Reassignment of the Si_2^- photodetachment spectra

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Upon reanalysis of our silicon cluster data, we have discovered that our analysis of our Si_2^- photoelectron and threshold photodetachment spectra reported previously[1] is incorrect. The mistake lies in improperly correlating peaks seen in the photoelectron spectrum (PES) with those found in the threshold photodetachment (or zero electron kinetic energy—ZEKE) spectrum. Figure 1 shows the PES of Si_2^- with the detachment laser wavelength of 355 nm (3.493 eV) and polarization 90° with respect to the electron detection. Figure 2 shows the ZEKE spectrum of Si_2^- corresponding to the 1.1–1.4 eV region in the PES. Originally, we believed that peaks *d* and *C* in the PES corresponded, respectively, to the triplet feature at 555 nm and the doublet feature found at 570 nm in the ZEKE spectrum. However, a more careful calibration indicates that the triplet corresponds to peak *D* in PES, and that peak *d* is absent in the ZEKE spectrum. The energy interval between 570 and 555 nm is 532 cm^{-1}. Peaks *d* and *C* on the PES are separated by only 350 cm^{-1}, while *D* and *C* are separated by 550 cm^{-1}. The ZEKE spectrum shown in Fig. 2 has been relabeled to correctly reflect the correspondence with the PES peaks.

This change affects the relative energies of the low-lying states of Si_2 and Si_2^-, which are displayed in Fig. 3. Peaks *A* through *F* are assigned to transitions between two nearly degenerate doublet states of the anion and the two nearby triplet states of the neutral. The assignment of the ZEKE spectrum is the same as before: the triplets (peaks *D*, *E*) are due to $^3\Pi_u \leftarrow {}^2\Sigma_g^+$ transitions, and the doublets (peaks *B*,*C*) are from $^3\Sigma_g^- \leftarrow {}^2\Pi_u$ transitions. (The triplet and doublet structure is from the spin–orbit fine structure in the $^3\Pi_u$ and $^2\Pi_u$ states, respectively.) However, the PES assignment is now altered: peak *D* is the $^3\Pi_u \leftarrow {}^2\Sigma_g^+$ transition, while peak *d* is the $^3\Pi_u \leftarrow {}^2\Pi_u$ transition; this assignment was reversed in our previous paper. Peak *d* is observed in the PES but not the ZEKE spectrum because it is a *p*-wave transition involving ejection of a photoelectron with orbital angular momentum $l=1$; the threshold photodetachment spectrometer is sensitive only to *s*-wave ($l=0$) photodetachment transitions, since, according to the Wigner threshold law,[2] these are the only transitions with substantial cross sections near the detachment threshold. The implications of this reassignment are as follows. Since peak *D* corresponds to a higher energy transition than peak *d*, the $^2\Sigma_g$ state of the anion must lie below, rather than above, the $^2\Pi_u$ stated. This means that the energy of peak *C* no longer corresponds to the electron affinity of Si_2 because it is not the transition between the lowest electronic states of the anion and neutral. The "electron affinity" transition, from the anion $^2\Sigma_g$ state to the neutral $^3\Sigma_g^-$ state, is a two-electron transition, involving both photodetachment and rearrangement of the remaining electrons. Such a transition is, in general, too weak to be observed in either the PES or ZEKE spectrum. We therefore do not see the electron affinity transition here, although the electron affinity can be extracted from the observed transitions.

A similar error was made in the singlet manifold, peaks *G*–*L*. The transitions are shown in Fig. 3. Figure 4 shows the threshold photodetachment spectrum in the 0.6 to 0.95 eV energy region in the PES. The peak found at 451 nm was originally believed to correspond to peak *I* in the PES. However, with our improved PES data calibration, we now know that it corresponds to peak *J* in the PES. The 451 nm peak was correctly assigned to the $b\,^1\Pi_u \leftarrow {}^2\Sigma_g^+$ transition. Peak *I* in the PES is then assigned to the $b\,^1\Pi_u \leftarrow {}^2\Pi_u$ transition, a *p*-wave transition that will not be observed in the ZEKE spectrum. The relative position of

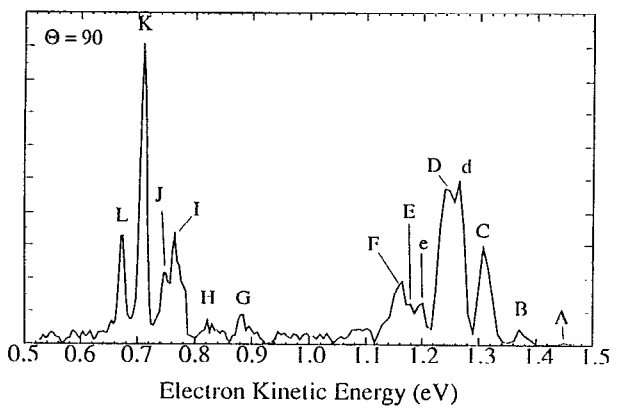

FIG. 1. Photoelectron spectrum of Si_2^-. The detachment wavelength is 355 nm.

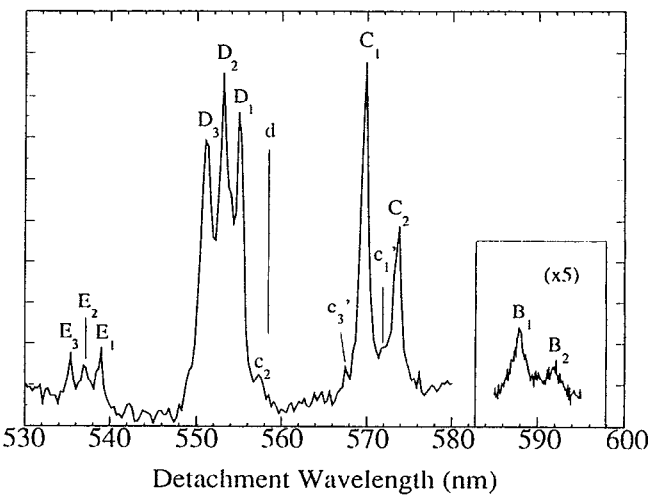

FIG. 2. ZEKE spectrum of Si_2^- showing transitions to the triplet states of Si_2.

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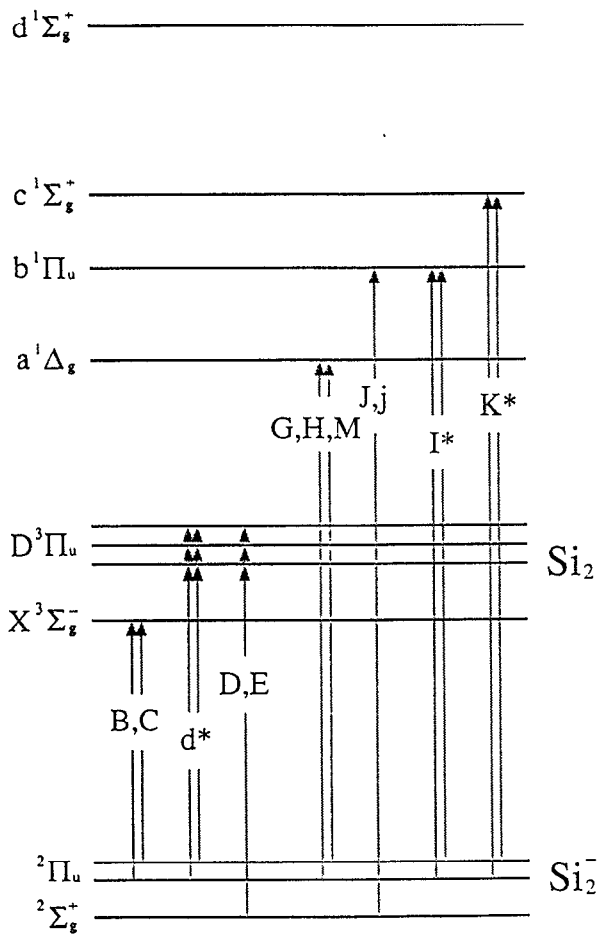

FIG. 3. One-electron transitions between the low-lying states of Si_2^- and Si_2. Those marked with an asterisk are *p*-wave transitions. Multiple letters correspond to different vibrational transitions (see Table I).

these two peaks is consistent with the $^2\Sigma_g^+$ state being the ground state of the anion.

Several of the peak labels in Figs. 5 and 6, and Table I in Ref. 1 should be changed in order to properly reflect the

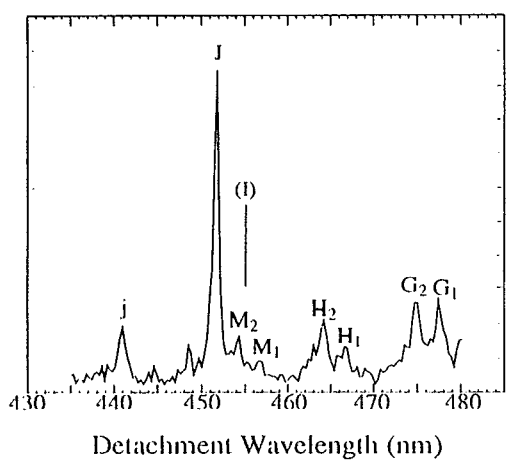

FIG. 4. ZEKE spectrum of Si_2^- showing transitions to the singlet states of Si_2.

TABLE I. Peak positions and assignments for the ZEKE spectrum of Si_2^-. Peaks marked with an asterisk were not seen on the ZEKE spectrum, and are taken from the PES spectrum.

Peak	Position (eV)	Assignment
B_2	2.096	$X\,^3\Sigma_g(v'=0) \leftarrow ^2\Pi_{1/2}(v''=1)$
B_1	2.110	$X\,^3\Sigma_g(v'=0) \leftarrow ^2\Pi_{1/2}(v''=1)$
C_2	2.162	$X\,^3\Sigma_g(v'=0) \leftarrow ^2\Pi_{1/2}(v''=0)$
c_1'	2.166	$D\,^3\Pi_2(v'=0) \leftarrow ^2\Sigma_g^+(v''=1)$
C_1	2.177	$X\,^3\Sigma_g(v'=0) \leftarrow ^2\Pi_{3/2}(v''=0)$
c_3'	2.186	$D\,^3\Pi_0(v'=0) \leftarrow ^2\Sigma_g^+(v''=1)$
d^*	2.222	$D\,^3\Pi_u(v'=0) \leftarrow ^2\Pi_u(v''=0)$
c_2	2.225	$X\,^3\Sigma_g(v'=1) \leftarrow ^2\Pi_{1/2}(v''=0)$
D_1	2.235	$D\,^3\Pi_2(v'=0) \leftarrow ^2\Sigma_g^+(v''=0)$
D_2	2.243	$D\,^3\Pi_1(v'=0) \leftarrow ^2\Sigma_g^+(v''=0)$
D_3	2.251	$D\,^3\Pi_0(v'=0) \leftarrow ^2\Sigma_g^+(v''=0)$
e^*	2.287	$D\,^3\Pi_u(v'=1) \leftarrow ^2\Pi_u(v''=0)$
E_1	2.304	$D\,^3\Pi_2(v'=1) \leftarrow ^2\Sigma_g^+(v''=0)$
E_2	2.310	$D\,^3\Pi_1(v'=1) \leftarrow ^2\Sigma_g^+(v''=0)$
E_3	2.317	$D\,^3\Pi_0(v'=1) \leftarrow ^2\Sigma_g^+(v''=0)$
F^*	2.326	?
G_1	2.598	$a\,^1\Delta_g(v'=0) \leftarrow ^2\Pi_{1/2}(v''=0)$
G_2	2.612	$a\,^1\Delta_g(v'=0) \leftarrow ^2\Pi_{3/2}(v''=0)$
H_1	2.658	$a\,^1\Delta_g(v'=1) \leftarrow ^2\Pi_{1/2}(v''=0)$
H_2	2.672	$a\,^1\Delta_g(v'=1) \leftarrow ^2\Pi_{3/2}(v''=0)$
M_1	2.716	$a\,^1\Delta_g(v'=2) \leftarrow ^2\Pi_{1/2}(v''=0)$
M_2	2.729	$a\,^1\Delta_g(v'=2) \leftarrow ^2\Pi_{3/2}(v''=0)$
I^*	2.722	$b\,^1\Pi_u(v'=0) \leftarrow ^2\Pi_u(v''=0)$
J	2.746	$b\,^1\Pi_u(v'=0) \leftarrow ^2\Sigma_g^+(v''=0)$
K^*	2.787	$c\,^1\Sigma_g^+(v'=0) \leftarrow ^2\Sigma_g^+(v''=0)$
j	2.812	$b\,^1\Pi_u(v'=1) \leftarrow ^2\Sigma_g^+(v''=0)$
L^*	2.826	?

relationship between the PES and the threshold photodetachment spectrum. As mentioned before, $d_{1,2,3}$ and $e_{1,2,3}$ in Fig. 5, Ref. 1 should be changed to $D_{1,2,3}$ and $E_{1,2,3}$. Likewise, peaks *I* and *i* in Fig. 6, Ref. 1 should be changed to *J* and *j*. Figures 2 and 4 presented here have these new labels. Also indicated by vertical lines in Figs. 2 and 4 are the positions of peaks *d* and *I* taken from the newly calibrated PES data.

Table I lists these threshold spectral peaks by the new label along with the position and assignment. Additionally, the *p*-wave transitions observed only in the PES are included in Table I with the improved energy position. These are marked by an asterisk (*). Several of these peaks have different assignments than they were given in Ref. 1 as a result of the above discussion. Table II summarizes the excitation energies of the anion and neutral states based on

TABLE II. Excitation energies for the low-lying states of Si_2 and Si_2^-.

	State	T_e (eV)
	$d\,^1\Sigma_g^+$	1.152±0.010
	$c\,^1\Sigma_g^+$	0.586±0.010
Si_2	$b^1\Pi_u$	0.544±0.010
E.A.=2.202±0.010 eV	$a\,^1\Delta_g$	0.435±0.002
	$D\,^3\Pi_u$	0.041±0.010
	$X\,^3\Sigma_g$	0
	$^2\Pi_u$	0.025±0.010
Si_2^-	$^2\Sigma_g^+$	0

the correct ordering of the anion states.[3] The correct electron affinity of Si_2, 2.202 ± 0.01 eV, is also given. Vibrational frequencies and spin–orbit splittings remain unchanged for all of the states. Note that r_e for the $^3\Pi_u$ state is 2.155 Å;[4] a typographical error was made in Ref. 1.

Interestingly, calculations performed on the anion by Bruna *et al.*,[5] Nimlos, Harding, and Ellison,[6] and Raghavachari and Rohlfing[7] predict the $^2\Sigma_g^+$ state to be the ground state. In fact, the highest level calculation performed by Raghavachari predicted the Π state to lie 22 meV above the Σ state, which is remarkably close to our experimental value of 25 meV.

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