bands is to overlapping transitions to the closely spaced $^2\Delta_g$ and $^2\Sigma_g^-$ states. The excitation energies for both states (Table 5) agree with the position of the C_1 band to within the estimated accuracy of the calculation (~ 0.3 eV). Fig. 3(b) suggests that both will have better Franck–Condon (FC) overlap with the ground state than for the A–X transition. The calculated oscillator strengths are about twice that of the A–X excitation, in agreement with the relative intensities of these bands in the matrix spectrum.[24] There are several possible candidates for the excited states accessed by the B system. The lowest frequency band (B_1) is close to the calculated positions of the $^2\Phi_g$ and $^4\Sigma_g^-$ states; the former state might be accessed through vibrational coupling with a π_g mode and the latter in a spin-forbidden transition. The transition to the second $^2\Pi_g$ state cannot be ruled out given the accuracy of the calculated excitation energy and its FC overlap and oscillator strength suggest that it should be much weaker than other allowed transitions. The weakness of the B system is supportive of a transition to any or all of these states but the vibrational structure is perhaps most consistent with a vibronically allowed transition and the $^2\Phi_g$ state is tentatively favoured. The separation of the groups of bands (~ 550 cm^{-1}) is closer to the calculated wavenumbers for the $\nu_6(\pi_g)$ mode in the ground state (433 cm^{-1}, 361 cm^{-1}[25]) than for any other fundamental.

Discussion and conclusions

Optical transitions to excited states of C_3^- and C_5^- above the electron detachment energy have been observed and assigned to Feshbach resonances on the basis of *ab initio* calculations. There are several important implications of these results.

The spectroscopic experiments provide much higher energy resolution than is currently achievable by electron scattering techniques which up to now have been the main route to study Feshbach resonances. The energy resolution is limited by the laser linewidth, which in the present experiment is ~ 0.15 cm^{-1}. This has enabled the lifetimes for the observed resonant states to be estimated from the band profiles; for C_3^- and C_5^- lifetimes in the range from 3 ps to 200 fs are obtained. The lifetime obtained for the B $^2\Sigma_g^-$ state of C_3^- is in excellent agreement with the value recently obtained by fs pump–probe measurements.[34] The detection window of the current set-up allows the observation of resonances with lifetimes up to ~ 1 μs. The observed states have all been assigned as closed-channel Feshbach resonances. The latter are comparatively long-lived and give rise to narrow bands in the spectra. No assignments have been made to the open-channel shape and core excited shape resonances, which are expected to be more shortly lived, giving much broader bands.

Feshbach resonances are difficult to detect in electron transmission spectra. They have low cross-sections for electron capture because this process involves the concerted excitation of one electron and the attachment of the incoming electron. These resonances have been most commonly observed in dissociative attachment and threshold electron spectra.[14] The optical preparation of Feshbach resonances has the further advantage that while electron scattering can only be performed on stable neutral molecules this method starts from anions in their ground states which are formed in a suitable source. It is therefore to be considered as a complementary method to electron scattering. Resonances with lifetimes ~ 100–200 μs have been measured for N_2^-, in a storage ring or tandem accelerator and assigned as sextet states where autodetachment to the low lying singlet or triplet states of the neutral is spin forbidden.[35,36] These experiments, however, provide no information about the energetics of these resonances.

The threshold photodetachment spectrum of C_5^- reveals a band system about 0.26 eV to higher energy of the $^1\Sigma_g^+$–$^2\Pi_u$ transition, which has a similar intensity but differs considerably in

its band structure.[23] The band system was assigned as a transition to an excited state of C_5 despite the fact that *ab initio* calculations indicate that the lowest linear excited states are triplets at energies between 2.5 and 2.7 eV above the ground state.[33] Recent calculations for C_3^- have predicted a cyclic $^3A_2'$ state, which correlates with $^2\Pi_u$ in the linear limit, at only about 1 eV above the $^2\Pi_g$ ground state.[27] A low lying cyclic or bent form of C_5 would be consistent with the band structure of this transition.

The alternative possibility that this band system corresponds to a transition to an autodetaching state of C_5^- was excluded as this was expected to give rise to electron energies of more than ~ 10 cm^{-1}. The B_1 and B_3 bands observed in the photodetachment spectrum of C_5^- (Fig. 2) are in quite good agreement with strong features in this band system but to higher energy the bands die off rapidly in intensity in the threshold spectrum whilst they remain strong in the photodetachment spectrum. This coincidence suggests that the second band system in the threshold spectrum might in fact be an autodetaching state of C_5^-. The production of threshold electrons in this case could occur following a transition to an excited anion eigenstate which probes a region of the potential close to a crossing point with the neutral ground state. The higher bands in the photodetachment spectrum might not be seen in the threshold spectrum owing to the production of higher kinetic energy electrons in autodetachment from these levels. Fig. 3 shows that there are several states which cross the ground state of C_5 less than 1 eV above its energy minimum. These include the second $^2\Pi_g$, $^2\Phi_g$ and $^4\Sigma_g^-$ states which were previously considered as the most likely assignments for the B band system.

The results for C_3^- and C_5^- suggest that stabilization by the matrix environment does not need to be invoked to explain the observation of transitions to states above the photodetachment threshold in C_5^-, C_7^- and C_9^-.[24] The observation of Feshbach states above the photodetachment threshold is most likely a quite general phenomenon, at least for carbon clusters where a manifold of states arises from the conjugated π-systems. This opens the possibility of detecting optical absorptions which had previously been discounted on the basis of the electron affinities. It has been shown that these absorptions may be narrow enough to exhibit rotational structure.

The observation of a new class of optically accessible anion states is of significance to various areas of chemistry, for example, as a means of identifying and monitoring anion concentrations in atmospheric and combustion processes. It is of particular interest in astrophysics as the presence of carbon chains has been established in interstellar and stellar environments. The neutral C_3 molecule has been detected in both the ISM[37] and, along with C_5, in the circumstellar shell of carbon-rich stars.[38,39] The suggestion that carbon chains may be carriers of the diffuse interstellar bands (DIBs)[40] has gained credence with the identification of several close coincidences between DIBs and bands in the lowest electronic system of C_7^- in the gas phase.[4] The removal of the electron affinity as a limit on the optical range for the observation of anion states greatly increases the number of possible carriers of the DIBs. Interestingly, the spectrum of C_3^- shows a close match between the strongest band (A $^2\Delta_u$–X $^2\Pi_g$ 0_0^0) and a tentatively identified DIB at 404 nm.[41] The rest of the spectrum is not in the range of any currently recorded DIB.

Acknowledgements

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