VOLUME 90, NUMBER 21 PHYSICAL REVIEW LETTERS week ending 30 MAY 2003

Rotational Spectrum and Structure of Si_3

M. C. McCarthy and P. Thaddeus

Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138, USA,
and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA

(Received 15 January 2003; published 30 May 2003)

The rotational spectrum of a pure silicon cluster, the Si_3 trimer, has been observed for the first time. From the rotational constants of the normal and the ^{29}Si and ^{30}Si isotopic species, a precise geometrical structure has been derived: the trimer is an isosceles triangle with a bond to the apex Si of length 2.177(1) Å and an apex angle of 78.10(3)°. The substantial inertial defect and fairly large centrifugal distortion suggest that the molecule possesses a shallow bending potential. Si_3 is a good candidate for astronomical detection because radio lines of comparably massive silicon molecules (e.g., SiC_2, SiC_4, and SiS) are readily observed in at least one astronomical source. The rotational spectra of Si_6, Si_9, and even larger polar silicon clusters may be detectable with the present technique, as well as similar germanium clusters.

DOI: 10.1103/PhysRevLett.90.213003 PACS numbers: 33.20.Bx, 36.40.Mr, 61.46.+w

Small silicon clusters differ significantly in bonding and structure from carbon clusters of the same size and have been the subject of a number of theoretical and experimental studies [1–5]. They play an important role in the vapor deposition of amorphous silicon films [6] and in the photochemistry of some silicon-rich evolved stars [7], and they are a first step towards understanding the properties of larger clusters. Several of the smaller silicon clusters are calculated to be polar, with dipole moments of a few tenths of one Debye, and are therefore good candidates for detection by Fourier-transform microwave (FTM) spectroscopy, where rotational line intensities are proportional to the first power of μ, not μ^2, as in conventional spectroscopy. With this technique we have now detected Si_3, the smallest polar silicon cluster, and by isotopic substitution determined its geometrical structure to high precision.

The present work is the first high-resolution spectroscopic study of a silicon cluster. *Ab initio* calculations [3,8–11] and infrared and optical [12] studies of Si_3 trapped in inert gas matrices indicate that the most stable isomer has the C_{2v} symmetry shown in Fig. 1, and a singlet electronic ground state $^1A_1$; a nonpolar triplet isomer with D_{3h} symmetry is calculated to lie within 1 kcal/mol. Vibrational and electronic energies for the ground and several excited states of Si_3 have been obtained from vibrationally resolved anion photoelectron and zero electron kinetic energy spectra of Si_3^- [2]. The calculated dipole moment of the singlet isomer in Fig. 1 is 0.3–0.4 D [4].

The rotational spectrum of Si_3 was detected with a FTM spectrometer recently used to identify nearly 100 new reactive molecules [13]—mainly organic radicals and carbenes, but silicon molecules as well, including the Si_2H_3 radical and a novel monobridged isomer of Si_2H_4. Reactive molecules are created in the throat of a small supersonic nozzle by applying a low-current dc discharge to a short gas pulse created by a fast mechanical valve, the gas in the present work being silane SiH_4 (0.1%) heavily diluted in a neon or argon buffer. Free expansion from the nozzle into a large vacuum chamber forms a Mach 2 supersonic beam with a kinetic and rotational temperature in the moving reference frame as low as 1 K. As the beam passes through a large high-Q Fabry-Perot microwave cavity, a rotational transition is excited by a short (1 μsec) pulse of resonant microwave radiation, which dies out very rapidly once the microwaves are turned off by a fast *p-i-n* diode switch. Line radiation by the coherently rotating molecules is then detected by a sensitive receiver which, to enhance sensitivity, can be cooled by liquid nitrogen.

The silicon trimer was first observed by accident. In the course of searches for new silicon hydrides, a very strong unidentified line was observed near 12.6 GHz, which is only produced in the presence of an electrical discharge, and does not exhibit a detectable Zeeman effect when a permanent magnet is brought near the molecular beam. Elemental tests using normal and fully deuterated silane,

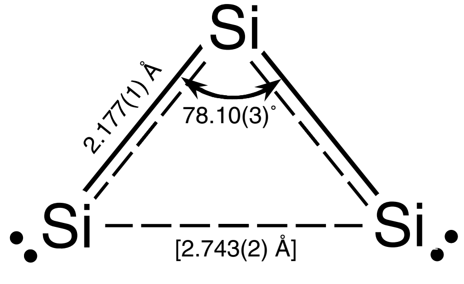

FIG. 1. Experimental structure of Si_3, an asymmetric top molecule with C_{2v} symmetry. Estimated uncertainties in units of the last significant digit are given in parentheses. Following Raghavachari [8] and Grev and Schaefer [9], dashed lines indicate the π electrons delocalized over the three-membered ring.

and argon and neon buffer gases, then showed that the carrier of this line contains only silicon—a surprising result because of the low polarity of most single element clusters. That objection was quickly overcome, however, when a plausible assignment was found: on the basis of *ab initio* calculations, the frequency of the line agrees closely with that of the fundamental $1_{1,1} \rightarrow 0_{0,0}$ transition of singlet Si_3, predicted to lie at 12.7 GHz [3,8–11]. Owing to the high signal to noise, the corresponding $1_{1,1} \rightarrow 0_{0,0}$ lines of the two ^{29}Si and the two ^{30}Si isotopic species (see Fig. 2) were then readily detected, in spite of their low fractional abundances (4.7% and 3.1%, respectively). The extremely close agreement between the observed frequency shifts of the isotopic species and those predicted from the geometry in Fig. 1 is crucial confirmation that the assigned lines are produced by Si_3 and no other silicon cluster.

A total of 21 *b*-type transitions of Si_3 up to $J = 6$ and $K_a = 4$ between 8 and 42 GHz have now been measured. Spectroscopic constants were determined by fitting a theoretical spectrum calculated from a standard asymmetric top Hamiltonian with centrifugal distortion to the observed frequencies. With three rotational constants and all five quartic centrifugal distortion terms (Table I), the rms of the fit is only 66 kHz, in good agreement with the data, but still more than an order of magnitude larger than the 2 kHz measurement uncertainty.

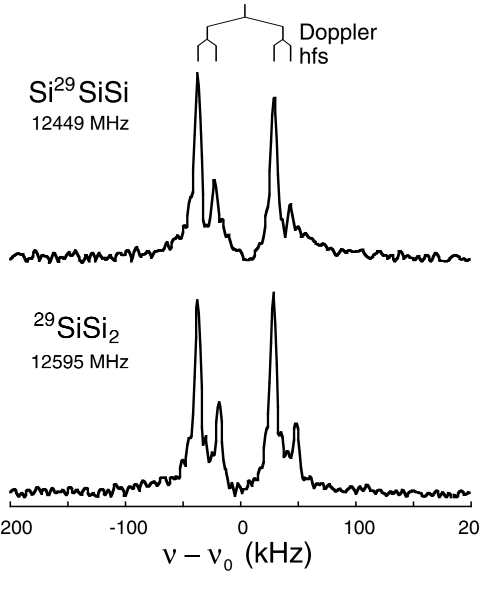

FIG. 2. The $1_{1,1} \rightarrow 0_{0,0}$ transitions of Si^{29}SiSi and ^{29}SiSi$_2$ showing the small hyperfine splittings (of order 10–20 kHz) which arise in both spectra from the interaction of the $I = 1/2$ spin of the ^{29}Si nucleus with the rotationally induced magnetic field. The double-peaked line shape is the result of the Doppler shift of the Mach 2 molecular beam relative to the two traveling waves that compose the confocal mode of the Fabry-Perot. The integration time for each spectrum was approximately 1 min.

TABLE I. Spectroscopic constants of Si_3 (in MHz).

Constant	This work[a]	Ref. [8]	Ref. [3]	Ref. [9]	Ref. [10]
A	9506.07(2)	9585	9501	9630	9562
B	4809.26(2)	4855	4864	4878	4592
C	3185.94(1)	3222	3217	3237	3102
Δ[b]	0.379 48(10)				

[a] Note: 1σ uncertainties (in parentheses) are in the units of the last significant digits. The best fit centrifugal distortion constants (in MHz) are $\Delta_J = 7.0(3) \times 10^{-3}$, $\Delta_{JK} = -31(2) \times 10^{-3}$, $\Delta_K = 59(1) \times 10^{-3}$, $\delta_J = 2.8(1) \times 10^{-3}$, and $\delta_K = 6(2) \times 10^{-3}$.

[b] The inertial defect, $\Delta = I_c - I_a - I_b$, is given in units of amu Å^2.

Additional centrifugal distortion terms improve the fit only slightly. Sixth-order constants have a negligible effect on the rms of the fit, and constants derived from truncated subsets of the data omitting transitions between levels with high J or high K_a are similar to those derived from the full set of data. The inability of the present nearly rigid-body Hamiltonian to reproduce the observed frequencies to within the measurement uncertainties suggests that Si_3 is readily deformed, with a shallow potential to vibrational distortion similar to that of isovalent SiC_2 [14], causing the centrifugal distortion expansion to converge slowly.

Theoretical calculations and other experimental evidence also point to nonrigidity. Raghavachari concludes on the basis of high-level *ab initio* (MP4/6-31G*) calculations [8] that the bending potential surface of Si_3 is extremely shallow; the present bent isomer is only about 9.5 kcal/mol lower in energy than linear Si_3, even though the two differ in bond angle by more than 100°. The experimentally derived inertial defect $\Delta = I_c - I_a - I_b$ is also consistent with a low frequency bend. In a triatomic molecule the major contribution to Δ comes from the lowest frequency vibration, $\Delta \approx h/2\pi^2\nu$, where ν is the vibrational frequency in cm^{-1} [15]. Our Δ from Table I yields $\nu = 178 \pm 11$ cm^{-1} for Si_3 [16], in fairly good agreement with the computed value of $\nu = 146$ cm^{-1} [10]. In comparison, SiC_2 has a 5.8 kcal/mol barrier to linearity [17], and a similarly large inertial defect ($\Delta = 0.363$ amu Å^2; Ref. [18]) and low frequency (196 cm^{-1}; Ref. [14]) bending vibration.

Twenty-one lines of ^{29}SiSi$_2$ and of ^{30}SiSi$_2$ and 12 lines of Si^{29}SiSi and of Si^{30}SiSi have been measured and analyzed in the same way as those of the normal isotopic species (see Table II). Nearly twice as many lines have been measured for ^{29}SiSi$_2$ and ^{30}SiSi$_2$ than for Si^{29}SiSi and Si^{30}SiSi because ^{29}Si or ^{30}Si substitution at one of the equivalent silicon atoms breaks the C_{2v} symmetry, enabling the symmetry-forbidden transitions to be observed. A more complete account of the laboratory measurements and data analysis will appear elsewhere.

Because of the symmetry of Si_3, only two geometrical parameters are needed to describe its structure. An

TABLE II. Rotational constants of isotopic Si_3 (in MHz).[a]

Constant	$Si^{29}SiSi$	$^{29}SiSi_2$	$Si^{30}SiSi$	$^{30}SiSi_2$
A	9287.915(2)	9452.200(4)	9084.731(3)	9403.725(5)
B	4809.180(2)	4725.505(3)	4809.105(2)	4645.800(4)
C	3160.956(1)	3143.003(2)	3136.984(1)	3102.258(2)
Δ^b	0.382 856(1)	0.381 053(7)	0.386 002(1)	0.382 480(7)

[a] Note: 1σ uncertainties (in parentheses) are in the units of the last significant digits. Centrifugal distortion constants were constrained to those of normal Si_3 (see Table I).

[b] The inertial defect, $\Delta = I_c - I_a - I_b$, is given in units of amu Å^2.

empirical (r_0) structure was derived (Fig. 1) by adjusting the length of the Si-Si bond to the apex atom of the triangle and the apex angle to reproduce the three measured rotational constants of the five isotopic species. This structure is compared with *ab initio* predictions in Table III. The agreement between the two is very good: the difference in the apex angle is less than 0.3° for all but the QCISD(T) calculation, and the experimental and theoretical bond lengths agree to within 0.02 Å. The length of the Si-Si bond (2.177 Å) is close to that of a double bond (2.12 Å), indicating substantial multiple bonding character in Si_3. The length of the Si-Si bond (2.743 Å) opposite the apex angle is considerably longer than that of a single bond (2.35 Å), but calculations show that there is significant bonding even at this separation [8].

In excess of 10^{13} Si_3 clusters are produced in our molecular beam per gas pulse. This abundance, derived by comparison of line intensities in the beam with those of the stable molecule carbonyl sulfide (OCS), at a known fractional abundance (i.e., 1% OCS in Ne), is more than an order of magnitude higher than that reported for SiC_3 (3×10^{11}/pulse; Ref. [19]) and about a factor of 3 lower than SiC_2 (4×10^{13}/pulse; unpublished data). At this high concentration, the gas-phase infrared and optical spectra of Si_3 should be detectable with fairly standard spectroscopic techniques.

Si_3 is of astronomical interest because SiC_2, SiC_4, and SiS, a molecule with two second-row elements, have been detected in the circumstellar shells of evolved carbon-rich stars by radioastronomy. SiC_2, for example, is so abundant in IRC + 10216 that lines of $^{29}SiC_2$ are readily detected there [20]. We find no evidence for Si_3 in two published radioastronomical surveys of IRC + 10216 [21], but this failure is plausibly the result of the small dipole moment (~ 0.35 D vs 2.39 D for SiC_2; Ref. [22]); at the same column density as SiC_2, lines of Si_3 would be 100 times weaker (because emission line intensities are proportional to μ^2). Dedicated searches at frequencies provided by the present work might improve detection limits by a factor of 3 or more. A list of the most interesting astronomical lines will be published elsewhere.

Because of the high concentration achieved here for Si_3, larger Si clusters may be detectable with the present technique. They are of considerable interest because, owing in part to higher coordination numbers, their structures are predicted to be quite different from that of the bulk material, to that derived from microcrystal geometries [23], and to carbon clusters of similar size. The larger atomic radius of Si compared to that of C (by roughly ~30%), for example, generally restricts Si to single bonding, resulting in three-dimensional structures for Si clusters; in contrast, C can readily form either single or multiple bonds, and C clusters consequently possess either linear or monocyclic structures.

Theoretical calculations predict that Si_6, Si_9, and Si_{10} have singlet ground or extremely low-lying electronic states that are polar (see Fig. 3), with dipole moments comparable to that of Si_3. Si_6 is of particular interest because it is one of several important "magic" clusters whose ground state geometry and symmetry have been the subject of controversy [4,24]. Laser photoionization time-of-flight mass spectra of the products of a silane discharge measured in this laboratory indicate that Si_6 is only 15 times less abundant than Si_3, more than adequate for FTM detection. The distorted (edge-capped) trigonal bipyramidal structure with C_{2v} symmetry shown in Fig. 3 is expected to produce a number of accessible rotational transitions.

The rotational spectra of other semiconductor and mixed metal clusters may also be detectable. The ground

TABLE III. Experimental and theoretical Si_3 structures.

Parameter	This work[a]	Ref. [8] (HF/6-31G*)	Ref. [3] (MP4/6-31G*)	Ref. [9] (CISD/DZP)	Ref. [10] [QCISD(T)/6-31G*]
Si-Si (Å)	2.177(1)	2.165	2.17	2.160	2.191
Apex angle (°)	78.10(3)	77.8	77.8	78.1	79.6

[a] Structure that best reproduces the observed rotational transitions of the five isotopic species. Estimated uncertainties in the last significant digit are given in parentheses.

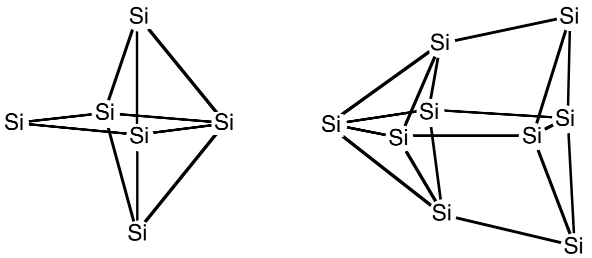

FIG. 3. Predicted geometries from Ref. [4] for the polar isomers of Si_6 and Si_9. Calculated dipole moments are 0.19 D for Si_6 and 0.36 D for Si_9.

state structure of Ge_n is thought to be similar [25] to that of Si_n, and germane, GeH_4, is probably a good source for Ge_n clusters. Ge_3, for example, is thought to have the same C_{2v} symmetry as Si_3, and a comparable b-dipole moment of 0.45 D [4]. If a laser vaporization source is used as a cluster source, mixed metal clusters such as $GaAs_2$ may be detectable as well.

The rotational analysis presented here provides new information on the structure and abundance of the silicon trimer, a cluster of both fundamental and applied interest. Despite the considerable importance of silicon clusters, motivated in part by the theoretical prediction of compact ground state structures which differ markedly from those of carbon and the bulk tetrahedral arrangement, no detailed spectroscopic information of the structure and chemical bonding of any cluster beyond the dimer has been previously reported. Because as shown here Si_3 is copiously produced in a supersonic molecular beam through the discharge products of silane and because its rotational lines are readily detected by the FTM spectroscopy despite its small dipole moment, it may be possible to detect larger clusters by the same method. Structural information derived from such high-resolution studies should be useful in understanding how the chemical and physical properties evolve with cluster size in the transition from small clusters to the bulk semiconductor.

We thank C. A. Gottlieb, S. G. Kukolich, J. Dudek, J. K. G. Watson, P. R. Bunker, and W. Klemperer for helpful discussions. This work is supported by NASA Grant No. NAG5-9379 and NSF Grant No. AST-9820722.

[1] M. F. Jarrold, Science **252**, 1085 (1991); J. Phys. Chem. **99**, 11 (1995).
[2] C. Xu, T. R. Taylor, G. R. Burton, and D. M. Neumark, J. Chem. Phys. **108**, 1395 (1998).
[3] K. Raghavachari and V. Logovinsky, Phys. Rev. Lett. **55**, 2853 (1985).
[4] I. Vasiliev, S. Öğüt, and J. R. Chelikowsky, Phys. Rev. Lett. **78**, 4805 (1997); B. K. Panda, S. Mukherjee, and S. N. Behera, Phys. Rev. B **63**, 045404 (2001).
[5] N. Binggeli and J. R. Chelikowsky, Phys. Rev. Lett. **75**, 493 (1995); B.-X. Li and P.-L. Cao, Phys. Rev. B **62**, 15 788 (2000); I. Vasiliev, S. Öğüt, and J. R. Chelikowsky, Phys. Rev. B **65**, 115416 (2002).
[6] *Chemical Vapor Deposition, Principles and Applications*, edited by M. L. Hitchman and K. F. Jensen (Academic Press, New York, 1993); J. M. Jasinski, B. S. Meyerson, and B. A. Scott, Annu. Rev. Phys. Chem. **38**, 109 (1987).
[7] A. E. Glassgold and G. A. Mamon, in *Chemistry and Spectroscopy of Interstellar Molecules*, edited by D. K. Bohme, E. Herbst, N. Kaifu, and S. Saito (University of Toyko Press, Tokyo, 1992), p. 261; M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, Mol. Phys. **101**, 697 (2003).
[8] K. Raghavachari, J. Chem. Phys. **83**, 3520 (1985).
[9] R. S. Grev and H. F. Schaefer, Chem. Phys. Lett. **119**, 111 (1985).
[10] C. M. Rohlfing and K. Raghavachari, J. Chem. Phys. **96**, 2114 (1992).
[11] J. A. Hayward, Sudarko, J. M. Hughes, E. I. von Nagy-Felsobuki, and L. P. Alderidge, Mol. Phys. **92**, 177 (1997); G. H. F. Diercksen, N. E. Grüner, J. Oddershede, and J. R. Sabin, Chem. Phys. Lett. **117**, 29 (1985).
[12] S. Li, R. J. Van Zee, W. Weltner, Jr., and K. Raghavachari, Chem. Phys. Lett. **243**, 275 (1995); J. Fulara, P. Freivogel, M. Grutter, and J. P. Maier, J. Phys. Chem. **100**, 18 042 (1996).
[13] M. C. McCarthy, W. Chen, M. J. Travers, and P. Thaddeus, Astrophys. J. Suppl. Ser. **129**, 611 (2000).
[14] S. C. Ross, T. J. Butenhoff, E. A. Rohlfing, and C. M. Rohlfing, J. Chem. Phys. **100**, 4110 (1994).
[15] W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (Wiley, New York, 1984), p. 687.
[16] The uncertainty has been estimated from other three and four atom molecules, where this approximation is generally accurate to about 10%. See, e.g., J. K. G. Watson, J. Chem. Phys. **98**, 5302 (1993).
[17] I. M. B. Nielsen, W. D. Allen, A. G. Császár, and H. F. Schaefer III, J. Chem. Phys. **107**, 1195 (1997).
[18] C. A. Gottlieb, J. M. Vrtilek, and P. Thaddeus, Astrophys. J. **343**, L29 (1989).
[19] A. J. Apponi, M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, J. Chem. Phys. **111**, 3911 (1999).
[20] J. Cernicharo, C. Kahane, J. Gómez-González, and M. Guélin, Astron. Astrophys. **167**, L9 (1986).
[21] K. Kawaguchi, Y. Kasai, S. I. Ishikawa, and N. Kaifu, Publ. Astron. Soc. Jpn. **47**, 853 (1995); J. Cernicharo, M. Guélin, and C. Kahane, Astron. Astrophys. Suppl. Ser. **142**, 181 (2000).
[22] R. D. Suenram, F. J. Lovas, and K. Matsumura, Astrophys. J. **342**, L103 (1989).
[23] T. T. Tsong, Appl. Phys. Lett. **45**, 1149 (1984); L. A. Bloomfield, R. R. Freeman, and W. L. Brown, Phys. Rev. Lett. **54**, 2246 (1985).
[24] A. D. Zdetsis, Phys. Rev. A **64**, 023202 (2001); C. Zhao and K. Balasubramanian, J. Chem. Phys. **116**, 3690 (2002).
[25] J. M. Alford, R. T. Laaksonen, and R. E. Smalley, J. Chem. Phys. **94**, 2618 (1991).