# Vibrationally resolved photoelectron spectra of $Si_3^-$ and $Si_4^-$

T. N. Kitsopoulos, C. J. Chick[a], A. Weaver, and D. M. Neumark[b]
*Department of Chemistry, University of California, Berkeley, California 94720*

(Received 30 July 1990; accepted 13 August 1990)

The study of elemental clusters has received a great deal of experimental attention in recent years. A major goal of this effort is to understand how the structure and properties of a cluster depend on its size. However, little is known about the spectroscopy of clusters with three or more atoms. For example, spectra showing resolved vibrational features have been observed for only a handful of such clusters in the gas phase.[1-7] The measurement of vibrational frequencies is an important first step towards understanding the nature of chemical bonding in a cluster.

Negative ion photoelectron spectroscopy offers a promising experimental technique for the study of size-selected elemental clusters. In a typical experiment, a mass-selected beam of negative cluster ions is photodetached and the resulting electron kinetic energy distribution is analyzed, thereby probing the electronic and vibrational states of the neutral cluster formed by photodetachment. This technique offers the considerable advantage of eliminating any ambiguity concerning the size of the cluster under investigation, and has been used by Lineberger,[5,8] Smalley,[9-11] Bowen,[12] Meiwes-Bröer,[13] and their co-workers to study polyatomic metal and semiconductor clusters. However, the resolution of a photoelectron spectrometer is, at best, 50–100 $cm^{-1}$, and only Lineberger's spectra[5] of $Pd_3^-$ and $Pt_3^-$ have shown resolved vibrational structure.

In this Communication, we present photoelectron spectra of $Si_3^-$ and $Si_4^-$ which show resolved vibrational progressions in several electronic states of the neutral clusters. The photoelectron spectra of these anions were first reported by Smalley,[9] but the resolution of his spectra was around 1200 $cm^{-1}$. Our spectra are obtained at considerably higher resolution, thereby enabling the observation of vibrational structure. The interpretation of these spectra is aided by the *ab initio* calculations on small neutral Si clusters which have been performed by several investigators,[14-21] and by recent calculations on Si cluster anions by Raghavachari and Rohlfing.[22]

The instrument used in these studies is a modified version of our negative ion time-of-flight photoelectron spectrometer described in detail elsewhere.[23] The instrument is similar to that first described by Johnson and co-workers.[24] A beam of cold anions is mass selected using a time-of-flight mass spectrometer, and the mass-selected anions are photodetached with a pulsed laser. A small fraction ($10^{-4}$) of the ejected photoelectrons is energy analyzed by time of flight. The electron energy resolution is 8 meV (64 $cm^{-1}$) for electrons with 0.65 eV of kinetic energy and degrades as $(KE)^{3/2}$. The spectra below were obtained with third and fourth harmonics of a Nd:YAG laser (20 Hz repetition rate) at 355 nm (3.49 eV) and 266 nm (4.66 eV), respectively, and each was signal averaged for 250 000 laser shots. The laser polarization was set at the "magic angle" ($\theta = 54.7°$) with respect to the direction of electron detection. This eliminates any intensity effects due to anisotropy in the electron angular distribution.

The silicon cluster anions are generated with a laser-vaporization/pulsed molecular beam source.[25] In this source, the output of a XeCl excimer laser (308 nm, 5–15 mJ/pulse) is focused onto the surface of a rotating and translating silicon rod. The resulting plasma is entrained in a gas pulse of He from a pulsed beam valve and passes through a 0.25 cm diameter, 1.25 cm long channel before expansion into the vacuum chamber. The He backing pressure behind the pulsed valve (0.05 cm diameter orifice) is typically 100 psig. This source configuration produces $Si_n^-$ clusters with $n \leqslant 15$.

The photoelectron spectra of $Si_3^-$ obtained at 355 and 266 nm are shown in Figs. 1(a) and 1(b). The 355 nm spectrum shows two distinct bands, labeled *X* and *B*. The *X* band shows a resolved vibrational progression of nine peaks with an average spacing of $360 \pm 40$ $cm^{-1}$, while the *B* band consists of a single sharp (20 meV FWHM) peak. In the 266 nm spectrum, a band between the *X* and *B* bands becomes apparent. This band, labeled *A*, consists of five peaks with an average spacing of $480 \pm 40$ $cm^{-1}$. In addition, two more bands labeled *C* and *D* appear at the higher photon energy. The *C* band shows extended, irregular vibrational structure, while the *D* band consists of two peaks separated by 480 $cm^{-1}$. We expect the cluster anions to be sufficiently cold that the peak spacings in each band correspond to vibrational frequencies in the neutral cluster, rather than to anion frequencies due to "hot band" transitions.

Assuming these transitions originate from the ground electronic state of $Si_3^-$, each band corresponds to a different electronic state of $Si_3$, with the *X* band corresponding to the ground state. The estimated origin of each band is indicated by an arrow. From the *X* band origin in Fig. 1(a), we obtain 2.33 eV for the electron affinity of $Si_3$. This assumes that the weak signal at electron energies $> 1.16$ eV is due to transitions from vibrationally excited $Si_3^-$. The energies of the excited $Si_3$ electronic states relative to the ground state are then *A*(0.45 eV), *B*(0.89 eV), *C*(1.10 eV), and *D*(1.67 eV).

The photoelectron spectra of $Si_4^-$ obtained at 355 and 266 nm are shown in Figs. 2(a) and 2(b). We observe four bands corresponding to transitions to various electronic states of the neutral tetramer. The electron affinity of the $Si_4$ ground state, labeled *X*, is 2.15 eV, and the three excited

[a]NSF Predoctoral Fellow.
[b]NSF Presidential Young Investigator and Alfred P. Sloan Fellow.

 0021-9606/90/206108-03$03.00 © 1990 American Institute of Physics

Downloaded 03 Mar 2003 to 128.32.220.150. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

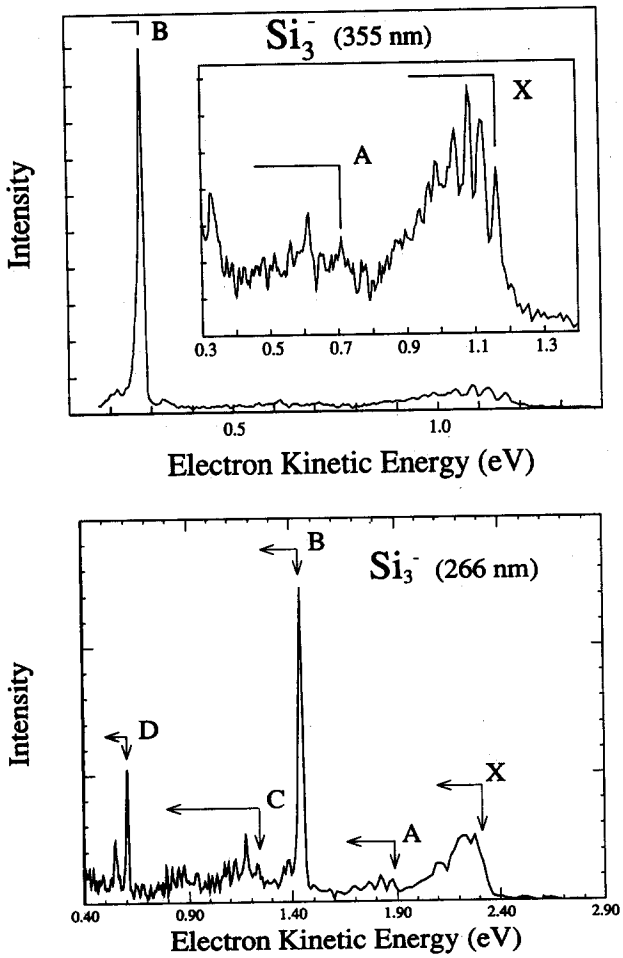


FIG. 1. Photoelectron spectra of $Si_3^-$ at (a) 355 nm and (b) 266 nm. Estimated band origins are indicated with arrows. The inset in (a) shows the *X* and *A* bands magnified in intensity by a factor of 10. The A band origin is obtained from the 255 nm spectrum.

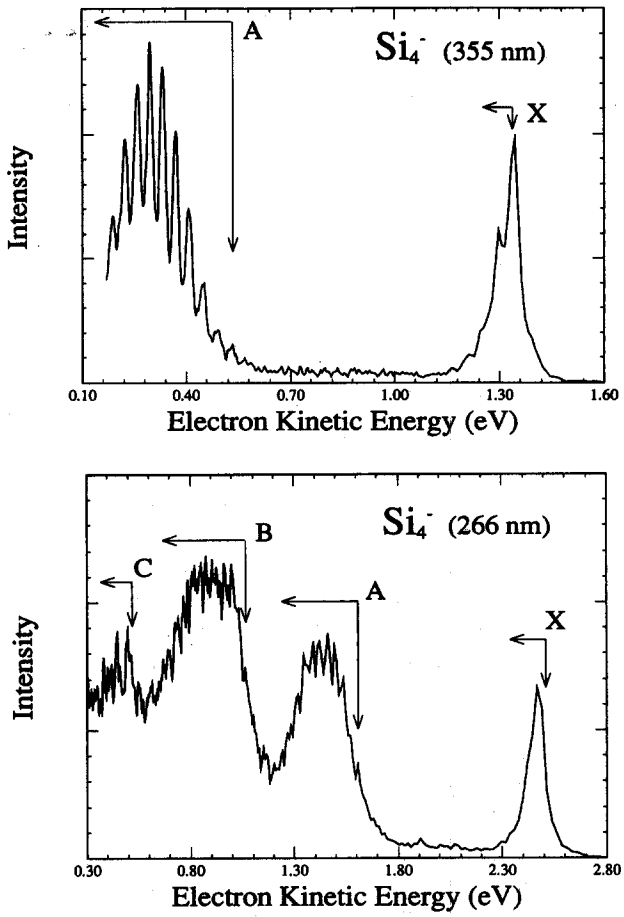


FIG. 2. Photoelectron spectra of $Si_4^-$ at (a) 355 nm and (b) 266 nm. Estimated band origins are indicated with arrows.

states *A*, *B*, and *C* lie 0.81, 1.45, and 2.01 eV, respectively, above the ground state. In the 355 nm spectrum, the *X* band is considerably narrower than the *A* band. The *X* band exhibits a partially resolved vibrational progression of three peaks with frequency $360 \pm 25$ cm$^{-1}$, and the *A* band shows a well-resolved progression of ten peaks with frequency $300 \pm 25$ cm$^{-1}$. In the 266 nm spectrum, the *B* band shows irregular vibrational structure, while a four peak progression with frequency $450 \pm 65$ cm$^{-1}$ is observed in the *C* band.

In order to interpret our spectra, we consider the previous *ab initio* calculations of electronic energies and vibrational frequencies in neutral $Si_3$ and $Si_4$,[15,16,18,19] as well as the recently calculated ground state geometries for $Si_3^-$ and $Si_4^-$.[22] Although we cannot be certain which vibrational modes are responsible for the observed progressions, photoelectron spectra are usually dominated by progressions in totally symmetric modes, with the length of the progressions determined by the geometry change between the anion and neutral.

We first consider the silicon tetramer. A planar rhombus geometry with $D_{2h}$ symmetry is predicted for both the anion $^2B_{2g}$ and neutral $^1A_g$ ground states. The bond lengths differ by only 0.02 Å.[16,22] The relatively short progression we observe in the *X* band is consistent with this small geometry change. In addition, the experimental frequency (360 cm$^{-1}$) is close to the calculated frequency[16] of 380 cm$^{-1}$ for one of the totally symmetric modes of the neutral $^1A_g$ ground state. Thus, our spectra are qualitatively consistent with the calculated anion and neutral ground states.

Raghavachari[16] calculates the first excited state of $Si_4$ to be a nonplanar $D_{2d}$ species ($^3A_2$ term symbol) 1.1 eV above the ground state. This lies between the observed *A*–*X* and *B*–*X* spacings of 0.81 and 1.45 eV, respectively. Photodetachment to this state from a $D_{2h}$ anion should yield extended vibrational progressions, and both the *A* and *B* bands are considerably more extended than the ground state progression. Thus, either the *A* or *B* state could correspond to the predicted $^3A_2$ state. The calculated frequencies for the two totally symmetric modes of the $^3A_2$ state are 166 and 425 cm$^{-1}$. These disagree with the experimental *A* state frequency of 300 cm$^{-1}$, but excitation of both modes could lead to a congested spectrum such as the *B* band. In another calculation, Balasubramanian[19] finds a square excited state of $Si_4$ 1.41 eV above the ground state. This agrees with the experimental *B*–*X* splitting. However, Raghavachari finds that this state is not a local minimum and undergoes out-of-plane distortion to the $D_{2d}$ state.

The interpretation of the $Si_3^-$ spectrum is more complicated. $Si_3^-$ is predicted[22] to have a $^2A_1$ ground state with



Downloaded 03 Mar 2003 to 128.32.220.150. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

$C_{2v}$ symmetry and a bond angle of 66°. The calculations on $Si_3$ predict a $^1A_1C_{2v}$ ground state with a bond angle near 78° and a low-lying $^3A_2'D_{3h}$ excited state which lies between 0.03[16] and 0.16 eV[19] above the ground state. This suggests that the $X$ band consists of two overlapping electronic states, a definite possibility considering the irregular appearance of the band. However, the $X$ band vibrational frequency of 360 $cm^{-1}$ disagrees with the calculated frequencies 206 and 582 $cm^{-1}$ [16] for the totally symmetric modes of the $^1A_1$ ground state, and with the calculated value[15] of 528 $cm^{-1}$ for the totally symmetric mode in the $^3A_2'$ state.

Balasubramanian[19] calculates the $^1B_2$ and $^3B_1$ excited states of $Si_3$ to lie 0.41 and 0.89 eV, respectively, above the ground state. These values are very close to the experimental $A$–$X$ and $B$–$X$ spacings. This agreement may be fortuitous, however, since the excited states were constrained to a $D_{3h}$ geometry in the calculation; the extended progression for the $A$ band and the single peak for the $B$ band indicate that the $A$ and $B$ states have different geometries. In particular, the $B$ state must have a geometry similar to that of the anion.

In summary, the $Si_4^-$ photoelectron spectrum is qualitatively consistent with the predicted $D_{2h}$ ground state geometries for $Si_4^-$ and $Si_4$. The correspondence between experiment and theory is not as clear for the trimer or the excited states of the tetramer. We hope that the results presented here stimulate further *ab initio* studies of these species. On the experimental side, we plan to investigate these clusters at higher resolution (3–5 $cm^{-1}$) using our negative ion threshold photodetachment spectrometer.[26] This should provide considerably more information on the vibrational frequencies and low-lying electronic states of small silicon clusters.

This research is supported by the Office of Naval Research Chemistry Division and Young Investigator Program under Grant No. N0014-87-0485. We thank Krishnan Raghavachari and Celeste Rohlfing for communicating their results on Si cluster anions prior to publication.

[1] A. Herrmann, M. Hofmann, S. Leutwyler, E. Schumacher, and L. Wöste, Chem. Phys. Lett. **62**, 216 (1979); J. L. Gole, S. A. Pace, D. R. Preuss, and G. J. Green, J. Chem. Phys. **76**, 2247 (1982); G. Delacrétaz, E. R. Grant, R. L. Whetten, L. Wöste, and J. W. Zwanziger, Phys. Rev. Lett. **56**, 2598 (1986).
[2] M. D. Morse, J. B. Hopkins, P. R. R. Langridge-Smith, and R. E. Smalley, J. Chem. Phys. **79**, 5316 (1983); W. H. Crumley, J. S. Hayden, and J. L. Gole, *ibid.* **84**, 5250 (1986); E. A. Rohlfing and J. J. Valentini, Chem. Phys. Lett. **126**, 113 (1986).
[3] P. Y. Cheng and M. A. Duncan, Chem. Phys. Lett. **152**, 341 (1988).
[4] Z. Fu, G. W. Lemire, Y. M. Hamrick, S. Taylor, J.-C. Shui, and M. D. Morse, J. Chem. Phys. **88**, 3524 (1988).
[5] K. M. Ervin, J. Ho, and W. C. Lineberger, J. Chem. Phys. **89**, 4514 (1988); R. W. Woodward, S. H. Cobb, and J. L. Gole, J. Phys. Chem. **92**, 1404 (1988).
[6] M. F. Jarrold and K. M. Creegan, Chem. Phys. Lett. **166**, 116 (1990).
[7] P. F. Bernath, K. H. Kinkle, and J. J. Keady, Science **244**, 562 (1989); J. R. Heath, A. L. Cooksy, M. H. W. Gruebele, C. A. Schmuttenmaer, and R. J. Saykally, *ibid.* **244**, 564 (1989); N. Moazzen-Ahmadi, A. R. W. McKellar, and T. Amano, J. Chem. Phys. **91**, 2140 (1989).
[8] D. G. Leopold, J. Ho, and W. C. Lineberger, J. Chem. Phys. **86**, 1715 (1987).
[9] O. Cheshnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, Y. Liu, and R. E. Smalley, Chem. Phys. Lett. **138**, 119 (1987).
[10] S. H. Yang, C. L. Pettiette, J. Conceicao, O. Cheshnovsky, and R. E. Smalley, Chem. Phys. Lett. **139**, 233 (1987); S. Yang, K. J. Taylor, M. J. Craycraft, J. Conceicao, C. L. Pettiette, O. Cheshnovsky, and R. E. Smalley, *ibid.* **144**, 431 (1988).
[11] K. J. Taylor, C. L. Pettiette, M. J. Craycraft, O. Cheshnovsky, and R. E. Smalley, Chem. Phys. Lett. **152**, 347 (1988).
[12] K. 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**, 3702 (1989).
[13] G. Gantefor, M. Gausa, K. H. Meiwes-Bröer, and H. O. Lutz, Z. Phys. D **9**, 253 (1988); Faraday Discuss. Chem. Soc. **86**, 197 (1988).
[14] G. H. F. Diercksen, N. E. Gruner, J. Oddershede, and J. R. Sabin, Chem. Phys. Lett. **117**, 29 (1985).
[15] R. S. Grev and H.F. Schaefer, Chem. Phys. Lett. **119**, 111 (1985).
[16] K. Raghavachari, J. Chem. Phys. **83**, 3520 (1985); **84**, 5672 (1986).
[17] D. Tomanek and M. A. Schluter, Phys. Rev. Lett. **56**, 1055 (1986).
[18] G. Pacchioni and J. Koutecky, J. Chem. Phys. **84**, 3301 (1986).
[19] K. Balasubramanian, Chem. Phys. Lett. **125**, 400 (1986); **135**, 283 (1987).
[20] P. Ballone, W. Andreoni, R. Car, and M. Parrinello, Phys. Rev. Lett. **60**, 271 (1988).
[21] K. Raghavachari and C. M. Rohlfing, J. Chem. Phys. **89**, 2219 (1988).
[22] K. Raghavachari and C. M. Rohlfing (private communication).
[23] R. B. Metz, A. Weaver, S. E. Bradforth, T. N. Kitsopoulos, and D. M. Neumark, J. Phys. Chem. **94**, 1377 (1990).
[24] L. A. Posey, M. J. DeLuca, and M. A. Johnson, Chem. Phys. Lett. **131**, 170 (1986).
[25] T. G. Dietz, M. A. Duncan, D. E. Powers, and R. E. Smalley, J. Chem. Phys. **74**, 6511 (1981); V. E. Bondybey and J. H. English **74**, 6978 (1981).
[26] T. N. Kitsopoulos, I. M. Waller, J. G. Loeser, and D. M. Neumark, Chem. Phys. Lett. **159**, 300 (1989).



Downloaded 03 Mar 2003 to 128.32.220.150. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp