The electronic spectrum of Si_3 I: Triplet D_{3h} system

N. J. Reilly', D. L. Kokkin, X. Zhuang, V. Gupta, R. Nagarajan, R. C. Fortenberry, J. P. Maier, T. C. Steimle, J. F. Stanton, and M. C. McCarthy

Citation: The Journal of Chemical Physics **136**, 194307 (2012); doi: 10.1063/1.4704672
View online: http://dx.doi.org/10.1063/1.4704672
View Table of Contents: http://aip.scitation.org/toc/jcp/136/19
Published by the American Institute of Physics

The electronic spectrum of Si_3 I: Triplet D_{3h} system

N. J. Reilly,[1,a)] D. L. Kokkin,[1] X. Zhuang,[2] V. Gupta,[3] R. Nagarajan,[3] R. C. Fortenberry,[4] J. P. Maier,[3] T. C. Steimle,[2] J. F. Stanton,[5] and M. C. McCarthy[1]
[1]*Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138, USA and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, Massachusetts 02138, USA*
[2]*Department of Chemistry & Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, USA*
[3]*Department of Chemistry, University of Basel, Klingebergstrasse 80, CH-4056 Basel, Switzerland*
[4]*Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, USA*
[5]*Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712-0165, USA*

(Received 14 October 2011; accepted 28 March 2012; published online 18 May 2012)

We report the measurement of a jet-cooled electronic spectrum of the silicon trimer. Si_3 was produced in a pulsed discharge of silane in argon, and the excitation spectrum examined in the 18 000–20 800 cm^{-1} region. A combination of resonant two-color two-photon ionization (R2C2PI) time-of-flight mass spectroscopy, laser-induced fluorescence/dispersed fluorescence, and equation-of-motion coupled-cluster calculations have been used to establish that the observed spectrum is dominated by the $1\,^3A_1'' - \tilde{a}\ ^3A_2'$ transition of the D_{3h} isomer. The spectrum has an origin transition at 18 600 $\pm$ 4 cm^{-1} and a short progression in the symmetric stretch with a frequency of ~445 cm^{-1}, in good agreement with a predicted vertical transition energy of 2.34 eV for excitation to the $1\,^3A_1''$ state, which has a calculated symmetric stretching frequency of 480 cm^{-1}. In addition, a ~505 cm^{-1} ground state vibrational frequency determined from sequence bands and dispersed fluorescence is in agreement with an earlier zero-electron kinetic energy study of the lowest D_{3h} state and with theory. A weaker, overlapping band system with a ~360 cm^{-1} progression, observed in the same mass channel ($m/z = 84$) by R2C2PI but under different discharge conditions, is thought to be due to transitions from the (more complicated) singlet C_{2v} ground state ($^1A_1$) state of Si_3. Evidence of emission to this latter state in the triplet dispersed fluorescence spectra suggests extensive mixing in the excited triplet and singlet manifolds. Prospects for further spectroscopic characterization of the singlet system and direct measurement of the energy separation between the lowest singlet and triplet states are discussed. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4704672]

I. INTRODUCTION

Small silicon clusters play an important role in the photochemistry of silicon- and carbon-rich evolved stars[1] and in vapor deposition of silicon films,[2] and they are a first step in developing an understanding of larger clusters. To date, 11 silicon-containing molecules have been detected in the interstellar medium, primarily via their pure rotational transitions, with some so abundant that their rare isotopomers are easily observed.[3] The study of Si_3 in the optical region is of astronomical interest because it is isovalent with SiC_2 - a highly conspicuous ionic ring - and C_3, both of which have been detected in space by their electronic spectra.[4–6] Because of its small permanent electric dipole moment (0.3–0.4 D; Refs. 7 and 8), astronomical detection of Si_3 may be more favorable in the optical rather than the radio band.

Understanding the differences in structure and bonding between silicon- and carbon-rich species provides further motivation for the experimental study of small silicon clusters. Although silicon is isovalent with carbon, its larger atomic radius results in weaker π-bonding. Calculations predict that silicon prefers to form non-linear and three-dimensional structures containing single bonds,[9] a conclusion which is broadly supported experimentally by photoelectron and matrix infrared spectroscopy of Si_3–Si_7.[9,10] This is in contrast to carbon, which forms single and multiple bonds and generally prefers linear and planar monocyclic structures.[11]

The silicon trimer is the most thoroughly studied small polyatomic silicon cluster. *Ab initio* calculations predict that the singlet C_{2v} form is the electronic ground state[12–15] while a non-polar triplet D_{3h} isomer lies within ~1 kcal/mol. The first experimental evidence for the C_{2v} form was obtained by Li *et al.*,[9] who recorded infrared absorption spectra of several silicon clusters including Si_3 in three different rare gas matrices. They measured vibrational frequencies of approximately 550 cm^{-1} and 525 cm^{-1}, in agreement with those calculated for the symmetric and asymmetric stretching modes, respectively, of the C_{2v} form. Four electronic transitions, all assigned to the C_{2v} form, were observed in absorption by Fulara *et al.*,[16] following deposition of mass-selected silicon clusters in a neon matrix. Two of the transitions lie in the near infrared and ultraviolet regions, with origin bands reported at 778.9 nm and 388.3 nm, respectively, while two lie within the spectral region (555–480 nm) covered in this work. Of these latter two transitions, the stronger one, assigned as $\tilde{E}\ ^1A_1 - \tilde{X}\ ^1A_1$ in Ref. 16, has an origin near 580 nm and a vibrational spacing of 235–270 cm^{-1}, which has been assigned to the bending mode (ν_2). The other transition, $\tilde{F}\ ^1B_1 - \tilde{X}\ ^1A_1$, has a progression in a ~360 cm^{-1} vibrational mode, and an origin tentatively assigned near 522 nm. These assignments

a)nreilly@cfa.harvard.edu.

agree with a recent theoretical investigation of the structures and electronic spectra of small silicon clusters by Park and coworkers.[17] Most recently, McCarthy and Thaddeus[18] measured the rotational spectrum of the C_{2v} form and showed that it is strongly bent, with a bond angle of 78.10°, in marked contrast to C_3, which is linear.[19] From the inertial defect, a frequency of 178 cm^{-1} was estimated for ν_2.

Further experimental attempts to understand the electronic structure of the silicon trimer by photoelectron spectroscopy have furnished little additional insight on the lowest C_{2v} state but instead much new information on the D_{3h} triplet isomer. In 1990, Kitsopoulos *et al.* measured the 266 nm photoelectron spectrum (PES) of Si_3^- and observed five bands which correspond to electronic states of the neutral.[20] The unusual profile of the lowest energy band (the X-band in their reported PES), corresponding to the Si_3 ground electronic state, was proposed to result from a convolution of features from both the C_{2v} and D_{3h} forms, a view supported in an *ab initio* study of the Si_3^- PES.[15] Subsequently, the near threshold photodetachment zero-electron kinetic energy (ZEKE) spectrum of Si_3^-, probing the same band at much higher resolution, was reported by Arnold and Neumark in 1994.[21] The spectrum showed well-resolved vibrational structure, and was assigned to transitions from a Jahn-Teller distorted anion to the $^3A_2'$ electronic state of the D_{3h} neutral. The frequencies of the symmetric stretch and degenerate e' modes in the $^3A_2'$ state were determined to be 501 and 337 cm^{-1} (±10 cm^{-1}), respectively, in good agreement with earlier calculations[22,23] performed on the lowest triplet state. Surprisingly, the X-band probed in the ZEKE spectrum contained no evidence of the C_{2v} neutral, a result attributed to a lower photodetachment cross section near threshold for this isomer. A recent *ab initio* simulation of the vibrationally resolved PES (Ref. 10) by Garcia-Fernadez *et al.* confirmed that the major contribution to the X-band is from the $^3A_2'$ electronic state.[24]

In light of the substantial effort to understand the electronic structure of the silicon trimer, it is surprising that no gas-phase excitation spectrum has been reported for either isomer. In this article, we focus on the jet-cooled gas-phase spectrum of Si_3 in the 555–480 nm region, probed by resonant mass-selected two-color two-photon ionization (R2C2PI) and laser-induced fluorescence (LIF)/dispersed fluorescence (DF) spectroscopy. The excitation spectrum is dominated by the $1\,^3A_1'' - \tilde{a}\ ^3A_2'$ transition of the D_{3h} form, and is assigned on the basis of vibrational sequence band analysis and dispersed fluorescence spectra from several of the strongest bands. The assignment is supported by *ab initio* calculations of electronic states in the singlet and triplet manifolds using the equation-of-motion coupled-cluster (EOM-CCSD) approach.[25,26] A weaker band system, overlapped with the D_{3h} transition and extending to the blue, is tentatively assigned to the C_{2v} form that has been observed in the matrix by Fulara *et al.*,[16] and will be discussed elsewhere. The electronic structure of Si_3 is conveniently represented in terms of the electron configuration and resulting states at the high symmetry D_{3h} geometry, where the electron configuration is $(5a_1')^2(2a_2'')^2(6e')^2(2e'')^0$, and the transitions comprised in the current spectra are those involving promotion of an electron from the (half-filled) $6e'$ orbital to the $2e''$ orbital (see Fig. 1 and its caption).

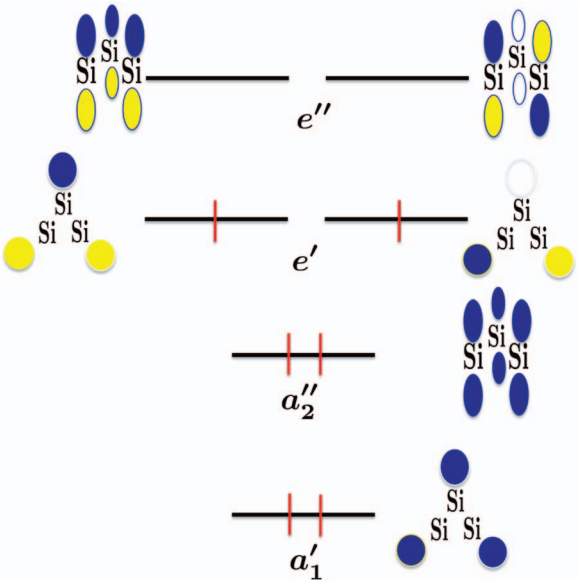

FIG. 1. Ground state electron configuration of Si_3 at the symmetric (D_{3h}) geometry. All of the electronic transitions that occur in the range of wavelengths under study correspond to promotion of an electron from the e' HOMO to the e'' LUMO orbital. Thus, the lower electronic states are $^3A_2'$, $^1A_1'$, and $^1E'$, where the two singlet states couple strongly (see, for example, Figure 2 in Ref. 24) to ultimately yield the $^1A_1$ C_{2v} structure and the triplet state is far simpler in constitution. The upper states in the electronic transition are numerous: A_1'', A_2'', and E'' for both singlets and triplets. The triplet transition that is studied in this work is $^3A_1'' \leftarrow {}^3A_2'$ and is the only dipole-allowed process available to the triplet. On the other hand, in the singlet manifold, a number of transitions are possible, all of which are profoundly affected by the Jahn-Teller and pseudo-Jahn-Teller mechanisms. In terms of D_{3h} symmetry, these are the $^1A_2'' \leftarrow {}^1A_1'$ and $^1E'' \leftarrow {}^1E'$ transitions, which correlate with $b_1 \leftarrow a_1$ processes from the C_{2v} (Jahn-Teller distorted) ground state, and a dark $a_2 \leftarrow a_1$ transition, which unquestionably contributes to the complexity of the spectra.

II. EXPERIMENTAL DETAILS

Resonance-enhanced multi-photon ionization experiments were performed in parallel at two laboratories, one in Cambridge, the other in Basel. The experimental setups in both laboratories are similar and each has been described elsewhere.[27,28] At Cambridge, Si_3 was produced in the throat of a supersonic nozzle by electrical discharge (varying from 500 V to 1.5 kV, with 10 kΩ ballast resistance) through a gas stream containing a dilute mixture of SiH_4 (1%) in argon, just prior to supersonic expansion into a vacuum chamber. The discharge nozzle is based on the design in Ref. 29. The stagnation pressure was varied from 3 to 8 atm; typical operating pressure within the chamber was 10^{-6} Torr. At Basel, Si_3 was produced by laser ablation of a pure silicon rod in the presence of supersonically expanding helium. The pressure behind the pulsed valve was ∼10 atm and the chamber operating pressure was 7×10^{-5} Torr.

In these experiments, tunable radiation between 480 and 555 nm was generated by a 355 nm-pumped dye laser operating with Coumarin 500 and 540 A. The typical dye laser output over the tuning range was ∼10 mJ per pulse, with a linewidth of ∼0.4 cm^{-1}. Absolute wavelength calibration was provided by an external wavemeter. Because Si_3 has an ionization potential of ∼8.5 eV,[30] the excimer laser was operated with ArF (193 nm or 6.42 eV) to be certain that the

$1+1'$ process was sufficiently energetic (~8.7 eV at 540 nm) to yield a positive ion.

Fluorescence experiments were also performed at Arizona State University, with a reactive molecule source similar to that used in Cambridge. Specifically, a discharge (700 V, 20 μs, 6 kΩ ballast resistor) was struck in a 1% SiH_4 in Ar gas pulse. The backing pressure was 15 atm, the repetition rate 20 Hz, and the operating chamber pressure 7×10^{-5} Torr. The supersonic free jet expansion was crossed with pulsed laser radiation approximately 5 cm downstream from the source. Two types of experiments were performed: (a) LIF excitation in the 510–550 nm range; (b) DF emission in the 500–610 nm range. In both experiments, the excitation source was a pulsed dye laser pumped by 308 nm radiation from an excimer laser. The fluorescence signal was viewed through a 0.67 m scanning monochromator, detected with a cooled photomultiplier tube and processed using gated photon counting. In the LIF excitation measurements, the slits on the monochromator were opened to 3 mm, resulting in a resolution of ±3.7 nm, and the peak transmission scanned to track the laser wavelength. In the DF measurements, the slits on the monochromator were reduced to 1 mm for a resolution of ±1.24 nm. Typically, 50 pulses were averaged at each step of the laser or monochromator.

III. COMPUTATIONAL METHODOLOGY

Ab initio calculations were performed on the triplet D_{3h} isomer of the silicon trimer. Vertical excitation energies were calculated using the EOM-CCSD approach. Geometries of the ground and first excited state were optimized using analytical gradients; this was done at the CCSD level[31] for the ground state ($\tilde{a}\ ^3A_2'$), and at the EOM-CCSD level[25,26] for the excited state ($1\,^3A_1''$). The basis set used in these calculations was the correlation-consistent polarized weighted core-valence triple-zeta (cc-pwCTZ) basis of Peterson and Dunning.[32] Harmonic vibrational frequencies at the equilibrium geometries were obtained for the ground and excited states from analytic second derivatives for CCSD,[33] and numerical differentiation of analytic first derivatives for EOM-CCSD, respectively. At the geometry of the ground state, the vertical excitation energy was also calculated with the quite sophisticated EOM-CCSDT method for the triplet state, using the atomic natural orbital basis of Widmark *et al.*,[34] in which only the valence shell electrons were correlated. All calculations were performed using the CFOUR package of electronic structure programs.[35] Table I summarizes the key results of our calculations.

IV. RESULTS AND ASSIGNMENT

R2C2PI spectra of the $m/z = 84$ products of a SiH_4 (1%) in Ar discharge, recorded between 18000 and 20500 cm^{-1} (555–480 nm) under two different expansion conditions, are shown in Fig. 2; a similar $m/z = 84$ spectrum was also observed using the pure silicon rod ablation source at Basel. The lower spectrum in Fig. 2 was recorded under "cold" discharge conditions, i.e., using a low discharge voltage, a short discharge pulse, and a high (8 atm) backing pressure.

TABLE I. Experimental (in italics) and calculated vibrational frequencies (cm^{-1}) and T_0 (eV) for the $\tilde{a}\ ^3A_2'$ and $1\,^3A_1''$ states of Si_3.

	$\tilde{a}\ ^3A_2'$		$1\,^3A_1''$	
	Calc.	Exp.	Calc.	Exp.
ν_1 (a_1')	520	*505*[a]	480	*445*[a]
ν_2 (e')	351	*337*[b]	133	*~137*[c]
Excitation energy (eV)			2.34[d]	*2.31*

[a]This work.
[b]Ref. 21.
[c]Derived from Ref. 21 and tentative sequence band assignment of 2^1_1.
[d]Vertical excitation energy obtained with EOM-CCSDT.

At least two overlapping progressions are evident: a stronger progression, with a ~445 cm^{-1} interval and an origin near 18 600 cm^{-1}; and a much weaker one, with a regular spacing of ~360 cm^{-1} but which does not have the same origin. As indicated in Fig. 2, the two progressions have a coincidental overlap near 19 500 cm^{-1}. Under the experimental conditions which produced the best S/N for the 445 cm^{-1} progression, no strong or sharp spectral features were observed in survey scans that extended down to 17 240 cm^{-1}, near where the strongest transition of the C_{2v} form was observed in a neon matrix.[16]

The same wavelength region was re-scanned under "hotter" beam conditions (higher discharge voltage, longer discharge pulse, backing pressure reduced to 3 atm). The resulting spectrum is shown in the upper trace in Fig. 2. The increase in the intensity of the 360 cm^{-1} progression relative to the 445 cm^{-1} progression suggests that they do not share a common *lower* state. A second 360 cm^{-1} progression, presumably due to vibrational hot bands, is now evident under these conditions.

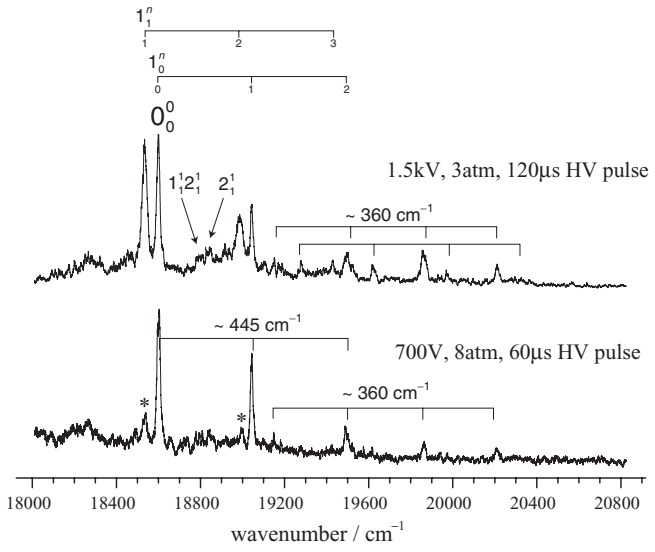

FIG. 2. Mass-selected resonant two-color two-photon ionization spectra of Si_3, recorded under two different expansion conditions. Features designated with an asterisk in the lower trace are hot vibrational sequence bands; these are enhanced in the upper trace, which was measured using a lower backing pressure and a discharge pulse of higher voltage and longer duration. The 445 cm^{-1} progression belongs to the triplet manifold and the 360 cm^{-1} progression to the singlet.

Two band systems of Si_3, both from the C_{2v} singlet ground state, have been observed in this spectral region in a neon matrix:[16] the first, assigned $\tilde{E}\ ^1A_1 - \tilde{X}\ ^1A_1$, has an origin at 580 nm and a 235–270 cm^{-1} progression in ν_2; the second, assigned $\tilde{F}\ ^1B_1 - \tilde{X}\ ^1A_1$, has a tentatively assigned origin near 520 nm and a ~360 cm^{-1} progression. On the basis of the reported matrix spectrum, transitions within the $\tilde{E}\ ^1A_1 - \tilde{X}\ ^1A_1$ band system are expected to be weak in this region but probably contribute to the broad background observed to the red of the 18 600 cm^{-1} feature. The second band system is likely responsible for the 360 cm^{-1} progression observed in Fig. 2. These "singlet" features, which exhibit richer vibrational structure, result from transitions within a manifold of states that correlate to degenerate states in D_{3h} symmetry (see Fig. 2 in Ref. 24). Unlike the quite simple triplet manifold, vibronic interactions are both numerous and complicated in the singlet spectrum, and their study will be addressed in a forthcoming publication. Assignment of the transition that exhibits the 445 cm^{-1} progression is the primary focus of the present study.

The features at 18 534 cm^{-1} and 18 986 cm^{-1} are remarkably strong in the hotter spectrum. Both of these bands (indicated in the cold spectrum with asterisks) appear red-shifted from bands in the 445 cm^{-1} progression by approximately 60 cm^{-1}. Assigning them as sequence bands of the 445 cm^{-1} progression yields a putative lower state frequency of ~505 cm^{-1}, in excellent agreement with 501 ± 10 cm^{-1} observed by ZEKE for the symmetric stretch (ν_1) of the D_{3h} $\tilde{a}\ ^3A_2'$ state.[21] We calculate ν_1 frequencies in the $\tilde{a}\ ^3A_2'$ and $1\ ^3A_1''$ states of Si_3 of 520 cm^{-1} and 480 cm^{-1}, respectively (see Table I), in reasonable agreement with experiment, and a vertical transition between these states at 2.34 eV (compared to the observed origin at 18600 cm^{-1} (2.31 eV)) with an oscillator strength of 0.0037. In addition, we calculate an excited state frequency of 133 cm^{-1} for the degenerate deforming mode ν_2, and a lower state one of 351 cm^{-1}, also in agreement with the 337 cm^{-1} determined in the same ZEKE study. One might therefore expect 2_1^1 sequence bands to appear approximately 200 cm^{-1} red-shifted from the 1_0^n progression in the D_{3h} spectrum. While we hesitate to make such an assignment with certainty until the 360 cm^{-1} progression is better understood, the appearance in the hotter spectrum of a weak band at 18 845 cm^{-1}, 200 cm^{-1} to the red of the 1_0^1 band, is consistent with this interpretation; furthermore, this feature is accompanied by a slightly weaker feature approximately 50–60 cm^{-1} to the red, the latter of which can be plausibly assigned as $1_1^2 2_1^1$, reminiscent of the other sequence bands in the D_{3h} spectrum.

For the $\tilde{a}\ ^3A_2'$ state, the calculated CCSD/cc-pwCTZ equilibrium structure has an Si-Si bond length of 2.280 Å which increases to 2.294 Å in the $1\ ^3A_1''$ state. Unlike many of the states in the singlet manifold, neither triplet state is Jahn-Teller active; as a result, one might expect the $1\ ^3A_1'' - \tilde{a}\ ^3A_2'$ transition to have a simple spectrum consisting only of a short progression in the symmetric stretch (ν_2 is Franck-Condon inactive), as shown in Fig. 2. The strength of the sequence bands in the hotter spectrum provides additional evidence that the 360 cm^{-1} progression must arise from a different lower state, as none of these bands have a comparably intense band ~60 cm^{-1} to the red. While this proposed assignment seemed reasonable, the absence of the 1_2^n sequence is puzzling, given the strength of the 1_1^n sequence. Some confirmation was therefore sought using fluorescence spectroscopy.

Figure 3 contains the LIF spectrum (left) of the 1% SiH_4/Ar discharge in the region 18100–19200 cm^{-1}. The

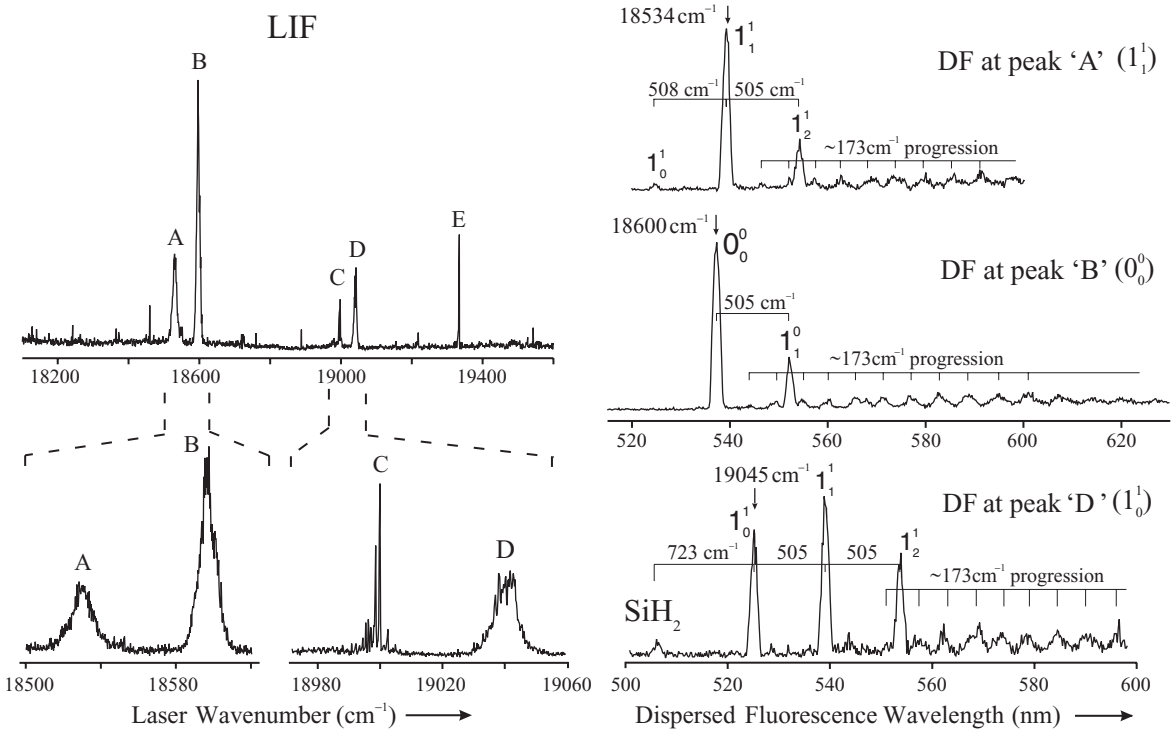

FIG. 3. Laser-induced fluorescence spectrum of Si_3 (left) and (right) dispersed fluorescence spectra obtained from the LIF bands labeled A, B, and D.

spectrum contains no evidence of the 360 cm^{-1} progression, possibly because the fluorescence was selectively detected using a monochromator with a 3.7 nm bandwidth that tracked the laser excitation. The ν_1 progression is also shorter, probably due to lower laser power in the region of the 1_0^2 band. The spectrum also includes some sharp features (C and E) near 19 300 cm^{-1} and 19 334 cm^{-1}; based on a ground state frequency of ~540 cm^{-1} from DF (not shown), an excited state interval of ~334 cm^{-1}, and a very recent theoretical study,[36] these bands almost certainly belong to the $2^3\Pi_g \leftarrow \tilde{D}\ ^3\Pi_u$ transition of Si_2, which is predicted to occur near 19 000 cm^{-1}.

DF spectra recorded from the LIF bands labeled A (1_1^1), B (0_0^0), and D (1_0^1) are also shown in Fig. 3. The spectra are similar: each contains a short 505 cm^{-1} progression, and a relatively weak but long one with a spacing of ~173 cm^{-1}. The assignment of the 505 cm^{-1} intervals in each spectrum to ν_1 is entirely consistent with our assignment of sequence band structure in the R2C2PI spectra. For example, the 1_1^1 DF spectrum contains a feature blue-shifted from the laser frequency by 505 cm^{-1} - coincident with the $\tilde{a}\ ^3A_2'$ ν_1 frequency inferred earlier - that has an obvious assignment of 1_0^1. On the basis of the R2C2PI spectra, the dominant features in the DF spectra, and our calculations on the $\tilde{a}\ ^3A_2'$ and $1\ ^3A_1''$ states, assignment of the 445 cm^{-1} progression to the $1\ ^3A_1'' - \tilde{a}\ ^3A_2'$ transition is therefore secure and is summarized in Table II.

V. DISCUSSION

While the singlet manifold is replete with Jahn-Teller and pseudo-Jahn-Teller interactions, the triplet transition probed in this work is free of such effects and exhibits a very simple spectrum (once the overlapping singlet transitions are identified). However, there are several aspects of this seemingly uncomplicated system that are surprising, and worthy of further discussion.

A. Evidence of the $\tilde{X}\ ^1A_1$ state in triplet emission

The dominant features in the triplet DF spectra are readily assigned to ν_1 in the $\tilde{a}\ ^3A_2'$ state, but rationalizing the long ~173 cm^{-1} progression that appears in all three spectra is more problematic. Calculations on the $\tilde{X}\ ^1A_1$ ground state of the C_{2v} isomer of Si_3 have predicted a frequency for the bending mode of 146 cm^{-1} (Ref. 15) and 196 cm^{-1}.[24] From the

TABLE II. Observed bands from the R2CP2I spectrum in Fig. 2 and assignments for the $1\ ^3A_1'' - \tilde{a}\ ^3A_2'$ transition of Si_3.

Frequency (cm^{-1})	Assignment
18 534	1_1^1
18 600	0_0^0
18 790	$1_1^2 2_1^1$
18 845	$1_0^1 2_1^1$
18 986	1_1^2
19 045	1_0^1
19 430	1_1^3
19 497	1_0^2

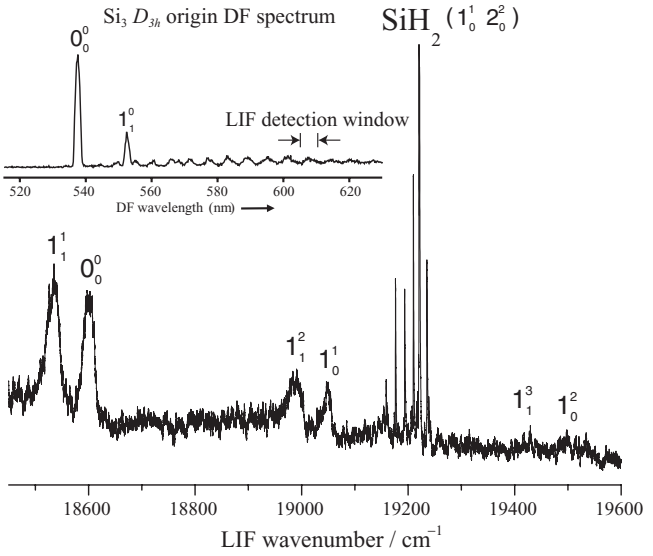

FIG. 4. LIF spectrum of Si_3 measured using the detection window indicated above the dispersed fluorescence spectrum (reproduced from Fig. 3) shown in the inset.

rotational spectrum of the C_{2v} isomer, McCarthy and Thaddeus estimated a frequency of 178 cm^{-1} based on the inertial defect,[18] in fairly close agreement with the spacing in the DF progressions. If these weaker features in the $1\ ^3A_1'' - \tilde{a}\ ^3A_2'$ DF spectra are indeed due to the C_{2v} form, they may have at least two distinct explanations. First, if either the C_{2v} $\tilde{E}\ ^1A_1 - \tilde{X}\ ^1A_1$ and $\tilde{F}\ ^1B_1 - \tilde{X}\ ^1A_1$ band systems accidentally coincide in wavelength with the triplet transitions that have been probed by DF, emission to the singlet ground state might be observed. However, we have been so far unable to observe by LIF any of the putative C_{2v} features that were observed in REMPI (see Sec. V C).

A more likely explanation for the ~173 cm^{-1} progression is that the $1\ ^3A_1''$ state undergoes an intersystem crossing, and emission then follows to the $\tilde{X}\ ^1A_1$ state through either the $\tilde{E}\ ^1A_1 - \tilde{X}\ ^1A_1$ and $\tilde{F}\ ^1B_1 - \tilde{X}\ ^1A_1$ transitions. Seeking evidence in support of the latter hypothesis, the LIF spectrum was re-measured with the monochromator tuned to 610 nm using a bandpass of approximately 3 nm (see Fig. 4, in which the detection window is indicated above the origin DF spectrum). Because the progression in ν_1 is quite short, we can be confident that any Si_3 bands observed by LIF at this detection wavelength emit to a member of the ~173 cm^{-1} progression, rather than through the symmetric stretching mode of the triplet. Other than a strong, unrelated band centered on 19 200 cm^{-1} (due to the $\tilde{A}\ ^1B_1 - \tilde{X}\ ^1A_1$ transition of SiH_2 (Ref. 37)), the resultant spectrum contains only the previously observed $1\ ^3A_1'' - \tilde{a}\ ^3A_2'$ features, and none of the other Si_3 features observed by R2C2PI. Consequently, the argument that overlapping transitions of the C_{2v} isomer contribute to the DF spectra can almost certainly be rejected. Instead, a singlet-triplet mixing in the upper state is probably responsible for the long ~173 cm^{-1} progressions that are observed in the DF spectra, which arises from bending levels in the ground singlet state. Because of the large change in geometry between the triplet and singlet states, emission to many ν_2 levels in the $\tilde{X}\ ^1A_1$ ground state occurs facilely.

B. Discharge temperature effects

Two unusual temperature effects observed in the hotter R2C2PI spectrum require comment. The first is that, although the 1_1^n sequence bands are similar in intensity to the origin and 1_0^1 bands, the 1_2^n sequence is absent. For the $\tilde{a}\ ^3A_2'$ state, with experimentally determined vibrational frequencies of $\nu_1 = 505\ \text{cm}^{-1}$ and $\nu_2 = 337\ \text{cm}^{-1}$, the 1_2 and 2_3 levels are almost coincident; intramolecular vibrational redistribution from 1_2 into the 2_3 level, which can be cooled more effectively in the free jet, is a plausible explanation for the absence of higher sequences.

More puzzling is the relative strength of the singlet and triplet transitions under the two different expansion conditions employed. Because the C_{2v} isomer is slightly more stable, one might expect it to be the more abundant isomer in the discharge. However, experimental evidence suggests that the D_{3h} form is instead much more abundant under "cold" experimental conditions, while "hot" conditions slightly enhance the relative strength of the C_{2v} features. Although the D_{3h} form lacks a rotational spectrum owing to its high symmetry, rotational lines of the C_{2v} isomer[18] were observed with the same discharge source and similar experimental conditions to those used to record the hotter R2C2PI spectrum (Fig. 2). Because Si_3 is almost certainly formed by recombination of smaller silicon fragments in the discharge, symmetry arguments may be relevant in formation. For example, Si and Si_2 both possess triplet ground states, suggesting that recombination might facilely produce triplet Si_3; singlet Si_3 may instead require recombination of electronically excited fragments.

C. Singlet-triplet mixing and the search for singlet fluorescence

The observation of what seems to be singlet emission following triplet excitation would appear to re-open the possibility of directly measuring the energy separation between the singlet and triplet ground states - one of the unresolved issues for the silicon trimer. On the basis of several calculations the singlet is predicted to lie approximately 1 kcal/mol below the triplet,[12–15] implying that emission to the vibrationless singlet ground state might appear a few hundred cm^{-1} to the blue of the laser in the triplet DF spectra. Unfortunately, with a bond angle change of ∼17° (Ref. 18) between the $\tilde{X}\ ^1A_1$ and $1\ ^3A_1''$ states, the Franck-Condon overlap at the geometry of the intersystem crossing for such emission is highly unfavorable. The 1_0^1 DF spectrum does show a feature approximately $720\ \text{cm}^{-1}$ to the blue of the laser, but this is most likely due to the presence of interfering SiH_2 (see Ref. 38 and also Refs. 37 and 39).

Evidence of the $\tilde{X}\ ^1A_1$ bending mode in emission also suggests that transitions of the singlet isomer should be detectable by fluorescence, enabling more detailed study of the ground singlet surface. The ν_2 progressions in the DF spectra are similar to the $360\ \text{cm}^{-1}$ progression assigned to ν_2 in the matrix absorption spectrum (both extending to at least 15 quanta), implicating the $\tilde{F}\ ^1B_1$ state in the singlet-triplet mixing. This state, which corresponds to the upper part of the conical intersection in the excited singlet manifold, is nearly degenerate with the excited triplet state at the D_{3h} geometry (based on the predicted 1 kcal/mol separation between the singlet and triplet ground states, and assuming an origin transition near 525 nm). By varying the temporal delay between the tunable and ionizing radiation in R2C2PI, upper state relaxation rates of approximately 20 μs were observed both for triplet and singlet transitions in the 500–540 nm region; for the triplet transitions, no short 1 μs component, corresponding to the triplet fluorescence lifetime, was observable above the slower relaxation component, suggesting that relaxation from the singlet is the dominant process. However, searches for the singlet transitions in LIF were unsuccessful. While small Franck-Condon factors resulting from the large bond angle change make this a challenging problem, the most severe obstacle to detection is spectral contamination by Si_2 (via the aforementioned $2^3\Pi_g \leftarrow \tilde{D}\ ^3\Pi_u$ transition[36]), which is abundantly produced under the experimental conditions that optimize singlet S/N, and exhibits extensive rotational contours overlapping most of the sought-after Si_3 transitions in this region; such contamination would be similarly problematic using an ablation source. Two-dimensional fluorescence, which has been applied to hydrocarbon discharges to extricate spectra which in 1D are obscured by C_2 and C_3,[40,41] could prove a powerful approach to detecting the singlet.

Detection of the C_{2v} isomer by LIF may also be more fruitful in the near-UV, as our calculations indicate stronger transitions in this region: in particular, the $\tilde{G}\ ^1B_2 - \tilde{X}\ ^1A_1$ transition,[16] which has been detected recently by R2C2PI by the Harvard group, has a calculated oscillator strength nearly an order of magnitude greater than any other transition of either isomer in the optical region. Spectral congestion from other abundant silicon species might also be less severe at these wavelengths.

VI. CONCLUSION

An optical excitation spectrum of the silicon trimer has been observed in a free jet expansion. While the C_{2v} form is believed to be the lower energy isomer of Si_3, mass-selective spectroscopic detection, laser-induced fluorescence, and *ab initio* calculations confirm that the observed spectrum near 535 nm is dominated by the $1\ ^3A_1'' - \tilde{a}\ ^3A_2'$ transition of the D_{3h} triplet isomer. Vibrational frequencies calculated for the $\tilde{a}\ ^3A_2'$ and $1\ ^3A_1''$ states are generally in good agreement with those determined from the R2C2PI and DF spectra, and from an earlier ZEKE study of the $\tilde{a}\ ^3A_2'$ state. Weak overlapping features from the $\tilde{E}\ ^1A_1 - \tilde{X}\ ^1A_1$ and $\tilde{F}\ ^1B_1 - \tilde{X}\ ^1A_1$ transitions of the C_{2v} isomer are evident in R2C2PI spectra, but we have so far been unable to observe the C_{2v} isomer in fluorescence. The $\tilde{X}\ ^1A_1$-state bending mode progressions observed in emission spectra from the triplet most likely result from intersystem crossing from the upper triplet state. Follow-up studies of the C_{2v} form in the vicinity of its relatively strong $\tilde{G}\ ^1B_2 - \tilde{X}\ ^1A_1$ transition in the near UV are now underway.

ACKNOWLEDGMENTS

The work in Cambridge is supported by National Science Foundation (NSF) Grant No. CHE-1058063. The work

in Basel is supported by the Swiss National Science Foundation (Project No. 200020-124349/1). T.C.S. acknowledges the NSF (Grant No. CHE-1011996) for funding support. R.C.F. wishes to thank the Virginia Space Grant Consortium for a graduate research fellowship, and acknowledges T. Daniel Crawford for advice on this project. J.F.S. has been supported by the NSF and the Robert A. Welch Foundation (Grant No. F-1283) of Houston, Texas.

[1] M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, Mol. Phys. **101**, 697 (2003).
[2] M. Grass, D. Fischer, M. Mathes, G. Ganteför, and P. Nielaba, Appl. Phys. Lett. **81**, 3810 (2002).
[3] J. Cernicharo, C. Kahane, J. Gómez-González, and M. Guélin, Astron. Astrophys. **167**, L9 (1986).
[4] P. W. Merrill, Publ. Astron. Soc. Pac. **46**, 175 (1926).
[5] R. F. Sanford, Publ. Astron. Soc. Pac. **46**, 177 (1926).
[6] J. P. Maier, N. M. Lakin, G. A. H. Walker, and D. A. Bohlender, Astrophys. J. **553**, 267 (2001).
[7] I. Vasiliev, S. Öğüt, and J. R. Chelikowsky, Phys. Rev. Lett. **78**, 4805 (1997).
[8] B. K. Panda, S. Mukherjee, and S. N. Behera, Phys. Rev. B **63**, 045404 (2001).
[9] S. Li, R. J. V. Zee, J. W. Weltner, and K. Raghavachari, Chem. Phys. Lett. **243**, 275 (1995).
[10] C. S. Xu, T. R. Taylor, G. R. Burton, and D. M. Neumark, J. Chem. Phys. **108**, 1395 (1998).
[11] E. B. Jochnowitz and J. P. Maier, Annu. Rev. Phys. Chem. **59**, 519 (2008).
[12] K. Raghavachari and V. Logovinsky, Phys. Rev. Lett. **55**, 2853 (1985).
[13] K. Raghavachari, J. Chem. Phys. **83**, 3520 (1985).
[14] R. S. Grev and H. F. Schaefer III, Chem. Phys. Lett. **119**, 111 (1985).
[15] C. M. Rohlfing and K. Raghavachari, J. Chem. Phys. **96**, 2114 (1992).
[16] J. Fulara, P. Freivogel, M. Grutter, and J. P. Maier, J. Chem. Phys. **100**, 18042 (1996).
[17] S. Park, S. Lee, and D. Neuhauser, J. Phys. Chem. A **110**, 7173 (2006).
[18] M. C. McCarthy and P. Thaddeus, Phys. Rev. Lett. **90**, 213003 (2003).
[19] F. J. Northrup, T. J. Sears, and E. A. Rohlfing, J. Mol. Spectrosc. **145**, 74 (1991).
[20] T. N. Kitsopoulos, C. J. Chick, A. Weaver, and D. M. Neumark, J. Chem. Phys. **93**, 6108 (1990).
[21] C. C. Arnold and D. M. Neumark, J. Chem. Phys. **100**, 1797 (1994).
[22] D. A. Dixon and J. L. Gole, Chem. Phys. Lett. **188**, 560 (1992).
[23] R. Fournier, S. B. Sinnott, and A. E. DePristo, J. Chem. Phys. **97**, 4149 (1992).
[24] P. Garcia-Fernandez, J. E. Boggs, and J. F. Stanton, J. Chem. Phys. **126**, 074305 (2007).
[25] J. F. Stanton, J. Chem. Phys. **99**, 8840 (1993).
[26] J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993).
[27] D. L. Kokkin, N. J. Reilly, M. C. McCarthy, and J. F. Stanton, J. Mol. Spectrosc. **268**, 23 (2011).
[28] A. E. Boguslavskiy and J. P. Maier, Phys. Chem. Chem. Phys. **9**, 127 (2007).
[29] M. C. McCarthy, W. Chen, M. J. Travers, and P. Thaddeus, Astrophys. J., Suppl. Ser. **129**, 611 (2000).
[30] K. Fuke, K. Tsukanoto, F. Misaizu, and M. Sanekata, J. Chem. Phys. **99**, 7807 (1993).
[31] A. C. Scheiner, G. E. Scuseria, J. E. Rice, T. J. Lee, and H. F. Schaefer III, J. Chem. Phys. **87**, 5361 (1987).
[32] K. A. Peterson and J. T. H. Dunning, J. Chem. Phys. **117**, 10548 (2002).
[33] J. Gauss and J. F. Stanton, Chem. Phys. Lett. **276**, 70 (1997).
[34] P. O. Widmark, P. A. Malmqvist, and B. O. Roos, Theor. Chem. Acc. **77**, 291 (1990).
[35] CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R. Price, E. Prochnow, K. Ruud, F. Schiffmann, W. Schwalbach, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.
[36] D. H. Shi, J. F. Sun, Z. L. Zhu, and Y. F. Liu, J. Quant. Spectrosc. Radiat. Transf. **112**, 2567 (2011).
[37] M. Fukushima, S. Mayama, and K. Obi, J. Chem. Phys. **96**, 44 (1992).
[38] The strongest feature in Fig. 4 is the $1_0^1 2_0^2$ band of the $\tilde{A}\ ^1B_1 - \tilde{X}\ ^1A_1$ transition of SiH_2, as reported by Ishikawa and Kajimoto.[39] SiH_2 has harmonic bending frequencies in its $\tilde{X}\ ^1A_1$ and $\tilde{A}\ ^1B_1$ states of 1000 cm^{-1} and 854 cm^{-1}, respectively.[37] Its $1_0^1 2_1^3$ hot band thus occurs near 19040 cm^{-1}, coincident with the $Si_3 1_0^1$ band, and can emit to the blue of the laser in the DF spectrum. (Levels involving the bending mode of SiH_2 also coincide with the $Si_3 1_2$ level in this DF spectrum, so a Franck-Condon simulation of the Si_3 DF intensities has little value.) Under slightly different expansion conditions, this hot band was extremely strong in survey LIF spectra. The observed Si_3 fluorescence decay profile is characterized by a single exponential with a lifetime - about 1 μs - similar to that of SiH_2, so fluorescence from the latter cannot be temporally gated out. While a definitive assignment of the particular lower state involved in the blue-shifted transition is not obvious, there are several transitions of SiH_2 near 19 750 cm^{-1} that could produce the appropriate blue-shift, within the monochromator resolution.[39] Moreover, no transitions of Si_3 were observed when the laser was scanned with the monochromator fixed over the blue-shifted feature, and no such feature appears at the same blue-shift in DF spectra from the Si_3 origin and sequence bands. It thus seems unlikely that this blue-shifted feature comes from Si_3; in particular, it is not associated with the triplet system studied here.
[39] H. Ishikawa and O. Kajimoto, J. Mol. Spectrosc. **160**, 1 (1993).
[40] N. J. Reilly, T. W. Schmidt, and S. H. Kable, J. Phys. Chem. A **110**, 12355 (2006).
[41] N. J. Reilly, D. L. Kokkin, M. Nakajima, K. Nauta, S. H. Kable, and T. W. Schmidt, J. Am. Chem. Soc. **130**, 3137 (2008).