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Multiphoton ionization of SiH $_3$ and SiD $_3$ radicals: Electronic spectra, vibrational analyses of the ground and Rydberg states, and ionization potentials

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The electronic spectra of silyl radicals, SiH_3 and SiD_3 , were observed between 310 and 430 nm (46 000-64 000 cm⁻¹) by resonance enhanced multiphoton ionization (REMPI) mass spectroscopy. The spectra were generated through a 2 + 1 REMPI mechanism. Two Rydberg series originating from planar, D_{3h} point group states were observed. One series, of quantum defect $\delta = 1.45(2)$, is comprised of the $\tilde{E}^2 A_1''(4p)$, $\tilde{J}^2 A_2''(5p)$, and $\tilde{M}^2 A_1''(6p)$ Rydberg states which have origins at $v_{0-0} = 48438$, 56929, and 60341 cm⁻¹ in SiH₃ and at $v_{0-0} = 48391$, 56 874, and 60 267 cm⁻¹ in SiD₃. In SiD₃ the $\tilde{P}^2 A_2''(7p)$ Rydberg origin was observed at v_{0-0} = 62 002 cm⁻¹. The \tilde{H}, \tilde{K} , and \tilde{N} states observed in the SiD₃ spectrum comprise the second Rydberg series, $\delta = 2.09$, and were tentatively assigned as $ns^2A'_1$ Rydberg states (n = 5, 6, 7). The \tilde{K} and \tilde{N} origins were observed at $v_{0-0} = 58417$ and 61 005 cm⁻¹. A fit of the Rydberg formula to the $np^2A_{j}^{\prime\prime}$ ($n \ge 5$) origins found the adiabatic ionization potential of the SiH₃ and SiD₃ radicals to be IP_a = 8.135(+5, -2) eV and IP_a = 8.128(1) eV, respectively. Detailed vibrational analyses of these Rydberg states are presented. Analysis showed that in the $\tilde{E}^2 A''_{j}$ (4p) state of the SiH₃ radical ω'_2 (a''_2 symmetric bend) = 796(7) and $2\omega'_4/2(e')$ degenerate bend) = 870(5) cm⁻¹ and that in SiD₃ radical $\omega'_1(a'_1 \text{ SiH}_3 \text{ symmetric stretch}) = 1576(3), \omega'_2$ = 589(3), and $2\omega'_4/2 = 635(6)$ cm⁻¹. The REMPI spectra exhibited v''_2 hot bands from vibrational levels as high as $E_v = 2073 \text{ cm}^{-1}$ in the $\tilde{X}^2 A_1$ state. Modeling calculations, which fit the numerous v_2'' hot bands, predicted barriers to inversion of $B_{inv} = 1935$ cm⁻¹ and B_{inv} = 1925 cm⁻¹ for SiH₃ and SiD₃ $\tilde{X}^2 A_1$ radicals, respectively.

I. INTRODUCTION

The observation of electronic spectra belonging to members of the isovalent series: CH₃, SiH₃, and GeH₃ radicals, have challenged spectroscopists for decades. The methyl (CH₃) radical spectrum was first observed in 1956 by Herzberg using traditional flash-photolysis UV absorption spectroscopy.^{1,2} Despite substantial effort, silyl (SiH₃) radicals eluded spectroscopic discovery.³⁻⁵ Since Herzberg's pioneering work, discoveries of new states in these radicals have originated from studies that used resonance enhanced multiphoton ionization (REMPI) spectroscopy.⁶ In 1982 the special multiphoton selection rules accessible to REMPI spectroscopy enabled us to observe numerous "one-photon forbidden" bands of the CH₃ radical.^{7,8} More recently, the sensitivity and selectivity intrinsic to mass resolved REMPI detection enabled us to observe the first electronic spectra of SiH₃^{9,10} and GeH₃¹¹ radicals.

Interest in the SiH₃ radical has recently increased because of its potential importance to semiconductor manufacturing. SiH₃ radicals are believed to play a pivotal role during the manufacture of silicon films by electric discharge chemical vapor deposition (CVD).¹² The spectroscopic information and procedures described here should facilitate optical studies of the silyl radical in such CVD processes. In this account we present an electronic spectrum of the SiH₃ radical from 310 to 430 nm. This REMPI spectrum encompasses a broader wavelength range than described in our previous reports.^{9,10} We also present the first spectrum of the SiD₃ radical. During our analyses of these REMPI spectra we identified four $np^2A_2''(D_{3h})$ Rydberg states, identified three members of a second Rydberg series tentatively assigned as $ns^2A_1'(D_{3h})$ states, assigned the numerous vibrational bands associated with these Rydberg states, assigned the vibrational bands associated with the \tilde{X}^2A_1 (C_{3v}) state, and precisely determined the adiabatic ionization potentials of SiH₃ and SiD₃ radicals.

All prior experimental studies and most theoretical studies have focused upon the ground state properties of the silyl radical and cation. For an extensive review of the SiH, (n = 1-3) radical literature through 1985, we refer the reader to the paper by Allen and Schaefer.¹³ The SiH₃ radical was first observed in cryogenic matrices with ESR^{14,15} spectroscopy. Early workers established that the ground state is pyramidal and modeled the ESR signals with a simple s-p hybridization model to estimate that $\theta_m = 15.1^\circ$ (\angle H-Si-H = 113.5°).¹⁶ [The angle θ is formed by the intersection of the line through the Si-H axis and the plane formed from the three hydrogen atoms. θ_m is the angle(s) at which the potential energy is at a minimum. For planar D_{3h} structures, $\theta = 0^{\circ}$.] All theoretical calculations qualitatively agree with the ESR geometry but predict less acute pyramidal structures.13,17-24

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Examination of the molecular orbitals shows the basis for the pyramidal structure. The molecular orbital configuration of the ground state SiH₃ radical is

$$(1a_1)^2(2a_1)^2(3a_1)^2(1e)^4(4a_1)^2(2e)^4(5a_1)^1 \quad \tilde{X}^2A_1.$$

When the radical is planar, the $5a_1$ orbital is described as the silicon p_z orbital which is perpendicular to the silicon-hydrogen plane. The 2e orbitals incorporate silicon sp^2 hybrid orbitals. As the radical symmetrically deforms into a pyramid (or "umbrella" shape), the $5a_1$ radical orbital mixes in s-orbital character, the 2e orbital mixes in p_z -orbital character, the 2e orbital mixes. Thus, the potential energy function along the umbrella coordinate of the silyl radical contains two minima centered at $+\theta$ and $-\theta$. The barrier between these minima, B_{inv} , is centered at the planar structure, $\theta = 0^{\circ}$. Best fits of the photoelectron spectrum²⁵ of SiH₃⁻ and the infrared diode laser spectrum of the SiH₃ radical²⁶ have led to estimates that $B_{inv} = 1868-1900$ cm⁻¹.

Ionization of the $\tilde{X}^2 A_1$ silyl radical by ejection of the $5a_1$ electron produces the ground state silyl cation. The molecular orbital configuration (in C_{3v} notation) of the ground state SiH₃ cation is

 $(1a_1)^2(2a_1)^2(3a_1)^2(1e)^4(4a_1)^2(2e)^4 \quad \tilde{X}^1A_1'.$

Ab initio molecular orbital calculations^{27,28} predict that the SiH₃ $\tilde{X}^{1}A_{1}$ cation is planar and in the D_{3h} point group. The planar structure prevails because no p_{z} -orbital electron is

$$(1a_1)^2 (2a_1)^2 (3a_1)^2 (1e)^4 (4a_1)^2 (2e)^4 \qquad \dots (nd)^1 \qquad n = 3,4,5,\dots \\ \dots (ns)^1 \qquad n = 4,5,6,\dots \\ \dots (np)^1 \qquad n = 4,5,6,\dots \\ \dots (nf)^1 \qquad n = 4,5,6,\dots$$

available to stabilize a pyramidal structure. The photoelectron spectrum of the SiH₃ radical reported by Dyke *et al.*²⁷ also indicates that the SiH₃ cation is planar. The spectrum displayed a progression of regularly spaced vibrational bands separated by 820 ± 40 cm⁻¹. This progression was assigned to the v_2 umbrella mode. The constancy of the frequency intervals along the progression indicates that the v_2 umbrella mode potential energy function is harmonic, and thus, that the cation is planar.

Ab initio calculations have predicted values for the adiabatic ionization potential for the SiH₃ radical which range between 7.8 and 8.0 eV.^{20,22,27,28} Research groups have measured the adiabatic ionization potential of the SiH₃ radical with photoelectron spectroscopy,²⁷ photoionization mass spectrometry,²⁹ and guided ion beam tandem mass spectrometry.³⁰ The reported adiabatic ionization potentials range between 8.01 and 8.14 eV. Since these groups have presented their ionization potentials with stringent measurement precisions, these measurements disagree. We offer a new measurement of the adiabatic ionization potential based upon a fit of Rydberg series observed in the spectra of SiH₃ and SiD₃ radicals. This fit provides an order of magnitude improvement in the precision of the ionization potential.

Olbrich²² has reported informative multireference double-excitation configuration interaction (MRD CI) molecular orbital calculations of the ground, excited valence, and Rydberg states of SiH₃. Most excited states of silyl radicals that lie below ~ 10 eV are Rydberg states formed from the configurations:

The MRD CI calculations predict that all nondegenerate Rydberg states are planar. The lowest excited state, the $\tilde{A}^2A'_1$ (4s) Rydberg state, which lies at ~41 855 cm⁻¹, is predicted to be dissociative. Olbrich also reports that one excited valence state exists below the first ionization potential. This state has the configuration

$$(1a_1)^2(2a_1)^2(3a_1)^2(1e)^4(4a_1)^2(2e)^3(5a_1)^2 \quad \widetilde{C}^2 E.$$

The MRD CI calculations predict that this $\tilde{C}^2 E$ valence state possesses a pyramidal geometry and high inversion barrier. This high inversion barrier perturbs the lower energy 2E Rydberg states and impels them into pyramidal geometries.

II. VIBRATIONAL QUANTUM NUMBERING CONVENTIONS AND TRANSITION SELECTION RULES

This report describes transitions between electronic states that possess pyramidal C_{3v} and planar D_{3h} geometries. This section establishes the vibrational quantum numbering conventions and selection rules used in this report. The silyl radical possesses four normal vibrational modes. Descriptions of these modes in the C_{3v} and D_{3h} point groups and the

vibrational selection rules that govern transitions between electronic states are listed in Table I. In this report all vibrational levels are labeled using the ascending sequence, v = 0, 1,2,3,..., where the integer denotes the number of nodes in each vibrational wave function.

The v_2 umbrella mode possesses a double-minimum potential-energy surface. Because of the double-minimum potential, the intervals between v_2 vibrational energy levels are staggered. Previous calculations that have modeled vibrational spectra of silyl radicals^{25,26} predict that the $v_2'' = 0,1$ levels of SiH₃ are separated by ~0.13 cm⁻¹. Higher v_2'' = 2n, 2n + 1 (n = 1, 2, 3, ...) levels that lie below this inversion barrier energy are also nearly degenerate. In the literature the near degeneracy between pairs of vibrational states is often acknowledged by labeling vibrational levels with the quantum number sequence, $0^+, 0^-; 1^+, 1^-; ...; n^+, n^-$. While useful to IR spectroscopy, this numbering system is awkward when discussing selection rules of a transition where the vibrational mode changes from a double minimum to a harmonic potential. The only slight inconvenience of our present sequence, $v_2 = 0, 1, 2, 3, ...,$ is that we must explicitly

37:1	Sym	metry		Vibrational
wib. mode	<i>C</i> _{3v}	D _{3h}	descriptions	selection rule
	a,	a' ₁	Symmetric stretch	$\Delta v_1 = 0, \pm 1, \pm 2,$
<i>v</i> ₂	<i>a</i> 1	a''	Umbrella mode, Symmetric deformation, Out-of-plane bend, Inversion mode	$\Delta v_2 = 0, \pm 2, \pm 4, \dots$
<i>v</i> ₃	е	e'	Degenerate stretch	$\Delta v_3 = 0, \pm 1, \pm 2,$ except $v_3 = 1 \leftrightarrow v_3 = 0$ forbidden
<i>v</i> ₄	е	e'	Degenerate deformation	$\Delta v_4 = 0, \pm 1, \pm 2,$ except $v_4 = 1 \leftrightarrow v_4 = 0$ forbidden

TABLE I. The vibrational modes of the SiH₃ molecule in C_{3v} and D_{3h} point groups and the vibrational selection rules that govern electronic transitions between C_{3v} and D_{3h} (or C_{3v}) structures.

remember that the levels $v_2'' = (0,1)$, $v_2'' = (2,3)$, etc. in the ground $\tilde{X}^2 A_1(C_{3v})$ state are nearly degenerate. Due to this practical degeneracy, the $v_2'' = 0$ and $v_2'' = 1$ vibrational levels possess almost identical populations. Thus, we expect transitions from the $v_2'' = 0,1$ levels to appear in spectra with equal band intensities.

In standard derivations of selection rules³¹ the Born– Oppenheimer approximation is invoked to separate the electronic and nuclear wave functions. This separation permits independent solution of the electronic and vibrational interaction integrals which yield the electronic and vibrational selection rules. For two-photon electronic transitions of the type $C_{3v}-C_{3v}$ or $C_{3v}-D_{3h}$ the electronic selection rules permit transitions between all group symmetries.

In the Born–Oppenheimer approximation the vibrational interaction integral evaluated for multiphoton transitions is the same as the integral evaluated for one photon transitions.^{6,31} The vibrational selection rules that govern transitions between pairs of electronic states belonging to $C_{3v}-C_{3v}$ and $C_{3v}-D_{3h}$ point groups restrict the vibrational quantum number changes along each normal mode. The general selection rule dictates that the product of the symmetries of the two vibrational states must contain the a'_1 symmetry element.

The equilibrium geometries of $\tilde{X}^2 A_1$ and lower energy ²E state silyl radicals belong to the C_{3v} point group. Even so, all vibrational wave functions of C_{3v} silyl radical belong to the D_{3h} point group.³¹ This higher symmetry is present because the vibrational potential energy surfaces of pyramidal SiH₃ structures are symmetric across the x, y reflection symmetry plane and because the inversion barriers centered at the x, y plane are finite. Therefore, vibrational selection rules that govern transitions between pairs of D_{3h} states also govern transitions between pyramidal-planar and pyramidalpyramidal pairs of states. The selection rules for nondegenerate vibrations can be summarized: For totally symmetric vibrations $(a'_1) \Delta v = 0, \pm 1, \pm 2,...,$ for non-totally symmetric vibrations (a'_2, a''_1, a''_2) $\Delta v = 0, \pm 2, \pm 4, \dots$. The selection rules for degenerate vibrations of e' symmetry, for which every vibrational level above v = 1 contains the a'_1 symmetry, $\Delta v = 0, \pm 1, \pm 2,...$ except that levels $v_i = 0$ and $v_i = 1$ cannot intercombine (0 \leftrightarrow 1). Since the SiH₃ radical possesses no vibrational modes of e'' symmetry, this symmetry will not be discussed.

III. APPARATUS AND METHODS

The apparatus³² used in this study has been described elsewhere.¹¹ Briefly, it consisted of a flow reactor which produced the free radical species, an excimer-pumped dye laser or a Nd:YAG-pumped frequency-doubled dye laser which irradiated the radicals and drove the multiphoton ionization process, a time-of-flight mass spectrometer, and a computer/data acquisition system. Free radicals produced in the flow reactor effused into the ion source of the mass spectrometer, where they were ionized by a focused laser beam. The pressure within the ion source was about 5×10^{-5} Torr. The laser generated ions were mass selected and detected by the mass spectrometer. The ion flight time that corresponded to SiH₃⁺ (m/z 31) or to SiD₃⁺ (m/z 34) was sampled by a gated integrator and the ion signal was averaged, displayed, and recorded with a microcomputer.

The excimer-pumped dye laser (Lambda Physik model 2002E) was scanned stepwise at 0.0048 to 0.0072 nm per step (bandwidth ~0.2 cm⁻¹) and ten laser shots were averaged at each step. The Nd:YAG pumped dye laser (Quantel International model TDL-50) was continuously scanned at 0.02 nm/min (bandwidth = 0.16 cm^{-1} FWHM) to yield an effective resolution of $\Delta \nu \sim 0.42 \text{ cm}^{-1}$. Both laser beams were focused by a 250 mm lens into the ionization region. Table II summarizes the characteristics of the dye solutions (Exciton Chemical Co.) used during these studies. The data displayed in this report are uncompensated for variations in dye laser energy.

Both dye lasers were calibrated by the optogalvanic method³³ using a table of neon lines.³⁴ In conformity with custom, wavelengths are reported in reference to air.

Silane (15% SiH₄ in helium) was procured from Matheson Gas Products, Inc. Silane- d_4 (99.9% D) was procured from MSD Isotopes, Inc., diluted with helium to prepare a 15% SiD₄ solution, and stored in a steel bulb at 1 atm pressure. Fluorine and chlorine (10% in helium) were obtained from Spectra Gases.

TABLE II. The laser dyes, their spectral ranges, and maximum energies used during this study.

Laser dye	Spectral range (nm)	Maximum energy (mJ/pulse)
Excimer-pumped dye laser ^a		
Coumarin 440 ^b	420-440	30
Stilbene 420 ^b	415-435	14
DPS	400-415	12
PBBO	390-410	8
QUI	365-395	25
DMQ	340380	23
<i>p</i> -Terphenyl	330-350	24
Nd:YAG-pumped dye laser ^b		
DCM	320-335	5
LDS-698	305335	10

* p-Dioxane solutions except as noted.

^b Methanol solution.

IV. RESULTS AND ANALYSES

A. Radical generation and species characterization

In a flow reactor operated at a total pressure of ~ 2 Torr a 1% mixture of F₂, Cl₂, or O₂ in helium was passed through a microwave discharge to form halogen or oxygen atoms. Downstream from the discharge and a few mm above the sampling skimmer, a slight excess of silane (or silane- d_4) was introduced into the flow stream. The atomic halogen or oxygen reacted with silane via

$$F + SiH_4 \rightarrow SiH_3 + HF$$
, $\Delta H = -43$ kcal/mol, (1)

 $Cl + SiH_4 \rightarrow SiH_3 + HCl, \quad \Delta H = -11 \text{ kcal/mol}, \quad (2)$

 $O + SiH_4 \rightarrow SiH_3 + OH, \quad \Delta H = -10 \text{ kcal/mol.}^{35}$ (3)

Previous studies have established that reactions (1) and (2) produce silyl radicals.^{10,11,27,29,36} When O was reacted with SiH₄, rapid subsequent reaction of OH radicals with SiH₄ almost certainly contributed to SiH₃ radical production. In our previous reports^{10,11} we established upon chemical and spectroscopic grounds that REMPI ion signals were carried by SiH₃ radicals. In the present study we observed that the

mass of the spectral carrier shifted from m/z 31 to m/z 34 when reaction (1) was conducted with SiD₄ reagent. This mass shift demonstrates that the spectral carrier contains three hydrogen atoms and confirms that the present REMPI spectra originate from SiH₃ and SiD₃ radicals. Over the wavelength range of this study the silyl radical signals were carried only by the molecular ion (i.e., SiH₃⁺ or SiD₃⁺). No evidence for photodissociation of the silyl cations was observed.

B. The REMPI spectrum of silyl radicals between 350 and 435 nm

1. Assignment of the \tilde{E} ²A^{\prime_2} (4p) Rydberg states and v'_2 umbrella modes

Figure 1 displays the REMPI spectrum of SiH₃ between 350 and 415 nm. The REMPI spectrum displays one strong progression of ten, regularly spaced, vibrational bands. Along the progression the average two-photon energy interval between band maxima is 2hv = 796(7) cm⁻¹. (That the REMPI spectrum arises from two-photon resonances is shown below.) Numerous weaker bands lie on the shoulders of each progression member. Table III lists the laser wavelength, two-photon energy, and spectral assignment of each REMPI band of the SiH₃ radical observed between 355 and 430 nm.

All spectra presented in this report are composites assembled from portions of spectra obtained using the laser dye solutions listed in Table II. These composites are assembled to clearly present the REMPI bands. The data are uncorrected for the effects of laser intensity variation across the range of each figure. To guide the reader, in Fig. 1 the 2_0^4 band is the most intense. We estimate that if a spectrum of the SiH₃ radical were measured using a laser of constant beam intensity, linewidth, temporal profile, and divergence; it would show that the sequence of $2_{0,1}^n$ bands that lie above and below the 2_0^4 band diminish steadily in intensity. The 2_1^9 and 0_0^0 bands would be ~ 10% and ~ 1% as intense as the 2_0^4 band, respectively.

Figure 2 displays the REMPI spectrum of SiD_3 between 350 and 415 nm. The REMPI spectrum of SiD_3 displays one



FIG. 1. The composite REMPI spectrum of SiH₃ between 350 and 415 nm. The marked features are the transitions from the nearly degenerate $v_2^{\prime\prime} = 0,1$ vibrational levels of the ground state to the $\tilde{E}^2 A_2^{\prime\prime}$ (4p) Rydberg state. Hot bands and vibronic transitions involving other modes are not indexed. The marked features reflect the 4p state v_2^{\prime} mode vibrational spacings.

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TABLE	III. The	REMPI	bands	of the	SiH3	radical	(m/z	31)	observed
between 3	55 and 4	130 nm ai	nd their	r assigr	ıment	s.			

Spectral assignment	Band maximum λ _{air} (nm)	Two-photon energy (cm ⁻¹)	Energy rel. to $\tilde{E}^2 A_2'' (4p)$ origin (cm^{-1})
2 <mark>6</mark>	428.96	46 613	- 1825
2 <mark>4</mark>	424.42	47 111	- 1327
21/2	423.83	47 177	- 1261
2 ⁰ 2	419.08	47 712	- 726
2 ¹ ₅	418.08	47 826	- 612
4 <i>p</i> 0°	412.79	48 438	0
2 ¹ ₃	412.17	48 511	73
2 ² ₄	411.68	48 568	130
2 ¹	406.13	49 231	793
2^{2}_{2}	405.50	49 308	870
23	404.87	49 384	946
2 ² 0	399.69	50 024	1586
23	399.21	50 084	1646
24	398.54	50 169	1731
4 ²	398.40	50 187	1749
2 ³	393.47	50 815	2377
2 ⁴ ₂	392.88	50 891	2453
$2_1^1 4_0^2, 2_5^5$	392.21	50 979	2541
	391.81	51 030	2592
$(4_0^3)^a$	391.23	51 107	2669
2 <mark>4</mark>	387.36	51 618	3180
2 ⁵ ₃	386.95	51 672	3234
$2_0^2 4_0^2$	386.31	51 757	3319
2 ⁵	381.50	52 410	3972
2 ⁶ 2	380.93	52 488	4050
$2_1^3 4_0^2$	380.52	52 545	4107
2 <u>6</u>	375.74	53 213	4775
2 ⁷ ₃	375.27	53 281	4843
2 ⁴ ₀ 4 ² ₀	374.78	53 349	4911
27	370.14	54 018	5580
2 ⁵ ₁ 4 ² ₀	369.18	54 159	5721
2 ⁸	364.73	54 819	6381
2%	359.55	55 610	7172

* Tentative assignment.

strong progression of 13, regularly spaced, vibrational bands. Along the progression the average two-photon energy interval between band maxima is 2hv = 589(3) cm⁻¹. Numerous weaker bands lie on the shoulders of each member of the strong progression. Table IV lists the laser wavelength, two-photon energy, and spectral assignment of each REMPI band of the SiD₃ radical observed between 350 and 430 nm. In Tables III and IV we have assigned the electronic origin of each silyl radical spectrum to the red-most band of each regular progression, i.e., the bands at 412.79 and at 413.19 nm in the SiH₃ and SiD₃ spectra, respectively. As expected for origin bands, the hydrogen isotope shift between these origins is small $(2hv = 47 \text{ cm}^{-1})$.

The present REMPI spectrum can arise from resonances with either excited valence states or Rydberg states. The excited valence state has a doubly occupied silicon p_z orbital, which heightens the inversion barrier between the two radical pyramidal structures. In contrast, Rydberg states feature empty p_z orbitals, which favor planar ($\theta_m = 0^\circ$ and $B_{inv} = 0$) silyl radical geometries. The large change in the v_2 umbrella mode potential that accompanies transitions to any higher excited state implies large, nondiagonal Franck-Condon factors that favor $\Delta v_2 > 0$ transitions. Thus, all electronic spectra of silyl radicals should exhibit long vibrational progressions along the v_2 umbrella mode. Accordingly, we assign the strong vibrational progressions in the REMPI spectra to the v'_2 umbrella mode of the upper state.

Analysis of the ν'_2 umbrella mode of the excited state distinguishes the Rydberg from the excited valence state assignments. The uniform frequency intervals observed along the strong ν'_2 progressions in the SiH₃ and SiD₃ spectra indicate that the excited electronic state ν'_2 umbrella mode potential energy functions are harmonic. Harmonic ν_2 umbrella mode potentials in silyl radicals can occur only for planar structures. Since unperturbed Rydberg states of silyl radical are planar and the excited valence state is pyramidal, we assign the REMPI spectrum to Rydberg states.

The Rydberg state assignment resolves the REMPI excitation mechanism. In the absence of strong perturbations



FIG. 2. Composite REMPI spectrum of SiD₃ between 350 and 415 nm. The marked features are the transitions from the nearly degenerate $v_2'' = 0,1$ vibrational levels of the ground state to the $\tilde{E}^2 A_2''$ (4p) Rydberg state. Hot bands and vibronic transitions involving other modes are not indexed. The marked features reflect the 4p state v_2' mode vibrational spacings.

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TABLE IV. The REMPI bands of the SiD₃ radical (m/z 34) observed between 350 and 430 nm and their assignments.

	Band		Energy rel. to
	maximum	Two-photon	<i>̃E A</i> ″₂ (4 <i>p</i>)
Spectral	λ_{air}	energy	origin
assignment	(nm)	(cm ⁻¹)	(cm ⁻¹)
2%	426.18	46 916	- 1475
21	425.25	47 018	- 1373
2 ⁰	422.34	47 342	- 1049
2 ¹ ₇	421.45	47 442	- 949
2 ⁰ ₂	417.87	47 848	- 543
21	417.18	47 928	- 463
4p 00	413.19	48 391	0
2	412.75	48 442	51
2 ²	412.08	48 521	130
2	408.15	48 987	596
2 ²	407.73	49 039	648
2 ²	403.30	49 577	1186
23 23	402.92	49 623	1232
4 ²	402.52	49 673	1282
2.3	398.55	50 168	1777
24	398.15	50 219	1828
2^{1}_{2}	397.81	50 261	1870
4 ³	397 39	50 314	1923
-0 24	393 93	50 757	2366
20 25	393.59	50 800	2409
2^{2}	393.25	50 843	2465
20 + 0 $2^{1} 4^{3}$	392 54	50 036	2452
1 ¹ 2 ²	390.85	51 156	2345
1020 75	389.42	51 344	2953
26	389.12	51 384	2993
2^{2} $2^{3}4^{2}$	388.81	51 425	3034
2^{1}	388.03	51 528	3137
1173	386 30	51 747	3356
1 0 2 1 7 6	385.01	51 932	3541
$2_0^{3} 4^{3}$	383 58	57 125	3734
11.24	382.05	52 334	30/3
1 ₀ 4 ₀	380.67	52 524	4122
24 1 24 A ³	370.07	52 324	4133
20 TO 11 75	377.24	52 018	4537
1 ₀ 41 78	376 30	52 121	4720
40 11.26	373.70	53 504	5112
1 ₀ 2 ₀	373.70	53 705	5115
$\frac{4}{127}$	372.30	53 703	5700
1 ₀ 2 ₁	309.30	54 100	5004
40 11 08	365 67	54 515 \$4 679	J724 6799
	264 29	J4 0/9 54 007	0288
\mathcal{L}_1	262 22	J4 00/ 55 0/5	0490
(22 2 ₀) 1109	361 91	55 045	6077
$1_0 Z_1$	260 51	JJ 203 EE 861	00/2
$\frac{Z_0^{-1}}{(\tilde{H} 2^5)^2}$	300.31	JJ 401 55 653	/0/0
$(II \ 2_1)^{-1}$	337.41 356 95	33 032 #6 030	
$(\Pi \ 1_0^2 2_1^2)^2$ $(\Pi \ 1_0^2 2_1^2)^2$	330.83 255 AG	56 040	
111 401	JJJ.40		

^a Tentative vibrational assignment. See the text.

the energies of Rydberg state origins conform to the familiar equation:

$$v_{0-0} \ (\text{cm}^{-1}) = \text{IP}_a - \frac{109737}{(n-\delta)^2}$$

where v_{0-0} is the electronic origin, IP_a is the adiabatic ioniza-

tion potential, *n* is the principal quantum number, and δ is the quantum defect. We show in Sec. IV D that $IP_a = 8.135$ eV (65 610 cm⁻¹) for the SiH₃ radical and IP_a = 8.128 eV (65 560 cm⁻¹) for the SiD₃ radical. Quantum defects for *ns*, np, nd, and nf Rydberg states of silicon-centered radicals should lie near $\delta \sim 2.0$, 1.6, 0.1, and 0.0, respectively.³⁷⁻³⁹ Rydberg formula calculations using these quantum defects predict that all Rydberg states lie above $31\,000\,\mathrm{cm}^{-1}$, i.e., at the energy of two or more laser photons. For the present spectra the most sensible solution to the Rydberg formula gives a principal quantum number of n = 4 and a quantum defect $\delta = 1.47$. These values indicate that the REMPI spectra arise from two-photon preparation of 4p Rydberg states. The 4p Rydberg origins of of SiH_3 and SiD_3 radicals lie at 48 438 and 48 391 cm $^{-1}$, respectively. A silyl radical in the 4p Rydberg state must absorb one more laser photon to ionize and form the $\tilde{X}^{1}A_{1}$ cation. Thus, the ion signal is generated through a 2 + 1 REMPI mechanism.

The v'_2 vibrational data enable an assignment of the state symmetry of the 4p Rydberg state. In the C_{3v} point group the np Rydberg orbitals of SiH₃ radicals are divided into states of E and A_1 symmetries. MRD CI calculations by Olbrich²² predict that all ${}^{2}A_{1}$ (C_{3v} notation) Rydberg states are planar. Thus, spectra of ${}^{2}A_{1}$ Rydberg states should display regular v'_2 vibrational progressions. In contrast, the MRD CI calculations predict that the 2 ^{2}E valence states possesses a strongly pyramidal geometry and high inversion barrier. To avoid "forbidden" diabatic curve crossing of adjacent ²E states, the 2 ^{2}E valence basis function mixes strongly with 1 ^{2}E (3d), $3^{2}E(4p)$, and $4^{2}E(3d)$ Rydberg basis functions. The amount of mixing changes as a function of the umbrella coodinate angle. The resulting four ${}^{2}E$ electronic states possess complex v'_2 umbrella mode potentials with multiple potential energy minima and maxima. Thus, REMPI spectra of these lower energy ${}^{2}E$ states should display irregularly spaced v'_2 vibrational progressions.²² Since the present **REMPI** spectrum exhibits a regularly spaced v'_2 vibrational progression, we assign the upper state as the $4p^2A_1(C_{3n})$ Rydberg state. Since this Rydberg state is planar, belongs to the D_{3h} point group, and is the fifth excited state above the ground state, we will refer to this state as the $\tilde{E}^2 A_2''$ (4p) Rydberg state.

2. Assignment of the $v_2^{"}$ hot bands

Many of the weaker bands and shoulders observed throughout the $\tilde{E}^2 A_2''(4p) \leftarrow \tilde{X}^2 A_1$ REMPI spectra of silyl radicals arise from thermally populated v_2'' vibrational levels of the $\tilde{X}^2 A_1$ state, i.e., v_2'' hot bands. Figure 3 shows the composite REMPI spectrum between 410 and 435 nm of the SiH₃ radical. The spectrum of the SiH₃ radical shows v_2'' hot band transitions from populated $v_2'' = 0-7$ vibrational levels of the ground state to the $v_2' = 0$ and $v_2' = 1$ levels in the $\tilde{E}^2 A_2'''(4p)$ state. The populated $v_2'' = 2-5$ levels also account for many of the shoulders that appear on members of the $2_{0,1}^n$ progression. Table III lists these band assignments. Because the ground state potential energy surface along the v_2' umbrella coordinate possesses two minima, the ground state vibrational intervals are not regular.

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FIG. 3. Composite REMPI spectrum of SIH₃ between 410 and 435 nm. The marked features are the transitions from several vibrational levels of the ground state to the $v'_2 = 0,1$ vibrational levels of the $\tilde{E}^2 A''_2$ (4*p*) Rydberg state. The marked features reflect the ground state v''_2 vibrational spacings.

Figure 4 shows the composite REMPI spectrum between 410 and 435 nm of the SiD₃ radical. The spectrum of the SiD₃ radical shows transitions from populated $v_2'' = 0-7$ and $v_2'' = 9$ vibrational levels of the ground state to the lowest two $v_2' = 0$ and $v_2' = 1$ levels. The 2_8^0 band was not observed. The populated $v_2'' = 2-4$ levels also account for many of the shoulders on members of the $2_{0,1}^n$ progression. Table IV lists these band assignments.

Tables V and VI shows the $\tilde{E}^2 A_2''(4p) \leftarrow \tilde{X}^2 A_1$ Deslandres tables for the v_2 umbrella modes of SiH₃ and SiD₃ radicals, respectively. These tables display the $\Delta v_2 = 0, \pm 2$,



FIG. 4. Composite REMPI spectrum of SiD₃ between 410 and 435 nm. The marked features are the transitions from several vibrational levels of the ground state to the $v'_2 = 0,1$ vibrational levels of the $\tilde{E}^2 A''_2$ (4*p*) Rydberg state. The marked features reflect the ground state v''_2 vibrational spacings.

 $\pm 4,...$ vibrational bands and band differences of the ground state (rows) and of the $\tilde{E}\,^2A_2''(4p)$ Rydberg state (columns). In all, v_2 hot bands account for 22 REMPI bands in each of the silyl radical spectra. The agreement of the vibrational intervals along each row and down each column indicates the overall self-consistency of these band assignments throughout the $\tilde{E}\,^2A_2''(4p) \leftarrow \tilde{X}\,^2A_1$ REMPI spectrum. As described below, we will average these measurements of the $\tilde{X}\,^2A_1\,v_2''$ band intervals with other REMPI measurements to construct a manifold of v_2 vibrational energy levels.

Initially, the appearance of silyl radicals with up to $E_v \sim 2100 \text{ cm}^{-1}$ of internal energy may seem surprising. However, flow reactors are devices usually operated neither at thermal nor chemical equilibrium. In our present experimental configuration a small fraction of the SiH₄ can react with atomic fluorine within the sampling skimmer. Most SiH₃ radicals are sampled within 100 μ s of their production, i.e., within ~10³ SiH₃/He collisions. Under these conditions few vibrationally hot radicals will be quenched. Thus, the appearance of vibrational hot bands up to $v_2'' = 9$ in these spectra shows that the reaction of F + SiH₄ forms a small nascent fraction of the SiH₃ radicals with up to ~2100 cm⁻¹ of internal energy.

3. Assignment of the v'_4 degenerate deformation mode

Numerous bands appear in the $\tilde{E}^2 A_2'' \leftarrow \tilde{X}^2 A_1$ REMPI spectra of silyl radicals (Figs. 1 and 2; Tables III and IV) that are not assignable as ν'_2 bands. A portion of these bands are accounted for when they are assigned to the ν'_4 degenerate deformation mode of the $\tilde{E}^2 A_2''$ (4p) Rydberg state, both alone and in combination with ν'_2 bands.

Table VII lists the vibrational REMPI bands of the SiH₃ radical that involve the v'_4 mode. Because the v'_4 vibration is degenerate, the $v'_4 = 1 \leftarrow v''_4 = 0$ transition is symmetry forbidden³¹ (Table I); the 4¹₀ band does not appear in the spectrum. Since transitions to higher v'_4 levels are symmetry allowed, the 4²₀ and 4³₀ bands do appear in the spectrum. Table VII also lists the combination bands whose differences measure $2\omega'_4$. The average of all measurements gives $2\omega'_4$ = 1740(10) cm⁻¹. The one measurement which involves $3\omega'_4$ can be used to derive an ω'_{e4} of 791(25) cm⁻¹ and an x'_{e4} of 20(5) cm⁻¹, using the formula $G(v) = \omega_e (v + 1)$ $+ x_e (v + 1)^2$. However the difference in vibrational spacing may not be due to anharmonicity in the vibrational potential, but due to a splitting of the degenerate levels which comprise the v > 1 levels of v'_4 .

In SiD₃ the REMPI spectrum exhibits the corresponding v'_4 vibrational band structure. Table VIII lists the vibrational REMPI bands of the SiD₃ radical that involve the v'_4 mode. Consistent with our vibrational assignments, the 4^1_0 band does not appear but the 4^2_0 and 4^3_0 bands do. Table VIII also lists the intervals among the combination bands which reflect the 4^2_0 and 4^3_0 spacings. The averages of these combination differences are $2\omega'_4 = 1270(11)$ cm⁻¹ and $3\omega'_4$ = 1949(16) cm⁻¹. As for SiH₃, these can be used to derive an ω'_{e4} of 576(25) cm⁻¹ and an x'_{e4} of 15(5) cm⁻¹. The isotopic frequency ratio between the ω'_4 vibrational frequencies of the SiH₃ and SiD₃ radicals is 1.37(2). This ratio

TABLE V. The Deslandres tables which analyze the v_2 umbrella bands observed in the $\tilde{E}^2 A_2''$ (4p) $\leftarrow \tilde{X}^2 A_1$ REMPI spectrum of the SiH₃ radical. Energies and differences are in cm⁻¹.

v_2 even									
								A	Measured $\tilde{E}^2 A'' (Ar)$
	$v_{2}'' = 0$		$v_{2}'' = 2$		$v_{2}'' = 4$		$v_{2}'' = 6$	ω_2'	v'_2 interval
$v'_{2} = 0$	48 438	726	47 712	600	47 111	499	46 613		
	1 587		1 597					1592	2–0
$v_{2}' = 2$	50 024	716	49 308						
	1 593		1 583					1588	4-2
$v_2' = 4$	51 618	726	50 891						
	1 595		1 597					1596	6-4
$v_{2}' = 6$	53 213	725	52 488						
2	1 606							1606	8–6
$v'_2 = 8$	54 819								
Av. ω_2''		723(5)		600		499			
Measured									
$\tilde{X}^2 A_1$		2-0		4-2		6-4			
v ₂ "Interval									
v_2 odd									
2									Measured
								Av.	$\widetilde{E}^{2}A_{2}''$ (4p)
	$v_{2}'' = 1$		$v_{2}'' = 3$		$v_{2}'' = 5$		$v_{2}'' = 7$	ω_2'	v_2' interval
$v'_{2} = 1$	49 231	720	48 511	685	47 826	649	47 177	-	
	1 584		1 573		1 558			1572	3-1
$v'_{2} = 3$	50 815	731	50 084	700	49 384				
	1 595		1 588		1 595			1591	5-3
$v'_{2} = 5$	52 410	738	51 672	693	(50 979) ^a				
	1 609		1 609					1609	7–5
$v_{2}' = 7$	54 018	738	53 281						
	1 59							1 591	9–7
$v'_{2} = 9$	55 610								
Α ν. ω ₂ "		732(9)		692		649			
Measured									
$\tilde{X}^2 A_1$		3-1		5-3		7–5			
v_2'' interval									
					<u> </u>	Av.	$\omega_2'/2 = 796(7)$	cm^{-1} for $\tilde{E}^2 A_2''$	

* Blended band.

matches the ω_4 isotope ratio of 1.35 predicted from the ion structure.⁴⁰

In summary, the present ν'_4 vibrational assignments for the SiH₃ and SiD₃ radicals are supported by the absence of the 4¹₀ bands and the agreement of the observed isotopic shift ratio with the predicted value.

4. Assignment of the v'_1 Si–D₃ symmetric stretching mode

Between 390 and 361 nm the REMPI spectrum of the SiD₃ radical displays a progression of bands that we have assigned to $v'_1 = 1 \leftarrow v''_1 = 0$ transitions in combination with $2^m_{1,0}$ (m = 2-8) transitions (Fig. 3 and Table IV). Table IX shows the combination differences between pairs of $2^m_{1,0}$ and $1^1_0 2^m_{1,0}$ (m = 2-8) bands. The average difference between these bands gives a v'_1 Si-D₃ symmetric stretch frequency of

 $\omega'_1 = 1576(3) \text{ cm}^{-1}$. No corresponding ν'_1 band system was observed in the REMPI spectrum of the SiH₃ radical.

C. The REMPI spectrum of silyl radicals between 310 and 360 nm

With increasing principal quantum number the energy that separates the higher Rydberg states becomes smaller. As a result, the REMPI spectra at shorter wavelengths become increasingly more congested as vibrational progressions from adjacent Rydberg states overlap. Between 310 and 360 nm the REMPI spectra display features from six Rydberg states that belong to two Rydberg series. These are described below.

1. Assignment of the $\tilde{J}^2 A_2^{"}(5p)$ Rydberg states

Figure 5 displays the composite 2 + 1 REMPI spectra between 310 and 360 nm of the SiH radical (m/z 31). Table

TABLE VI. The Deslandres tables which analyze the v_2 umbrella bands observed in the $E^2A_2^{\prime\prime}(4p) \leftarrow X^2A_1$ REMPI spectrum of the SiD ₃ radical. End	ergies
and differences are in cm ⁻¹ .	

v ₂ even											
	$v_{2}'' = 0$			$v_{2}'' = 2$		$v_{2}'' = 4$		v ₂ " =	= 6	Αν . ω ₂ '	Measured $\tilde{E}^2 A_2'' (4p)$ v_2' interval
$v'_{2} = 0$	48 391	5	43	47 848	506	47 342	426	46 9	016		
	1 186			1 190						1188(2)	2-0
$v_2' = 2$	49 577	5	38	49 039							
	1 180			1 180						1180	4-2
$v'_{2} = 4$	50 757	5	38	50 219							
	1 175			1 165						1170(5)	6-4
$v_2' = 6$	51 932	5	49	51 384							
	1 174									1174	86
$v_{2}' = 8$	53 106										
	1 188									1188	10-8
$v_2' = 10$	54 294										
Av. ω"		542	2(4)		506		426				
Measured							<i>.</i> .				
X^2A_1		2	-0		4-2		6-4				
v_2'' interval											
v_2 odd											
										Av.	Measured $\tilde{E}^2 A_1''$ (4p)
	$v_2'' = 1$		$v_{2}'' = 3$		$v_{2}'' = 5$		$v_{2}'' = 7$		$v_{2}'' = 9$	ω'2	ν'_2 interval
$v'_{2} = 1$	48 987	545	48 442	514	47 928	486	47 442	424	47 018		
	1 180		1 181							1181	3-1
$v_2' = 3$	50 168	544	49 623								
	1 176		1 177							11 77	5–3
$v_{2}' = 5$	51 344	544	50 800								
_	1 180									1180	7–5
$v_{2}' = 7$	52 524										
	1 173									1173	9–7
$v'_{2} = 9$	53 698										
Α ν. ω ₂ "		545(1)		514		486		424			
Measured											
X'A		3–1		5-3		7-5		9 –7			
v ₂ interval								Av. $\omega_2'/2$	= 589(3) a	m^{-1} for $\tilde{E}^2 A_2''$	state

X lists the band maxima and spectral assignments. The most prominent progression in the SiH₃ radical spectrum is comprised of seven $2_{0,1}^n$ (n = 0-6) bands separated by $2hv = 821(4) \text{ cm}^{-1}$. The uniform spacing between these $2_{0,1}^n$ bands shows that the upper state is a planar Rydberg state. The red-most band in this progression at 351.22 nm is assigned as the electronic origin $(v_{0-0} = 56\ 929\ \text{cm}^{-1})$. Table XI presents the Deslandres table that analyzes the 11 observed 2_m^n (n = 0-6, m = 0-3) bands that constitute this part of the REMPI spectrum. The ground state $v_2'' = 2-0$ and $v_2'' = 3-1$ intervals derived in Table XI agree well with those derived from the analysis of the $\tilde{E} {}^2A {}''_2(4p) \leftarrow \tilde{X} {}^2A_1$ band system (Table V).

Figure 6 displays the composite 2 + 1 REMPI spectra between 310 and 360 nm of the SiD₃ radicals (m/z 34). Table XII lists the band maxima and spectral assignments. The spectrum of SiD₃ exhibits a regular progression of 13 v'_2 umbrella mode vibrational bands separated by $2hv = 608(3) \text{ cm}^{-1}$. The prominent $2_{0,1}^{m}$ (m = 0-12) band progression, marked in Fig. 6, terminates upon the origin at $351.56 \text{ nm} (v_{0.0} = 56\ 874 \text{ cm}^{-1})$. Observation of the 2^{0}_{2} hot band at 354.95 nm verifies the origin assignment in SiD₃. The small red shift of $\Delta v_{0-0} = 55 \text{ cm}^{-1}$ between the SiH₃ and SiD₃ origins also supports the 0_0^0 band assignments for both isotopic radicals. Table XIII presents the Deslandres table that analyzes the 19 observed $2_m^n = (n = 0-6, m = 0-6)$ 3) bands that constitute this part of the REMPI spectrum. The ground state $v_2'' = 2-0$ and $v_2'' = 3-1$ intervals derived in Table XIII agree well with those derived from the analysis of the $\tilde{E}^2 A_2''$ (4p) $\leftarrow \leftarrow \tilde{X}^2 A_1$ band system (Table VI).

Using the assigned origins, the solutions to the Rydberg equation for the SiH₃ and SiD₃ radicals give n = 5 and $\delta = 1.45$. This quantum defect is only 0.02 smaller than computed for the $\tilde{E}^2 A_2^{"}$ (4p) Rydberg state. Because of the

TABLE VII. The bands observed in the $\tilde{E}^2 A_1''(4p) \leftarrow \tilde{X}^2 A_1$ REMPI spectrum of the SiH₃ radical that involve the $v'_4(e')$ degenerate deformation mode. This table shows the band intervals between v'_4 levels and the combination differences used to derive ω'_4 .

Assignment	Two-photon energy (cm ⁻¹)	Band interval (cm ⁻¹)
000 402 403	48 438 50 187 51 107	1749 2669
Combination differences 2_1^1 $2_1^1 4_0^2$	49 231 50 979	1748
2 ² ₀ 2 ² ₀ 4 ² ₀	50 024 51 757	1733
2 ³ 2 ³ ₁ 4 ²	50 815 52 545	1730
2 ⁴ 2 ⁶ 4 ²	51 618 53 349	1731
2_1^5 $2_1^5 4_0^2$	52 410 54 159	1749
Av. $2\omega'_4 = 1740(10) \text{ cm}^{-1}$ $3\omega'_4 = 2669$		
$\omega'_{e4} = 791(25) \text{ cm}^{-1a}$ $x'_{e4} = 20(5)$		

 $a^{a}G(v) = \omega_{e}(v+1) + x_{e}(v+1)^{2}$.

TABLE VIII. The bands observed in the $\tilde{E}^2 A_2''$ (4p) $\leftarrow \tilde{X}^2 A_1$ REMPI spectrum of the SiD₃ radical that involve the v'_4 (e') degenerate deformation mode. This table shows the band intervals between v'_4 levels and the combination difference used to derive ω'_4 .

Assignment	Two-photon energy (cm ⁻¹)	Band interval (cm ⁻¹)
00 40 40 40	48 391 49 673 50 314	1282 1923
Combination differences 2_1^1 $2_1^1 4_0^2$ $2_1^1 4_0^3$	48 987 50 261 50 936	1274 1949
2_0^2 $2_0^2 4_0^2$ $2_0^2 4_0^3$	49 577 50 843 51 528	1266 1951
2_1^3 $2_1^3 4_0^2$ $2_1^3 4_0^3$	50 168 51 425 52 125	1257 1957
2 ⁴ ₀ 2 ⁴ ₀ 4 ³ ₀	50 757 52 722	1965
Av. $2\omega'_4 = 1270(11) \text{ cm}^{-1}$ Av. $3\omega'_4 = 1949(16)$ $\omega'_{e4} = 576(25) \text{ cm}^{-1a}$ $x'_{e4} = 15(5)$		

 ${}^{a}G(v) = \omega_{e}(v+1) + x_{e}(v+1)^{2}.$

similarity of quantum defects, we have assigned this portion of the spectrum to $\tilde{J}^2 A_2''$ (5p) $\leftarrow \tilde{X}^2 A_1$ transitions. Small shifts in quantum defect between the first and second members of a Rydberg series are commonly observed. In carbon-centered radicals quantum defects usually decrease by 0.02-0.05 between the two lowest energy members of a Rydberg series.^{2,8,41}

2. Assignment of the \widetilde{M} ²A₂(6p) and ∞P ²A₂(7p) Rydberg states

Between 313 and 332 nm higher members of the silyl radical $np^{2}A_{2}$ Rydberg series appear in the spectra (Fig. 5 and Tables X and XII). The spectrum of the SiH₃ radical displays a three member $2_{0,1}^n$ (n = 0-2) progression separated by $2h\nu = 800(30)$ cm⁻¹ (Table XIV). We have assigned the Rydberg origin to the progression member at 331.35 nm $(v_{0-0} = 60 341 \text{ cm}^{-1})$. Solution of the Rydberg equation gives n = 6 and $\delta = 1.45$. The similarity of these quantum defects to lower $np^{2}A_{2}$ series members supports our assignment of these REMPI bands to $\widetilde{M}^2 A_2''(6p) \leftarrow \widetilde{X}^2 A_1$ transitions.

Between 313 and 332 nm the $\widetilde{M}^2 A_2''$ (6p) $\leftarrow \leftarrow \widetilde{X}^2 A_1$ transitions of the SiD₃ radical appear as a six member progression of $2_{0,1}^n$ (n = 0-5) bands uniformly separated by $2h\nu = 615(4)$ cm⁻¹ (Fig. 6 and Table XIV). We have assigned the progression terminus at 331.76 nm as the origin $(v_{0-0} = 60\ 267\ \mathrm{cm}^{-1})$ which gives the Rydberg equation solution: n = 6 and $\delta = 1.45$. The isotope shift of $\Delta v_{0-0} = 74$ cm^{-1} between the SiH₃ and SiD₃ 0_0^0 bands supports these origin assignments.

The $\tilde{P}^2 A_2''$ (7p) $\leftarrow \leftarrow \tilde{X}^2 A_1$ REMPI spectrum of SiD₃ appears as a regular $2_{0,1}^n$ (n = 0-3) progression with four members evenly separated by $2h\nu = 615(3)$ cm⁻¹ (Table XV). The progression terminus at 322.48 nm is assigned as the origin ($v_{0-0} = 62\ 002\ \text{cm}^{-1}$). The Rydberg equation solution, n = 7 and $\delta = 1.45$, leads to the assignment of this band system as the $\tilde{P}^2 A_2''(7p)$ Rydberg state.

3. Assignment of the Ĥ, K, and Ñ states, the second Rydberg series

REMPI bands originating from a second Rydberg series of silyl radicals appear between 310 and 365 nm. In this section we present the spectral analyses in the order of descending energy, \tilde{N} , \tilde{K} , and \tilde{H} . This presentation order is chosen because the highest member of this second Rydberg series has the most secure origin assignment. This assign-

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TABLE IX. The combination differences between bands observed in the $\tilde{E}^2 A_2''(4p) \leftarrow \tilde{X}^2 A_1$ REMPI spectrum of the SiD₃ radical that lead to the $\nu'_1(a'_1)$ Si-D₃ symmetric stretch mode assignment and derivation of ω'_1 .

Assignment	Two-photon energy (cm ⁻¹)	Combination difference (cm ⁻¹)
$\frac{2_0^2}{1_0^1 2_0^2}$	49 577 51 156	1580
2_1^3 $1_0^1 2_1^3$	50 168 51 747	1579
2 ₀ ⁴ 1 ₀ ¹ 2 ₀ ⁴	50 757 52 334	1577
2 ⁵ 1 ¹ ₀ 2 ⁵	51 344 52 918	1574
26 1, 26	51 932 53 504	1572
2_1^7 $1_0^1 2_1^7$	52 524 54 100	1576
2 ⁸ ₀ 1 ¹ ₀ 2 ⁸ ₀	53 106 54 679	1573
	Av. $\omega'_1 = 1576 \pm 3 \text{ cm}^-$	- 1



FIG. 5. Composite REMPI spectrum of SiH₃ between 310 and 360 nm. The marked features are the transitions from the nearly degenerate $v_2'' = 0,1$ vibrational levels of the ground state to the $\tilde{J}^2 A_2''$ (5p) and $\tilde{M}^2 A_2''$ (6p) states.

ment helps establish the origin bands of lower series members.

The $\tilde{N} \leftarrow \tilde{X}^2 A_1$ spectrum of the SiD₃ radical shows a regular progression of $2_{0,1}^n$ (n = 0-5) bands separated by $2h\nu = 619(7)$ cm⁻¹ (Fig. 6 and Table XVI). This ν'_2 umbrella mode frequency indicates that the valence electron configuration in the core of this Rydberg state corresponds to the $\tilde{X}^1 A_1$ cation. The terminus of this progression at

327.75 nm is assigned as the \tilde{N} state origin ($v_{0-0} = 58417$ cm⁻¹). This origin assignment gains additional support from the appearance of the 2^{0}_{2} hot band at 330.64 nm. Solving the Rydberg equation yields two physically meaningful solutions: n = 7, $\delta = 2.09$ and n = 5, $\delta = 0.09$. These solutions correspond to the $7s^{2}A'_{1}$ (D_{3h}) Rydberg state or to one of the three 5d Rydberg states.

The next lower member of this Rydberg series, the K state, is also clearly identified. The $\tilde{K} \leftarrow \tilde{X}^2 A_1$ spectrum of the SiD₃ radical shows a weak four member progression of $2_{0,1}^n$ (n = 0-3) bands which are regularly separated by $2h\nu = 615(3) \text{ cm}^{-1}$ (Table XVI). We have assigned the red terminus of this progression at 342.27 nm as the \tilde{K} state

TABLE X. The REMPI bands of the SiH₃ radical (m/z 31) observed between 310 and 360 nm and their assignments.

Spectral assignment	Band maximum λ_{air} (nm)	Two-photon energy (cm ⁻¹)	Energy rel. to $\tilde{J}^2 A_2'' (5p)$ origin (cm ⁻¹)	Energy rel. to $\widetilde{M}^2 A_2''(6p)$ origin (cm^{-1})
$5p \ 0_0^0$	351.22	56 929	0	
$5p 2_1^1$	346.21	57 752	823	
5p 2 ² ₂	345.63	57 849	920	
$5p 2_0^2$	341.37	58 570	1641	
$5p 2_3^3$	340.85	58 661	1732	
$5p 2_1^3$	336.65	59 392	2463	
$5p 2_2^4$	336.02	59 503	2574	
5p 204	332.05	60 215	3286	
6p 00°	331.35	60 341		0
$5p 2_1^5$	327.57	61 038	4109	
5p 2 ⁶	327.05	61 135	4206	
6p 2¦	326.91	61 162		821
5p 2%	323.24	61 855	4926	
6p 2 ² ₀	322.79	61 941		1600

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		v ₂ " even		v ₂ " odd			Measured $\tilde{I}^2 A'' (5n)$
$v_2 = 0$		$v_{2}'' = 2$	$v_{2}'' = 1$		$v_{2}'' = 3$	ω'2	v'_2 interval
56 929							
1 646						1646	20
58 575	726	57 849					
1 639		1 654				1647(7)	4-2
60 214	711	59 503					
1 641		1 632				1637(5)	6-4
61 855	720	61 135					
			57 756				
			1 636			1636	3–1
			59 392	731	58 661		
			1 647			1647	5-3
			61 038				
	719(6)			731			
	20			3–1			
			Av. $\omega_2'/2 = 821(4) \text{ cm}^{-1}$				
	56 929 1 646 58 575 1 639 60 214 1 641 61 855	56 929 1 646 58 575 726 1 639 60 214 711 1 641 61 855 720 719(6) 2-0	56 929 1 646 58 575 726 57 849 1 639 1 654 60 214 711 59 503 1 641 1 632 61 855 720 61 135 719(6) 2-0	56 929 1 646 58 575 726 57 849 1 639 1 654 60 214 711 59 503 1 641 1 632 61 855 720 61 135 57 756 1 636 59 392 1 647 61 038 719(6) 2-0	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

TABLE XI. The Deslandres table which analyzes the v_2 umbrella bands observed in the $\tilde{J}^2 A_2''(5p) \leftarrow \tilde{X}^2 A_1$ REMPI spectrum of the SiH₃ radical. Energies and differences are in cm⁻¹.

origin ($v_{0-0} = 58 \ 417 \ \text{cm}^{-1}$). Solving the Rydberg equation yields the physically meaningful solutions: n = 6, $\delta = 2.08$ and n = 4, $\delta = 0.08$. The band system may arise from two-photon preparation of the $6s^2A'_1(D_{3h})$ Rydberg state or a 4d Rydberg state.



FIG. 6. Composite REMPI spectrum of SiD₃ between 310 and 360 nm. The marked features are the vibronic transitions from the nearly degenerate $v_2^{"} = 0,1$ vibrational levels of the ground state to the $\tilde{J}^2 A_2^{"}$ (5*p*), $\tilde{M}^2 A_2^{"}$ (6*p*), \tilde{N} , and $\tilde{P}^2 A_2^{"}$ (7*p*) states. The \tilde{K} state is not indexed.

According to the Rydberg formula, the origin of the next lower member of this second Rydberg series should appear near 380.1 nm ($v_{0-0} \simeq 52\ 602\ \text{cm}^{-1}$). A fragment of a Rydberg band system, made up of four REMPI bands, appears between 355 and 364 nm (Fig. 2 and Table IV). The three $H \leftarrow \leftarrow X$ bands at 363.23, 359.27, and 355.46 nm comprise a short progression. The interval between these bands, 2hv = 602(5) cm⁻¹, shows that the v'_2 umbrella mode is active. This v'_2 progression may extend further to the red. If it does, coincidences with the stronger bands of the $\widetilde{E}^{2}A_{2}''(4p) \leftarrow \subset \widetilde{X}^{2}A_{1}$ system have masked these lower members. In fact, if we were to assign the three member progression as the 2_0^4 , 2_1^5 , and 2_0^6 bands of the \tilde{H} state, the hypothesized progression would terminate upon an electronic origin at $v_{0-0} = 52.637(20)$ cm⁻¹, very close to the energy predicted by the Rydberg formula. In this view the band at 356.85 nm would be assigned as the $1_0^1 2_1^3$ transition. This $1_0^1 2_1^3$ assignment would predict that $\omega'_1 = 1587(30)$ cm⁻¹—nearly the same ω'_1 frequency as observed in the $\tilde{E}^{2}A_{2}^{"}(4p)$ Rydberg state. Based upon this incomplete spectral evidence, we tentatively assign the H state as a member of the second Rydberg series.

Regardless of the orbital assignment, no lower energy members of the second Rydberg series are expected. If the \tilde{H} state is a 3d Rydberg state, it is the lowest member of the nd

Spectral assignment	Band maximum λ_{air} (nm)	Two-photon energy (cm ⁻¹)	Energy rel. to $\tilde{J}^2 A_2'' (5p)$ origin (cm ⁻¹)	Energy rel. to $\widetilde{M}^2 A_2''(6p)$ origin (cm^{-1})	Energy rel. to $\tilde{P}^2 A_2''(7p)$ origin (cm^{-1})	Energy rel. to \tilde{K} state origin (cm ⁻¹)	Energy rel. to \widetilde{N} state origin (cm ⁻¹)
5p 2 ⁰ ₂	354.95	56 330	- 544	· _ · · · · · · · · · ·			
5 <i>p</i> 0°	351.56	56 874	0				
$5p 2_3^1$	351.13	56 942	68				
$5p 2_1^1$	347.81	57 487	613				
$5p 2_2^2$	347.43	57 549	675				
$5p 2_0^2$	344.16	58 095	1221				
$5p 2_3^3$	343.81	58 155	1281				
$\tilde{K} 0_0^0$	342.27	58 417				0	
$5p 2_1^3$	340.63	58 699	1825				
5p 24	340.23	58 767	1893				
\widetilde{K} 2 ¹	338.70	59 032				615	
5p 2°	337.12	59 309	2435				
5p 23	336.66	59 390	2516				
$\tilde{K} 2_0^2$	335.22	59 645				1228	
$5p 2_1^5$	333.71	59 915	3041				
5p 2 ⁶ ₂	333.35	59 980	3106				
$\tilde{K} 2_1^3$	331.79	60 263				1846	
6p 00	331.76	60 267		0			
\widetilde{N} 2 ⁰ ₂	330.64	60 472					- 533
5p 2°	330.39	60 517	3643				
$5p 2_3^7$	330.05	6 0 579	3705				
$6p 2_{1}^{1}$	328.41	60 882		615			
$\widetilde{N} 0_0^0$	327.75	61 005					0
$5p 2_1^7$	327.17	61 113	4239				
5p 2 ⁸	326.91	61 162	4220				
$6p \ 2_0^2$	325.10	61 502		1235			
\widetilde{N} 2 ¹	324.43	61 628					623
5p 28	323.95	61 721	4779				
7p 000	322.48	62 001			0		
$6p 2_1^3$	321.88	62 116		1849			
$\widetilde{N} 2_0^2$	321.18	62 252					1247
$5p 2_1^9$	320.77	62 333	5391				
7p 21	319.30	62 620			619		
$6p \ 2_0^4$	318.72	62 733		2466			
\widetilde{N} 2_1^3	318.05	62 865					1860
$5p 2_0^{10}$	317.64	62 946	6004				
$7p \ 2_0^2$	316.20	63 234			1233		
$6p 2_{1}^{s}$	315.65	63 343		3076			
\widetilde{N} 2 ⁴ ₀	314.92	63 490					2485
5p 211	314.64	63 546	6604				
$7p 2_1^3$	313.16	63 847			1846		
\widetilde{N} 2 ⁵	311.92	64 101					3096

TABLE XII. The REMPI bands of the SiD₃ radical (m/z 34) observed between 310 and 360 nm and their assignments.

Rydberg series. If the \tilde{H} state is the 5s ${}^{2}A'_{1}$ Rydberg state, it is the lowest bound member of the *ns* Rydberg series. The MRD CI calculation by Olbrich²² predict that the $\tilde{A} {}^{2}A'_{1}$ (4s) Rydberg state is unbound with respect to SiH₂($\tilde{a} {}^{3}B_{1}$) + H(${}^{2}S$) fragments. Rapid predissociation will preclude observation of the $\tilde{A} {}^{2}A'_{1}$ (4s) Rydberg state by REMPI.

D. Calculation of the adiabatic ionization potential of silyl radicals

The Rydberg series formed from the $np^2A_2^{"}$ band origins enables a direct determination of the first adiabatic ioni-

zation potential of the SiD₃ radical. The best fit of the $\tilde{J}^2 A_2''(5p)$, $\tilde{M}^2 A_2''(6p)$, and $\tilde{P}^2 A_2''(7p)$ Rydberg state origins yields a quantum defect of $\delta = 1.445 \pm 0.002$ and an ionization potential of 65 555 ± 10 cm⁻¹ (IP = 8.128 ± 0.001 eV). For SiH₃ an ionization potential of 65 650 cm⁻¹ (IP = 8.139 eV) and a quantum defect of $\delta = 1.45$ is found by solving the Rydberg equations for the $\tilde{J}^2 A_2''(5p)$ and $\tilde{M}^2 A_2''(6p)$ origins. Because of the obvious variation of the quantum defect, the $\tilde{E}^2 A_2''(4p)$ origins were not included as part of the fitted data.

Figure 7 shows the fit of the SiD_3 data graphically. The

<u> </u>	<i>v</i> ₂ " even			· · · · · · · · · · · · · · · · · · ·	v ₂ " odd		Av.	Measured $\tilde{J}^2 A_{*}^{*}(5n)$
	$v_{2}'' = 0$		$v_2''=2$	$v_{2}'' = 1$		$v_{2}'' = 3$	ω_2' ν_2' in	v'_2 interval
v ₂ ' even								
$v_{2}' = 0$	56 874	543	56 330					
	1 222		1 220				1221(1)	2–0
$v_{2}' = 2$	58 095	545	57 550					
	1 214		1 222				1218(4)	4-2
$v_{2}' = 4$	59 309	537	58 772					
	1 210		1 213				1211(2)	6-4
$v_2' = 6$	60 519	534	59 985					
	1 204						1204	86
$v_{2}' = 8$	61 723							
	1 223						1223	108
$v'_{2} = 10$	62 946							
v_2' odd								
$v_{2}' = 1$				57 487	545	56 942	,	
-				1 212		1 213	1212	3-1
$v'_{2} = 3$				58 699	543	58 155		
				1 220			1220	5-3
$v'_{5} = 5$				59 919				
-				1 195			1195	7–5
$v_{2}' = 7$				61 114	535	60 579		
-				1 219			1219	9–7
$v_{2}' = 9$				62 333				
				1 213			1213	11-9
$v'_{2} = 11$				63 546				
Α ν. ω ₂ "		540(6)			541(4)			
Measured								
$\tilde{X}^2 A_1$		2-0			3-1			
v_2'' interval								
				<u></u>	Av. ω'2/	$2 = 607(4) \text{ cm}^{-1}$	¹ for $\widetilde{J}^2 A_2''$ (5p)	······································

TABLE XIII. The Deslandres table which analyzes the v_2 umbrella bands observed in the $\tilde{J}^2 A_2''$ (5p) $\leftarrow \tilde{X}^2 A_1$ REMPI spectrum of the SiD₃ radical. Energies and differences are in cm⁻¹.

TABLE XIV. The $\tilde{M}^2 A_1^{"}$ (6p) $\leftarrow \tilde{X}^2 A_1$ REMPI transitions observed in the REMPI spectra of SiH₃ and SiD₃ radicals.

	Two-photon	Band
Band	energy	interval
assignment	(cm ⁻¹)	(cm^{-1})
SiH ₃ radical	······································	
00	60 341	
- 1		821
21	61 162	77 0
22	61 941	//9
2 0	01 941	
	Av. $\omega_2' = 800(30) \text{ cm}^{-1} \text{ for SiH}_3$	
SiD ₃ radical		
O ₀	60 267	
-1	60.000	615
2	60 882	(2)
22	61 500	621
2 0	01 502	614
23	62 116	014
-1		617
2 <mark>4</mark>	62 733	
		610
21	63 343	
	Av. $\omega_2' = 615(4) \text{ cm}^{-1} \text{ for } \text{SiD}_3$	

ionization potential is plotted as a function of quantum defect for the three Rydberg state origins. The point at which these curves intersect corresponds to the ionization potential and quantum defect. The curves would not have a common intersection if one or more of these Rydberg origins were misassigned even by one quantum of ν'_2 . Thus, the high precision of the Rydberg series fit also enhances the confidence

TABLE XV. The $\tilde{P}^2 A_2''$ $(7p) \leftarrow \leftarrow \tilde{X}^2 A_1$ REMPI transitions observed in the REMPI spectrum of the SiD₃ radical.

Band assignment	Two-photon energy (cm ⁻¹)	Band interval (cm ⁻¹)
00	62 002	
21	62 620	618
21	02 020	614
2 ² 0	63 234	613
2 ³	63 847	015

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TABLE	XVI.	The	Ã←←X̃	$^{2}A_{1}$ and	IÑ←←	$\tilde{X}^2 A_1$	REMPI	transitions	ob
served in	the R	EMI	PI spectr	um of th	ie SiD ₃	radica	1.		

Band assignment	Two-photon energy (cm ⁻¹)	Band interval (cm ⁻¹)
<i>K</i> state		
00 0	58 417	61 6
21	59 032	015
I.		613
2 ² ₀	59 645	(10
2 ³ ₁	60 263	618
	Av. $\omega'_{2} = 615(3) \text{ cm}^{-1}$ for \tilde{K} state	
\widetilde{N} state	2	
2 ⁰ ₂	60 472	500
00	61 005	- 533
00	01 000	624
2 ¹ ₁	61 628	
22	62.252	624
Zō	62 232	613
2_{1}^{3}	62 865	•••
-1	<i></i>	625
20	63 490	611
2 ⁵ ₁	64 101	011
	Av. $\omega_2' = 619(7) \text{ cm}^{-1} \text{ for } \tilde{N} \text{ state}$	

in the present Rydberg state origin assignments. The incorporation of the \tilde{K} and \tilde{N} Rydberg origins into the fitted data also yields IP_a = 8.128 eV for the SiD₃ radical.

Using the IP_a determined for the SiD₃ radical, we can also derive an adiabatic ionization potential of the SiH₃ radi-

IONIZATION POTENTIAL DETERMINATION



FIG. 7. The graphical determination of the ionization potential of SiD_3 is shown by plotting the ionization potential as a function of the quantum defect. Given the origins and the principal quantum numbers as shown, and using the rearranged Rydberg formula, a curve for each observed origin is drawn. The intersection of the three curves pinpoints the quantum defect and ionization potential.

cal by adding the net isotopic change in zero point vibrational energy, $\Delta(\Delta ZPE)$, caused by substituting hydrogen for deuterium in the vibrationless $\tilde{X}^2 A_1$ radicals and $\tilde{X}^1 A_1$ cations.⁴² $\Delta(\Delta ZPE)$ is available from measurements and from calculations. Rydberg spectra of SiH₃ and SiD₃ radicals give approximate direct measurements of $\Delta(\Delta ZPE)$. The isotope shift between the SiH₃ and SiD₃ $\tilde{J}^2 A_2''$ (5p) $\leftarrow \tilde{X}^2 A_1$ origins suggest that $\Delta(\Delta ZPE) = 55 \text{ cm}^{-1}$. Ab initio molecular orbital calculations also provide estimates of $\Delta(\Delta ZPE)$. To calculate $\Delta(\Delta ZPE)$ from *ab initio* results, we used the frequencies reported by Pople et al. for the SiH₃ cation¹⁹ and radical,²⁸ scaled the vibrational frequencies by 0.89, and derived vibrational frequencies for SiD₃ using the isotopic ratios for each harmonic vibrational mode. We calculate $\Delta(\Delta ZPE) = 55 \text{ cm}^{-1}$. Adopting $\Delta(\Delta ZPE) = 55 \text{ cm}^{-1}$, we derive an adiabatic ionization potential of $65\,615$ ($+\,40$; $(-20) \text{ cm}^{-1}$ [IP = 8.135 (+5; -2)] for the SiH₃ radical.

V. DISCUSSION

A. The ground state ν_2 umbrella mode of SiH_3 and SiD_3 radicals

In previous sections the Deslandres tables that analyze the v_2'' hot band structures for the $\tilde{E}^2 A_2''(4p) \leftarrow \tilde{X}^2 A_1$ spectra (Tables V and VI and the $\tilde{J}^2 A_2''(5p) \leftarrow \tilde{X}^2 A_1$ spectra (Tables XI and XIII) were presented. By averaging the ground state intervals shown in these tables, we have constructed the v_2 energy level manifolds of SiH₃ and SiD₃ radicals. Table XVII lists the observed v_2 vibrational energy levels of SiH₃ and SiD₃ radicals residing below $E_v = 2100$ cm^{-1.43}

Our results overlap with data reported previously by others. Using IR diode laser spectroscopy, Yamada and Hirota²⁶ have established with great accuracy that the $v_2'' = 1-2$ and $v_2'' = 0-3$ levels of the SiH₃ radical are separated by 721.0486 and 727.9438 cm⁻¹, respectively. In agreement with the IR diode laser results, our analogous measurements, which have greater uncertainty, give 723(5) and 732(9) cm⁻¹. Using photoelectron spectroscopy to observe silyl anions, Minlos and Ellison²⁵ measured the vibrational levels up to $v_2 = 14$ ($v_2 = 7^+$ in their notation; $E_v \leq 5210$ cm⁻¹) of the SiH₃ radical and levels up to $v_2 = 17$ ($v_2 = 8^-$; $E_{\nu} \leq 4520 \text{ cm}^{-1}$) of the SiD₃ radical. These photoelectron spectra are of lower resolution than the present REMPI spectra and do not resolve pairs of vibrational levels that lie at lower energies. Nevertheless, the overall agreement between the photoelectron and REMPI spectra is good.

Since the silyl radical is pyramidal, it possesses two potential energy minima along the umbrella mode coordinate. To model the observed energy levels of this double-well potential, we solved the Hamiltonian for a quartic oscillator with the potential $V = A(Z^4 - B \cdot Z^2)$, after the method described by Laane.⁴⁴ The umbrella coordinate is $Z = c_{\mu}r_e \Theta$. The constant c_{μ} includes the reduced mass, r_e is the Si-H bond length, and Θ is the out-of-plane angle. The reduced mass of the oscillator was approximated by the *G*-matrix element, $g_2 = (3m_{\rm H} + m_{\rm Si})/3m_{\rm H}m_{\rm Si}$. The mass-weighted coefficients *A* and *B* are derived from the variables: (1) Θ_m , the bending angle which corresponds to the minimum in the

TABLE XVII. The $v_1^{"}$ vibrational energy levels measured for the $\tilde{X}^2 A_1$ (C_{3v}) ground state of silyl radicals and calculated using a quartic potential, $V = A(Z^4 - B \cdot Z^2)$.

Quantum number, v ₂ "	Measured ω_2'' vibrational energy ^a (cm ⁻¹)	Calculated ω_2'' vibrational energy ^b (cm ⁻¹)	Difference (Obs Calc.) (cm ⁻¹)
SiH ₃ radical			
0	0	0	
1		0.03	
2	723	748.6	- 25.6
3	732	751.4	- 19.4
4	1326	1346	- 20
5	1424	1418	6
6	1825	1792	33
7	2073	2080	- 7
SiD ₂ radical			
0	0	0	
1		1.5E - 4	
2	542	556.01	- 14.0
3	545	556.04	- 11.0
4	1048	1062.6	- 14.6
5	1059	1064.5	- 5.5
6	1474	1478	4
7	1545	1519	26
8		1782	
9	1969	1963	6

* See Ref. 43.

^b For SiH₃, $V(\text{cm}^{-1}) = 98.40(Z^4 - 8.88 \cdot Z^2)$; ZPE = 402.7 cm⁻¹ and for SiD₃, $V(\text{cm}^{-1}) = 63.29(Z^4 - 11.03 \cdot Z^2)$; ZPE = 291.3 cm⁻¹.

potential, (2) r_e , the Si-H bond length, and (3) B_{inv} , the inversion barrier.

Table XVII lists the calculated v_2'' umbrella mode energy levels obtained with the quartic potential. Using a leastsquares procedure, the observed vibrational energy levels of the SiH₃ and SiD₃ radicals were fitted separately to find the best quartic coefficients. The coefficients A and B for each isotopic radical are listed in the footnotes of Table XVII. The



FIG. 8. Schematic of the potential function for the v_2'' (a_2'') umbrella mode of SiH₃ as a function of symmetric out-of-plane bending "umbrella" angle Θ (Ref. 16). The experimentally observed v_2'' vibrational levels are indicated. All energies are in cm⁻¹. The level splitting between $v_2'' = 0$ -1 is not shown.

inversion barriers calculated from these coefficients are $B_{inv} = 1935 \text{ cm}^{-1}$ for the SiH₃ radical and $B_{inv} = 1925 \text{ cm}^{-1}$ for the SiD₃ radical. To intepret the equilibrium coordinate value Z_m , we have adopted the *ab initio* bond length $r_e = 1.462 \ 32 \text{ Å}$, calculated by Allen and Schaefer.¹³ The Z_m 's give $\Theta_m = \pm 20.7^\circ$ for SiH₃ and $\Theta_m = \pm 21.3^\circ$ for SiD₃ radicals. The residuals listed in Table XVII indicate that the fit is reasonable. The consistency between the Θ_m 's and B_{inv} 's of SiH₃ and SiD₃ is very good.

Figure 8 diagrams the $v_2''(a_2'')$ umbrella mode potential function based upon the solution of the quartic potential. The experimentally observed intervals between vibrational levels are also shown. As is typical of vibrations described by double-minimum potentials, the vibrational levels below the potential barrier have collapsed into closely spaced doublet levels. Those levels that lie above the barrier are well separated.

Other groups have reported inversion barriers and potential minima for silyl radicals based upon spectroscopic data. Using a quartic potential to fit the $v_2 = 2 \leftrightarrow 1$, $3 \leftrightarrow 0$ transitions, Yamada and Hirota found $B_{inv} = 1768$ cm^{-1,26,45} By combining the fitted potential minimum with the observed rotational constant B_0 , they found that r_e (Si-H) = 1.456 Å and $\Theta_m = \pm 20.4^\circ$. Yamada and Hirota also solved for these levels using the three parameter potential function $V(Q) = 0.5 \cdot [kQ^2 + \Delta E - (\Delta E^2 + 4a^2Q^2)^{1/2}]$ to find $B_{inv} = 1868$ cm⁻¹, $r_e = 1.486$ Å, and Θ_m $= \pm 18.4^\circ$.^{26,45} To fit the photoelectron spectrum of the SiH₃ anion, Nimlos and Ellison used the three parameter function $V(Q) = 0.5 \cdot k \cdot Q^2 + D \cdot \exp(-\beta Q^2)$, and found that $\Theta_m = \pm (16 \pm 2)^\circ$ and $B_{inv} = 1900 \pm 300$ cm^{-1,25}

The barriers calculated with ab initio methods have depended strongly upon the orbital basis set size and theory level used in the calculation. Ab initio molecular orbital calculations have predicted $B_{inv} = 1400$,¹⁸ 1539,¹⁷ 1889,²² 1951,²⁴ 2046,²³ and 2174¹³ cm⁻¹. Allen and Schaefer¹³ have published the ab initio results for the SiH₃ radical that have the lowest variational energy. They predict that $B_{inv} = 2174$ cm⁻¹.¹³ All *ab initio* calculations calculate a more planar radical than derived from fits of the experimental data. Ab *initio* calculations all predict $\Theta_m = 18.4^{\circ}-16.1^{\circ}$.^{13,17,18,20-22} Allen and Schaefer calculate $\Theta_m = \pm 17.8^{\circ}.^{13}$ Some of the discrepancy between the present and *ab initio* values for Θ_m might be reconciled if we were to define more explicitly the normal mode path Z, and to add a shape factor for the inversion barrier. The improved definition of Z would include changes in bond length and reduced mass as a function of bending angle Θ . However, a discrepancy between the *ab* initio and experimentally derived bond angles is expected. Yamada and Hirota²⁶ have noted that the rotational constant B_0 calculated using the *ab initio* geometry does not reproduce the experimentally observed B_0 .

B. The Rydberg states of SiH₃ and SiD₃ radicals

This study has precisely established the energies of six excited electronic state origins. Evidence for a seventh Rydberg state was obtained. Figure 9 diagrams the excited state energy levels of the SiH₃ radical. Solid lines represent the Rydberg states observed during this study. Dashed lines rep-



FIG. 9. The energy level diagram which shows the excited states of silyl radicals. Energy levels indicated with solid lines were observed during this study. Energy levels indicated with dashed lines are predicted states. Interconnecting line show the state mixing predicted with MRD CI calculations by Olbrich (Ref. 22). Solid interconnecting lines among the ²E states symbolize the mixing which occurs along the umbrella coordinate. Dashed interconnecting lines symbolize the mixing which occurs as one Si-H bond is lengthened. The predicted predissociative nature of the $\tilde{A}^2A'_1$ (4s) is shown. The interconnected ²E states belong to the C_{3v} point group. All others belong to the D_{3h} point group.

resent predicted electronic states. The energies of the \tilde{A} , \tilde{B} , \tilde{C} , \tilde{D} , \tilde{G} , and \tilde{I} states are derived from term values calculated by Olbrich using the MRD CI method.²² The solid lines connecting the \tilde{B} , \tilde{C} , \tilde{F} , and $\tilde{G}^2 E$ states indicate the configurational mixing which occurs along the umbrella coordinate between the nonplanar $\tilde{C}^2 E$ valence state and the ²E Rydberg states. This configurational mixing, predicted by the MRD CI calculations,²² also causes the $\tilde{F}^2 E$ (4p) state to reside at higher energy than the $\tilde{E}^2 A_2''$ (4p) Rydberg state. In Fig. 9 we have retained this predicted energy ordering. Since the valence-Rydberg interactions may cause the lower ²E Rydberg states to assume pyramidal geometries, we have notated the \tilde{B} , \tilde{C} , \tilde{F} , and $\tilde{G}^2 E$ states as members of the C_{3v} point group.

In Fig. 9 we depict the \tilde{H} , \tilde{K} , and \tilde{N} states as the 5s, 6s, and 7s Rydberg states, respectively. These assignments are tentative. We base our preference for these *ns* Rydberg series assignments upon the bond dissociation curves calculated by Olbrich. These calculations²² predict that as one Si-H bond is lengthened, the $\tilde{A}^{2}A'_{1}$ (4s) Rydberg state couples with the $\tilde{C}^{2}E, \tilde{B}^{2}E$ (3d), and $\tilde{X}^{2}A'_{1}$ states through avoided crossing interactions. In Fig. 9 dashed interconnecting lines symbolize this mixing. The net potential along the Si-H coordinate of the $\tilde{A}^{2}A'_{1}$ (4s) Rydberg state leads directly to SiH₂ $(\tilde{a} {}^{3}B_{1}) + H({}^{2}S)$ fragments. Thus, rapid predissociation should prevent the $\tilde{A} {}^{2}A'_{1}$ (4s) Rydberg state from appearing in REMPI spectra. Since higher *ns* Rydberg states do not strongly mix to form a dissociative potential surface, they should appear in REMPI spectra. Our proposed assignment scheme, depicted in Fig. 9, fits the present observations.

An alternate assignment of the \tilde{H} state would be to the $3d^{2}E$ Rydberg state (labeled \tilde{G} in Fig. 9).⁴⁶ However, the mixing of the dissociative $\tilde{A}^2 A_1'$ (4s) state with the $\tilde{C}^2 E$ valence and $\tilde{B}^{2}E$ (3d) Rydberg states may also give some dissociative character to \tilde{C} and \tilde{B} . Additional mixing along the umbrella coordinate among the $\tilde{B}, \tilde{C}, \tilde{F}$, and \tilde{G} states may impart dissociative character to the $\tilde{F}^2 E(4p)$ and $\tilde{G}^2 E(3d)$ states. If this mixing scheme occurs, then we should not expect REMPI spectroscopy to detect these states. Such a mixing scheme can account for the absence of the $\tilde{F}^2 E$ (4p) Rydberg state from our REMPI spectra. We cannot completely dismiss the possibility that the \tilde{H} state should be assigned as the 3d ${}^{2}A_{1}$ state (labeled \widetilde{D} in Fig. 9).⁴⁶ However, the $\tilde{H} \leftarrow \tilde{X}^2 A_1$ bands appear at energies that seem too high to favor such an assignment. Future molecular orbital calculations may provide firmer assignments for this second Rydberg series.

The \tilde{E} , \tilde{J} , \tilde{M} , and \tilde{P} states comprise the $np^{2}A_{2}''(D_{3h})$ Rydberg series. We based the *p*-orbital assignment on the Rydberg series quantum defect, $\delta = 1.45$. The symmetry assignment of the entire Rydberg series depends upon the behavior of the v'_{2} umbrella mode in the $\tilde{E}(4p)$ state. MRD CI calculations by Olbrich²² lead to the prediction that the $4p^{2}A_{2}''$ Rydberg state will show a regular v'_{2} vibrational progression and that the $4p^{2}E'$ Rydberg state will show an irregular v'_{2} vibrational progression. Because the $\tilde{E}(4p)$ state exhibits a regular v'_{2} vibrational progression, we assigned the Rydberg series as having ${}^{2}A_{2}''(D_{3h})$ symmetry.

Analysis of a rotationally resolved spectrum of any **REMPI** band would confirm our ${}^{2}A_{2}''(D_{3h})$ symmetry assignment. Unfortunately, no rotational branches were resolved. The absence of rotational structure may indicate that nonradiative processes influence the REMPI spectra. The nonradiative paths may lead to predissociative states or to states that possess poor ionization cross sections. Coriolis coupling⁴⁷ of the ²A $\frac{7}{2}$ states to a background of ²A $\frac{7}{1}$ and ²E' states might explain the observations. Under the Hund's case (b) angular momentum coupling which we expect to govern SiH₃ Rydberg states, the strength of the Coriolis induced coupling from each $A_{2}^{"}$ vibrational level depends upon the N, K quantum numbers. For example, the average coupling strength between ${}^{2}E'$ and ${}^{2}A''_{2}$ vibrational levels is proportional to $[N(N+1) - K^2]$.⁴⁷ The coupling vanishes when N = 0 and is at a minimum for K = N levels. Thus, Coriolis induced coupling would permit observation of some rotational levels, yet quench most of the rotational spectrum.

Table XVIII summarizes the state assignments and spectroscopic constants of SiH₃ and SiD₃ radicals derived from the REMPI spectra. For comparison with experiment, Table XVIII also presents the vertical excitation energies T_{vert} , predicted with the MRD CI molecular orbital calculations.²² For each transition we also present a T_0 derived from TABLE XVIII. Summary of the experimentally observed and predicted origins and vibrational frequencies of Rydberg states.

$\begin{array}{c c c c c c c c c c c c c c c c c c c $			Experimental values		Predicted val	ues
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Rydberg state	SiH ₃ (cm ⁻¹)	SiD ₃ (cm ⁻¹)	Orig. shift (cm ⁻¹)	SiH ₃ (cm ⁻¹) ^a	SiD ₃ (cm ⁻¹) ^b
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\widetilde{\tilde{E}^{2}A_{2}^{\prime\prime}}(4p)$				$T_{\rm vert} = 50\ 708^{\rm c}$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$T_0 =$	48 438	48 391	47	47 776 ^d	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$(\delta = 1.47)$	$(\delta = 1.47)$			1.5/0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\omega_1' =$	70((7)	1 576(3) →		2 218	1568
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\omega_2' =$	/96(7)	589(3)		811	001 1616
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\omega_3 = \omega_1$	970/515	675/615		2 283	1010
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\omega_4 =$	870(3)	033(0)*		910	073
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\widetilde{J}^2 A_2''$ (5p)				$T_{\rm vert} = 60\ 850^{\rm c}$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$T_0 =$	56 929	56 874	55	57 918 ^d	
$\begin{split} \omega_2' &= & 821(4) & 608(3) & 811 & 601 \\ \tilde{M}^2 A_1^r (6p) \\ T_0 &= & 60 341 & 60 267 & 74 \\ (\delta = 1.44) & (\delta = 1.45) \\ \omega_2' &= & 800(30) & 615(4) & 811 & 601 \\ \tilde{P}^2 A_1^r (7p) \\ T_0 &= & (\delta = 1.44) \\ \omega_2' &= & 615(3) & 601 \\ \tilde{H} (5s)^r & & T_{vert} = 59 467^r \\ T_0 &= & [52 637(20)]^s & T_{vert} = 59 467^r \\ T_0 &= & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_1' &= & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_1' &= & 602(5) & 601 \\ \tilde{K} (6s)^h & & T_{vert} = 63 642^c \\ T_0 &= & (\delta = 2.08 \text{ or } \delta = 0.08) \\ \omega_1' &= & 615(3) & 601 \\ \tilde{N} (7s)^i \\ T_0 &= & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_1' &= & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_1' &= & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_1' &= & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_1' &= & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_1' &= & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_1' &= & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_1' &= & (\delta = 0.09) \\ \omega_1' &= & (\delta$	·	$(\delta = 1.45)$	$(\delta = 1.44)$			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\omega_2' =$	821(4)	608(3)		811	601
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\widetilde{M}^2 A_{*}^{"}(6n)$					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$T_0 =$	60 341	60 267	74		
$ \begin{split} \omega_{2}^{\prime} &= 800(30) & 615(4) & 811 & 601 \\ \\ \tilde{P}^{2}A_{2}^{\prime\prime}(7p) & & & & & & & & & & & & \\ T_{0} &= & 62002 & & & & & & & & & & \\ \omega_{2}^{\prime} &= & 615(3) & & & & & & & & & & & & & & & & & & &$	- 0	$(\delta = 1.44)$	$(\delta = 1.45)$			
$ \begin{split} \tilde{P}^{2}A_{2}^{r}(7p) \\ T_{0} = & 62002 \\ (\delta = 1.44) \\ \omega_{2}^{r} = & 615(3) & 601 \\ \tilde{H}(5s)^{f} & T_{vert} = 59467^{c} \\ T_{0} = & [52637(20)]^{s} & T_{vert} = 59467^{c} \\ (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{1}^{r} = & [1587(20)]^{s} & 1568 \\ \omega_{2}^{r} = & 602(5) & 601 \\ \tilde{K}(6s)^{h} & T_{vert} = 63642^{c} \\ T_{0} = & 58417 & 60710^{d} \\ \omega_{2}^{r} = & 615(3) & 601 \\ \tilde{N}(7s)^{i} & T_{0} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{1}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{1}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{1}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{1}^{r} = & (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 0.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 0.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 0.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 0.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 0.09 \text{ or } \delta = 0.09) \\ \omega_{2}^{r} = & (\delta = 0.09 $	$\omega'_2 =$	800(30)	615(4)		811	601
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\widetilde{P}^2 A'' (7n)$					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$T_{1} = T_{1}$		62 002			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1 ₀ —		$(\delta = 1.44)$			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\omega_2' =$		615(3)			601
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ũ (5c) ^f				T - 59 467°	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$T_{0} =$		[52 637(20)]8		56 535 ^d	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-0		$(\delta = 2.09 \text{ or } \delta = 0.09)$			
	$\omega'_1 =$		[1 587(20)] ^g			1568
$ \widetilde{K} (6s)^{h} \qquad T_{vert} = 63 \ 642^{c} \\ 60 \ 710^{d} \\ \omega'_{2} = & (\delta = 2.08 \ or \ \delta = 0.08) \\ \omega'_{2} = & 615(3) & 601 \\ \widetilde{N} (7s)^{i} \\ T_{0} = & 61 \ 005 \\ (\delta = 2.09 \ or \ \delta = 0.09) \\ \omega'_{4} = & 619(7) & 601 \end{array} $	$\omega_2' =$		602(5)			601
$T_{0} = 58 417 \qquad 60 710^{d}$ $\omega'_{2} = 61005 \qquad (\delta = 2.09 \text{ or } \delta = 0.09)$ $\omega'_{2} = 61005 \qquad (\delta = 2.09 \text{ or } \delta = 0.09)$ $\omega'_{3} = 601$	\widetilde{K} (6s) ^h				$T_{\rm eq} = 63.642^{\rm c}$	
$\omega_{2}^{\prime} = \begin{pmatrix} \delta = 2.08 \text{ or } \delta = 0.08 \\ 615(3) \end{pmatrix} \qquad 601$ $\widetilde{N} (7s)^{i}$ $T_{0} = \begin{pmatrix} 61005 \\ (\delta = 2.09 \text{ or } \delta = 0.09) \\ (\delta = 2.09 \text{ or } \delta = 0.09) \end{pmatrix}$ $\omega_{2}^{\prime} = \begin{pmatrix} 61005 \\ (\delta = 2.09 \text{ or } \delta = 0.09) \\ 619(7) \end{pmatrix} \qquad 601$	$T_0 =$		58 417		60 710 ^d	
	ũ		$(\delta = 2.08 \text{ or } \delta = 0.08)$			
$ \widetilde{N} (7s)^{i} T_{0} = 61 005 (\delta = 2.09 \text{ or } \delta = 0.09) 619(7) 601 $	$\omega_2' =$		615(3)			601
$T_{0} = 61005 \\ (\delta = 2.09 \text{ or } \delta = 0.09) \\ \omega_{0}^{\prime} = 619(7) $ 601	$\widetilde{N}(7s)^{i}$					
$\omega_{\lambda}^{\prime} = (\delta = 2.09 \text{ or } \delta = 0.09)$ 619(7) 601	$T_0 =$		61 005			
$\omega'_{2} = 619(7)$ 601	-		$(\delta = 2.09 \text{ or } \delta = 0.09)$			
	$\omega_2' =$		619(7)			601

* Except where noted, frequencies are those of Ref. 28 scaled by 0.89.

^b Scaled frequencies of Ref. 28 divided by isotope shift ratios given in Ref. 40.

^cCalculated vertical excitation energy from Ref. 22.

^d Derived using *ab initio* term value of Ref. 22, the IP_a of this work,

and the zero point vibrational energies: $T_0 = IP_a - (term value)$

+ ZPE(ion) - ZPE(radical).

the difference between the experimental IP_a and the MRD CI term value reported by Olbrich.²² This T_0 includes a ΔZPE correction.⁴² As seen in Table XVIII, the value for T_0 predicted with this procedure agrees reasonably well with the observed value.

Table XVIII also compares the observed Rydberg state vibrational frequencies with those calculated for the ground state cations. Because the bonding in the cation core of ${}^{2}A_{2}^{"}$ Rydberg radicals is nearly the same as the bonding of the SiH₃ cation, such comparisons are reasonable. In Table XVIII the predicted vibrational frequencies of the SiH₃ cation were derived from the *ab initio* results reported by Pople *et al.*²⁸ The *ab initio* vibrational frequencies were scaled by 0.89, a commonly used factor. To derive the vibrational frequencies for SiD₄ Rydberg radicals, the SiH₃ cation frequen $^{\circ}2\omega_{2}^{\prime}/2$ values used.

^fTentative assignment. Alternate assignment is (3d).

⁸ Extrapolated value. See the text.

^hTentative assignment. Alternate assignment is (4d).

ⁱTentative assignment. Alternate assignment is (5d).

cies were divided by the isotopic ratio of G-matrix elements of the cation.⁴⁰

As is shown in Table XVIII, the experimental and scaled *ab initio* vibrational frequencies agree extremely well. The $\tilde{E}^2 A_2''$ (4p) state provides the most comprehensive comparison. In this state the v'_1 , v'_2 , and v'_4 vibrational frequencies were measured. The scaled *ab initio* calculations have predicted the vibrational frequencies with better than 5% accuracy.

C. The ionization potential of silyl radicals

Our interpretation of the REMPI spectra supports the adiabatic ionization potentials, $IP_a = 8.135(+5, -2) \text{ eV}$ for the SiH₃ radical and $IP_a = 8.128(1) \text{ eV}$ for the SiD₃ radical. This paper is the first to report an ionization poten-

tial for the SiD₃ radical. The authority of our measurement resides in the fact that it is based upon meticulously assigned spectra of several states. The spectroscopic assignments of SiH₃ and SiD₃ concur with each other and converge to the same electronic origins. Precisely measured electronic origins were used to derive the IP_a . Hence, the present evaluation of the ionization potential appears completely secured by the spectroscopic data.

Ab initio molecular orbital calculations underestimate the IP_a of SiH₃ radicals by 0.1–0.3 eV. Olbrich calculated $IP_a = 7.81 \text{ eV}^{22}$ and Pople and Curtiss calculated IP_a = 7.99 eV.²⁸ This 0.1 eV calculational error is consistent with ab initio values for other silicon ground state radicals, SiH and atomic Si. For the $\tilde{X}^2 \Pi_r$, SiH radical the *ab initio* value is $IP_a = 7.81 \text{ eV}^{28}$ and the observed is $IP_a = 7.91$ eV.^{29,30} For the Si radical the *ab initio* value is $IP_a = 8.08$ eV^{28} and the observed is $IP_a = 8.152 eV.^{48}$

Before the present work two groups had reported precise but conflicting spectroscopic measurements of IP_a for the SiH₃ radical. Using photoelectron spectroscopy, Dyke et al. obtained a value of IP = 8.14 ± 0.01 eV.²⁷ Using photoionization mass spectrometry, Berkowitz et al. reported a value of IP = 8.01 ± 0.02 eV.²⁹ Photoionization spectroscopic methods determine the adiabatic ionization potential by observing the lowest energy onset of the photoionization signal. Because radicals, like SiH₃, undergo a large geometry change upon ionization, they possess small Franck-Condon factors near the photoionization threshold. Thus, identification of the weak ionization threshold band is difficult and governed by instrument sensitivity. These factors caused Berkowitz et al.²⁹ to conclude that poor Franck-Condon factors had prevented Dyke et al. from observing the true ionization threshold.

Our spectroscopic IP_a for SiH₃ radical agrees closely with the IP_a = 8.14(1) eV reported by Dyke et al.²⁷ We attribute the 0.13 eV difference between our recommended IP_a and the lower value reported by Berkowitz et al.²⁹ to the effects of vibrational hot bands in their spectrum. In their report Berkowitz et al. noted that the presence of vibrationally hot SiH₃ radicals would have corrupted their measurement by contributing signal at energies below the true ionization threshold energy.²⁹ To produce SiH₃ radicals for their experiments, they conducted the reaction $F + SiH_4$ in a flow reactor. They argued against the presence of hot bands based upon prior experience and the intensity ratios of the observed bands. In our REMPI experiments SiH₃ radicals were also produced in a flow reactor by the reaction $F + SiH_4$. The REMPI spectrum (Fig. 3) displays numerous vibrational hot bands. Although the direct comparison of equipment and experimental conditions between laboratories is not possible, our observation of hot bands makes the presence of vibrationally hot radicals during the studies by Berkowitz et al. likely.

Boo and Armentrout³⁰ reported IP_a = 8.11 ± 0.07 eV for the SiH₃ radical based upon measurements of the reaction rates of Si^+ with SiH_4 as a function of collision energy. This autonomous measurement agrees with our IP_a . Boo and Armentrout also derived heats of formation for several SiH_n (n = 1-3) radicals and cations. The 0.13 eV disparity between the previously published photoionization results caused them to express reservations regarding the correct heat of formation for the SiH₃ radical. The IP_a determined in this work sustains Boo and Armentrout's recommended value, $\Delta H_f^0(\text{SiH}_3) = 48.5 \text{ kcal/mol.}^{30}$

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- ⁴⁶In the event that future measurements or high quality calculations change these Rydberg orbital assignments, we recommend that the letter designation of each REMPI band system remain unchanged. New letters or prime designations may need to be introduced. For example, in the event that the \tilde{H} state becomes assigned as the $3d^2E$ state, then the reassigned state should be called $\tilde{H}^2E(3d)$, the $5s^2A_1$ state should acquire a primed letter designation (the letter determined by its energy), and the \tilde{G} designation should be discarded.
- ⁴⁷Coriolis induced predissociation appears in the spectrum of the H₃ radical. See I. Dabrowski and G. Herzberg, Can. J. Phys. 58, 1238 (1980); G. Herzberg and J. K. G. Watson, *ibid*, 58, 1250 (1980).
- ⁴⁸C. Moore, Atomic Energy Levels, Natl. Bur. Stand. Circ. 467 (U.S. GPO, Washington, D.C., 1949), Vol. 1.