

Threshold photodetachment spectroscopy of C_5^-

T. N. Kitsopoulos, C. J. Chick,^{a)} Y. Zhao, and D. M. Neumark^{b)}
Department of Chemistry, University of California at Berkeley, Berkeley, California 94720

(Received 9 July 1991; accepted 1 August 1991)

The importance of carbon clusters in astrophysics and combustion has made them the focal point of intense experimental effort. Carbon clusters come in a wide range of geometries, including linear chains, closed rings, and spheroidal fullerenes. The spectroscopy of these intriguing species has been reviewed by Weltner and Van Zee.¹ Although a great deal of progress has been made in understanding the physical and chemical properties of these carbon clusters, there remain many unanswered questions concerning the nature of the electronic, vibrational, and rotational structure of these species.

Over the years, negative ion photoelectron spectroscopy (PES) has offered a very promising technique for studying clusters.²⁻⁵ The first ultraviolet photoelectron spectra for carbon clusters C_n^- ($n=2-29$) were obtained by Smalley and co-workers⁶ at a resolution of about 1000 cm^{-1} , which allowed electronic bands to be mapped out but no vibrational progressions. More recently, Arnold *et al.*⁷ have obtained vibrationally resolved photoelectron spectra of C_n^- ($n=2-11$) at a resolution of about 100 cm^{-1} . This resolution is comparable to the lowest vibrational frequencies for these clusters, and not all features in the spectra were cleanly resolved. In this Communication, we report a considerably higher resolution ($6-10\text{ cm}^{-1}$) photodetachment study of C_5^- using threshold photodetachment spectroscopy.^{8,9} We observe considerably more vibrational structure than in the C_5^- photoelectron spectrum and obtain evidence for a low-lying excited electronic state of C_5 .

The threshold photodetachment spectrometer used in this study is described in detail elsewhere.^{8,10} A beam of cold anion carbon clusters is generated in a laser vaporization/pulsed molecular beam source and is mass-selected using time of flight. The cluster of interest is then photodetached using a excimer-pumped tunable dye laser operating at 20 Hz, and electrons with near zero kinetic energy (ZEKE) are collected as a function of photon energy. The selective detection of the ZEKE electrons is done using the method developed by Müller-Dethlefs *et al.*¹¹ In the spectra shown here, the electron signal was averaged for 1000 laser shots at each wavelength and normalized to both the laser power and the ion current. Four different laser dyes were utilized to obtain the C_5^- spectrum: Stilbene 3 (418–440 nm), Exalite 416 (408–427 nm), DPS (397–414 nm), and BiBuQ (375–400 nm).

Figure 1(a) shows the C_5^- threshold photodetachment spectrum in which the cluster beam was seeded in UHP helium; Fig. 1(b) shows a smaller region of this spectrum taken with neon as the seed gas. Two types of peaks appear in Fig. 1(a): Peaks *a*–*F* are all between 10 and 30 cm^{-1} wide, while a series of broader peaks (FWHM $\sim 100\text{ cm}^{-1}$) appears at slightly higher energy. The two sets of

peaks are labeled bands X and *a*, respectively. Peaks in each band represent transitions between vibrational levels of C_5^- and C_5 . The peaks in band X can be further grouped together according to their shape: peaks *a*, *A*, *D*, and *E* which are doublets split by 22 cm^{-1} , and peaks *b*, *B*, *c*, *C*, and *F* which are single peaks about 30 cm^{-1} wide.

Band X is the lower energy band observed and presumably results from transitions between the ground electronic states of the anion and neutral cluster. It is dominated by peak *A*, which is assigned to the $C_5(v'=0) \leftarrow C_5^-(v''=0)$ vibrational transition. The dominance of a single peak implies a small geometry change between the anion and the neutral cluster. Several high resolution infrared experiments¹²⁻¹⁴ have determined the structure of C_5 to be linear, in agreement with the prediction of Pitzer and Clementi,¹⁵ and our spectrum indicates C_5^- is linear as well. As mentioned above, peak *A* is actually two peaks (A_1, A_2) separated by 22 cm^{-1} . Molecular orbital considerations show that C_5 has a $^1\Sigma_g^+$ ground state and that the LUMO in C_5 is a π_u orbital, so C_5^- is expected to have a $^2\Pi_u$ ground state. We assign the 22 cm^{-1} splitting to the splitting between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ spin-orbit levels of the C_5^- $^2\Pi_u$ state. The smaller A_2 peak observed at higher wavelength originates from the excited $^2\Pi_{3/2}$ level and is

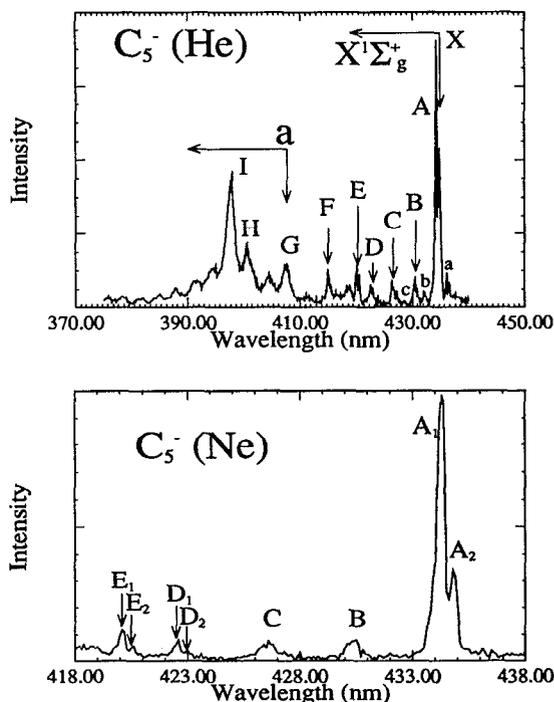


FIG. 1. (a) Threshold photodetachment spectrum of C_5^- generated in a helium expansion. (b) Section of the threshold photodetachment spectrum of C_5^- generated in a neon expansion.

TABLE I. Listed are the positions for the assigned peaks observed in band X, in the spectrum of Fig. 1. The uncertainty in the peak position is $\pm 10 \text{ cm}^{-1}$.

Peak	Position cm^{-1}	$\text{C}_5 \leftarrow \text{C}_5^-$ transition assignment
a_2	22 897	$^1\Sigma_g^+(v_7' = 1) \leftarrow ^2\Pi_{3/2}(v_7'' = 1)$
a_1	22 919	$^1\Sigma_g^+(v_7' = 1) \leftarrow ^2\Pi_{1/2}(v_7'' = 1)$
A_2	22 991	$^1\Sigma_g^+(v' = 0) \leftarrow ^2\Pi_{3/2}(v'' = 0)$
A_1	23 013	$^1\Sigma_g^+(v' = 0) \leftarrow ^2\Pi_{1/2}(v'' = 0)$
b	23 133	$^1\Sigma_g^+(v_7' = 3) \leftarrow ^2\Pi_u(v_7'' = 1)$
B	23 225	$^1\Sigma_g^+(v_7' = 2) \leftarrow ^2\Pi_u(v_7'' = 0)$
C	23 444	$^1\Sigma_g^+(v_5' = 2) \leftarrow ^2\Pi_u(v_5'' = 0)$
D_2	23 634	$^1\Sigma_g^+(v_7' = 2, v_5' = 2) \leftarrow ^2\Pi_{3/2}(v_7'' = 0, v_5'' = 0)$
D_1	23 656	$^1\Sigma_g^+(v_7' = 2, v_5' = 2) \leftarrow ^2\Pi_{1/2}(v_7'' = 0, v_5'' = 0)$
E_2	23 770	$^1\Sigma_g^+(v_2' = 1) \leftarrow ^2\Pi_{3/2}(v_2'' = 0)$
E_1	23 791	$^1\Sigma_g^+(v_2' = 1) \leftarrow ^2\Pi_{1/2}(v_2'' = 0)$
F	24 082	$^1\Sigma_g^+(v_6' = 2) \leftarrow ^2\Pi_u(v_6'' = 0)$

less intense because the population of this level is lower in our cold ion beam. Based on the intensity ratio A_2/A_1 , we obtain a spin-orbit temperature of 60 K for the He seeded beam and 30 K for the Ne seeded beam. The transition energy of the larger A_1 peak, $2.853 \pm 0.001 \text{ eV}$, is the electron affinity of C_5 .

Considering the other peaks in band X, we find that intensities for peaks a , b , and c vary considerably with the ion source conditions and we assign them to hot bands originating from vibrationally excited C_5^- . These hot band transitions are absent from Fig. 1(b) suggesting, in accordance with the spin-orbit temperatures, that the clusters formed in Ne expansions are colder than those seeded in He. The remaining peaks are transitions from $\text{C}_5^-(v'' = 0)$ to vibrationally excited C_5 . Their assignments, listed in Table I, are aided by *ab initio* calculated vibrational frequencies¹⁶ and the infrared absorption work on C_5 by Amano and co-workers.¹⁴ We observe transitions to the $v' = 1$ level of the ν_2 symmetric stretch and to the $v' = 2$ levels of the ν_5 , ν_6 , and ν_7 bending modes (since the bending modes are not totally symmetric, only transitions to even levels from the $v'' = 0$ anion level can occur¹⁷). We obtain the following C_5 vibrational frequencies: $\nu_2 = 779 \text{ cm}^{-1}$, $\nu_5 = 216 \text{ cm}^{-1}$, $\nu_6 = 535 \text{ cm}^{-1}$, $\nu_7 = 106 \text{ cm}^{-1}$. These agree reasonably well with the *ab initio* frequencies of Raghavachari and Binkley¹⁶ scaled by a factor of 0.89, the suggested correction factor for Hartree-Fock calculations.¹⁸

From the hot band positions in our spectrum, we can learn about the vibrational frequencies of C_5^- . Assuming the spin-orbit temperature of 60 K in Fig. 1(a) is representative of the anion vibrational temperature, then, based on Raghavachari's recent calculation of the C_5^- vibrational frequencies,¹⁹ only the lowest frequency vibrational mode will have non-negligible excitation. This is the $\nu_7 \pi_u$ bending mode, the frequency of which is calculated to be 162 cm^{-1} .²⁰ In our C_5 spectrum, the $0 \leftarrow 0$ transition is by far the most intense, so we expect the largest hot band, peak a , to correspond to a $v_7' = 1 \leftarrow v_7'' = 0$ transition. Peaks a and b are separated by twice the frequency of the ν_7 mode in C_5 . We therefore assign peak b to the $v_7' = 3 \leftarrow v_7'' = 1$ transition. Peak a is located 94 cm^{-1} to the red of A from which we

find $\nu_7 = 200 \text{ cm}^{-1}$ for C_5^- . This value is close to but somewhat higher than the *ab initio* value.

An interesting feature of band X is that the peak shapes vary considerably. Peak E , which corresponds to a transition involving the totally symmetric ν_2 mode, is a doublet split by the energy difference between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ anion spin-orbit states. In contrast, peaks B , C , and F appear as singlets; each of these peaks corresponds to a transition to the $v' = 2$ level of a degenerate bending mode of C_5 . The width of these peaks is about $30 \pm 10 \text{ cm}^{-1}$ and is considerably larger than the instrumental resolution under which the spectrum was obtained. We believe these peaks consist of closely spaced overlapping transitions and offer the following explanation.

For a linear molecule such as C_5 in a $^1\Sigma_g^+$ electronic state, the excitation of 2 quanta in a degenerate vibrational mode results in two states of symmetry Σ and Δ with vibrational angular momentum $l = 0$ and 2, respectively. These are degenerate for a two-dimensional harmonic oscillator, but anharmonicity can remove this degeneracy. If the splitting of these vibrational levels in C_5 is comparable to the spin-orbit splitting in C_5^- , then the $v' = 2 \leftarrow v'' = 0$ photodetachment transition could be composed of two overlapping pairs of transitions, namely, the $\Sigma \leftarrow ^2\Pi_{1/2,3/2}$ and $\Delta \leftarrow ^2\Pi_{1/2,3/2}$ transitions, yielding a single broad feature in the spectrum. The second pair of transitions (to the $\text{C}_5 \Delta$ state) is allowed only if there is vibronic coupling in the anion.²¹ The extent of this coupling is unknown, but we note that similar (although not identical) effects have been seen in the $^2\Sigma \leftarrow ^2\Pi$ electronic absorption spectra of NCO ,²² BO_2 ,²³ and the $^1\Sigma \leftarrow ^1\Pi$ absorption spectrum of C_3 .²⁴

Further insight into the nature of the vibrational levels of C_5 is provided by the intensity and shape of peak D . This peak is assigned to the transition to the $2\nu_7 + 2\nu_5$ level of C_5 on the basis of its position. However, this peak is nearly as intense as peaks B and C , which are transitions to the $2\nu_7$ and $2\nu_5$ vibrational levels, respectively, whereas a simple normal mode picture would lead one to expect a combination band such as peak D to be considerably less intense. One possible explanation of the anomalous intensity is the assignment of this peak to a Fermi-type resonance;²⁵ the component of the $2\nu_7 + 2\nu_5$ level with Σ symmetry and vibrational angular momentum $l = 0$ can interact with the nearby $\nu_2 = 1$ symmetric stretch level, and peak D therefore borrows intensity from peak E , the $v_2' = 1 \leftarrow v_2'' = 0$ transition. Peak D is a doublet split by 22 cm^{-1} , the anion spin-orbit splitting, indicating that only transitions to a single C_5 vibrational state are occurring. This is consistent with the idea of a Fermi resonance in which only transitions to the $l = 0$ component of the $2\nu_7 + 2\nu_5$ level borrow intensity. Hence, unlike peaks B , C , and F , peak D appears as a doublet, rather than an unresolved quartet.

In Fig. 1(a), we observe a second band labeled a at higher energy than band X. The peaks are noticeably broader in band a , and the most prominent peaks (G, H, I) do not appear to be transitions to vibrationally excited levels of the C_5 ground electronic state. Instead, band a appears to be a transition to an excited electronic state of C_5 .

If this state is linear, one can speculate on its nature by considering the molecular orbitals of C_5 and C_5^- . The valence molecular orbital configuration for C_5^- is $\sigma_g^2\sigma_u^2\pi_g^4\pi_u^1$. Removal of an electron from the HOMO (π_u) yields the $X^1\Sigma_g^+$ ground electronic state of C_5 . Similarly, the removal of other electrons will result in the formation of excited neutral electronic states. As discussed elsewhere,^{8,10} in threshold photodetachment spectroscopy we can only observe transitions which involve *s*-wave photodetachment, where the orbital angular momentum of the ejected electron is zero. Reed *et al.*²⁶ have shown that for $D_{\infty h}$ symmetry, *s*-wave photodetachment occurs *only* when the photoelectron is detached from either a π_u or σ_u orbital. Hence, if band **a** is a transition to a linear excited electronic state, it must involve the removal of a σ_u electron. The lowest state from the resulting $\sigma_g^2\sigma_u^1\pi_g^4\pi_u^1$ configuration is the $a^3\Pi_g$ state.

This assignment offers a qualitative explanation of the broad peaks in band **a**. Assuming Hund's case (a) coupling, the $a^3\Pi_g$ state will split into three spin-orbit components; all six possible transitions from the $^2\Pi_u$ anion state are allowed and should occur. If the magnitude of the spin-orbit splitting in the $a^3\Pi_g$ state is such that adjacent $a^3\Pi_{0,1,2} \leftarrow ^2\Pi_{1/2,3/2}$ transitions are too close in energy to be resolved, the six transitions will appear as an unresolved single peak, in agreement with our spectrum.

On the other hand, the vibrational structure in band **a**, while not assigned, looks more complex than expected for a linear anion \rightarrow linear neutral transition. In addition to the major peaks *G*, *H*, and *I*, we observe an extended progression of smaller peaks with an average separation of $200 \pm 50 \text{ cm}^{-1}$. Another point to consider is that an *ab initio* MRD CI calculations by Pacchioni and Koutecký²⁷ on linear excited electronic states of C_5 found the $^3\Pi_g$ state to lie 2.56 eV higher than the $^1\Sigma_g^+$ state, whereas band **a** begins about 0.26 eV above band **X** in our spectrum. Whether this substantial discrepancy arises from inaccuracies in the calculation or from an incorrect interpretation of our spectrum remains to be seen.

Another explanation of the peaks in band **a** is that they result from autodetachment from a metastable excited electronic state of C_5^- . Recently, Adamowicz²⁸ has predicted the existence of such a state 3.08 eV above the C_5^- ground state and is optically accessible ($a^2\Sigma_g^-$ state with configuration $\sigma_g^2\sigma_u^1\pi_g^4\pi_u^2$). The predicted energy is right in the middle of band **a**. However, there are two reasons we believe band **a** is not due to autodetachment. First of all, the major peaks in band **a** do appear in our lower resolution photoelectron spectrum,⁷ although the intensity of these peaks is higher in the threshold spectrum. Second, electrons generated by the decay of an autodetaching anion state are, in general, going to have more than 10 cm^{-1} of kinetic energy and are normally discriminated against by our detection scheme. To check for autodetachment we collected *all* the electrons generated by the photodetachment, but no structure was observed in the region of band **a**. We therefore believe band **a** is from direct detachment to an excited state of C_5 , but the nature of this state is open to question.

In conclusion, we have obtained the vibrationally re-

solved threshold photodetachment of C_5^- , and have presented a preliminary assignment which explains many of the features in our spectrum. Further analysis which involves modeling the potentials for both the C_5 and C_5^- ground and excited electronic states is necessary. We hope that our results will prompt more detailed theoretical work which will help us with our analysis. This report demonstrates that threshold photodetachment spectroscopy is a powerful technique for studying polyatomic clusters. We have recently obtained the threshold photodetachment spectra for other carbon clusters and will report on this in the near future.

This research is supported by the Office of Naval Research under Contract No. N0014-87-0495. We thank Krishnan Raghavachari for unpublished results on C_5^- .

^aNSF Predoctoral Fellow.

^bNSF Presidential Young Investigator and Alfred P. Sloan Fellow.

- ¹W. Weltner, Jr. and R. J. VanZee, *Chem. Rev.* **89**, 1713 (1989).
- ²J. Ho, K. M. Ervin, and W. C. Lineberger, *J. Chem. Phys.* **94**, 3670 (1991).
- ³L. A. Posey, M. J. Deluca, and M. A. Johnson, *Chem. Phys. Lett.* **131**, 170 (1986); L. A. Posey and M. A. Johnson, *J. Chem. Phys.* **88**, 5383 (1988).
- ⁴K. M. McHugh, J. G. Eaton, G. H. Lee, H. W. Sarkas, L. H. Kidder, J. T. Snodgrass, M. R. Manaa, and K. H. Bowen, *J. Chem. Phys.* **91**, 3792 (1989).
- ⁵G. Ganteför, M. Gausa, K. H. Meiwes-Broer, and H. O. Lutz, *Z. Phys.* **D 9**, 253 (1989).
- ⁶S. Yang, K. J. Taylor, M. J. Craycraft, J. Conceicao, C. L. Pettiette, O. Cheshnovsky, and R. E. Smalley, *Chem. Phys. Lett.* **144**, 431 (1988).
- ⁷D. W. Arnold, S. E. Bradforth, T. N. Kitsopoulos, and D. M. Neumark, *J. Chem. Phys.* (in press).
- ⁸T. N. Kitsopoulos, I. M. Waller, J. G. Loeser, and D. M. Neumark, *Chem. Phys. Lett.* **159**, 300 (1989).
- ⁹G. F. Ganteför, D. M. Cox, and A. Kaldor, *J. Chem. Phys.* **94**, 854 (1990).
- ¹⁰T. N. Kitsopoulos, C. J. Chick, Y. Zhao, and D. M. Neumark, *J. Chem. Phys.* **95**, 1441 (1991).
- ¹¹K. Müller-Dethlefs, M. Sander, and E. W. Schlag, *Z. Naturforsch.* **39a**, 1089 (1984).
- ¹²J. R. Heath, A. L. Cooksy, M. H. W. Gruebele, C. A. Schmuttenmaer, and R. J. Saykally, *Science* **244**, 564 (1989).
- ¹³P. F. Bernath, K. H. Hinkle, and J. J. Keady, *Science* **244**, 562 (1989).
- ¹⁴N. Moazzen-Ahmadi, A. R. W. McKellar, and T. Amano, *J. Chem. Phys.* **91**, 2140 (1989).
- ¹⁵K. S. Pitzer and E. Clementi, *J. Am. Chem. Soc.* **81**, 4477 (1959).
- ¹⁶K. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).
- ¹⁷G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ¹⁸J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, *Int. J. Quantum Chem. Symp.* **15**, 269 (1981).
- ¹⁹K. Raghavachari (private communication).
- ²⁰Actually, the degeneracy of this mode is split slightly because of the Π electronic state; the value given is the average.
- ²¹Reference 17, p. 159.
- ²²P. S. H. Bolman, J. M. Brown, A. Carrington, I. Kopp, and D. A. Ramsay, *Proc. R. Soc. London, Ser. A* **343**, 17 (1975).
- ²³J. W. C. Johns, *Can. J. Phys.* **39**, 1738 (1961).
- ²⁴E. A. Rohlfing and J. E. M. Goldsmith, *J. Opt. Soc. Am. B* **7**, 1915 (1990); F. J. Northrup and T. J. Sears, *J. Opt. Soc. Am. B* **7**, 1924 (1990).
- ²⁵G. Herzberg, *Infrared and Raman Spectra* (Van Nostrand Reinhold, New York, 1979).
- ²⁶K. J. Reed, A. H. Zimmerman, H. C. Andersen, and J. I. Brauman, *J. Chem. Phys.* **64**, 1368 (1976).
- ²⁷G. Pacchioni and J. Koutecký, *J. Chem. Phys.* **88**, 1066 (1988).
- ²⁸L. Adamowicz, *Chem. Phys. Lett.* **180**, 466 (1991).