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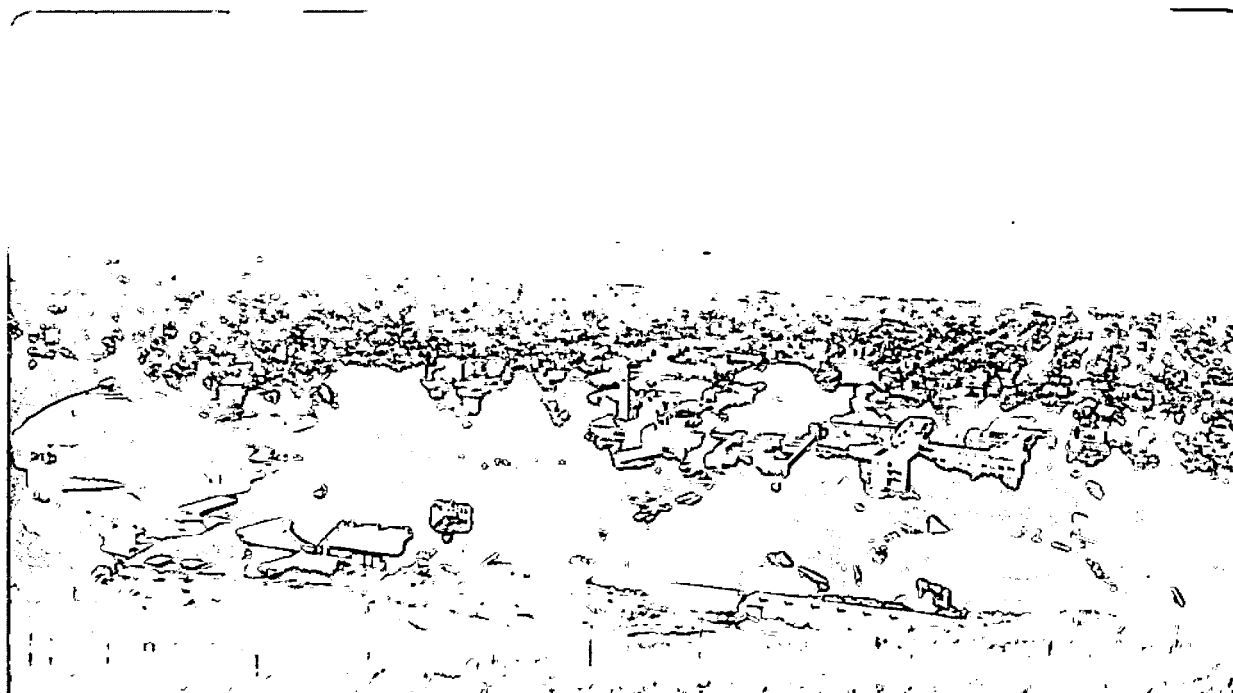
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Infrared Spectroscopy of the Siliconium Ion, SiH_5^+

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ABSTRACT

The infrared spectrum for the H-H stretching mode of the siliconium ion SiH_5^+ in the frequency range of 3650-3740 cm^{-1} is presented. The observed vibration-rotation transitions were fitted with the A-type rotational transitions of an asymmetric top using the Watson S-type asymmetric top rotational hamiltonian. The results suggested that the siliconium ion SiH_5^+ can be described as a complex between SiH_3^+ and a freely internally rotating H_2 groups, with a highly localized three-center two-electron bond.

1. INTRODUCTION

The siliconium ion SiH_5^+, an analogue of the carbonium ion CH_5^+, is of considerable interest in understanding the nature of nonclassical bonding. Nonclassical bonding is characterized by a three-center two-electron bond (3c2e) having a pentacoordinated central atom and bridged hydrogens.[1] Olah and coworkers reported recently that these pentacoordinated siliconium ions played as an intermediate in the electrophilic hydrogen-deuterium exchange reactions of trialkylsilanes widely used versatile synthetic reagents.[2]

The silicon hydride cations, $Si_xH_y^+$ were known to play an important role in the ion-molecule reactions during plasma-enhanced chemical vapor deposition (CVD) of silicon films. Among the $Si_xH_y^+$ ions in silane plasmas, SiH^+, SiH_2^+, SiH_3^+, and SiH_7^+ ions have been investigated extensively by employing several spectroscopic techniques such as vibrational[3] and electronic[4] predissociation spectroscopy, photoelectron spectroscopy of silicon hydride radicals,[5] and infrared laser absorption spectroscopy.[6] However, no spectroscopic study on SiH_5^+ has yet been performed to date, in spite of its importance.

Smith and coworkers[6] reported high resolution infrared spectra for SiH_3^+, a dominant ion in an ac glow discharge of silane and hydrogen gas mixtures. The results showed that the ground state structure of SiH_3^+ has a classical trigonal planar structure like CH_3^+. Okumura and coworkers[3] reported the infrared spectrum on SiH_7^+ obtained by employing the vibrational predissociation spectroscopy with a newly designed pulsed reflectron time-of flight mass spectrometer. They concluded that the structure of SiH_7^+ may be regarded as a symmetric complex between SiH_3^+ and two H_2 molecules, different from the structure of CH_7^+ proposed as $CH_5^+(H_2)$ in our previous work.[7] This is suggestive of the difference in nonclassical bonding between SiH_5^+ and CH_5^+.

Theoretical calculations[8-11] suggested that the minimum energy structure for SiH_5^+ is composed of SiH_3^+ and H_2 groups, and the H_2 group was predicted to rotate freely around the C_{3v} axis of SiH_3^+. Recent ab initio calculation at TZ2P CCSD, performed by Schaefer and coworkers, predicted that the scrambling motion involving a C_{2v} transition state structure[12-14] of SiH_5^+ was predicted to possess a high barrier (26.8 kcal/mole),[8] unlike CH_5^+. Therefore, the structure and dynamics of SiH_5^+ are expected to be analogous to, but distinct from those for

CH_5^+.

In this paper we present the first infrared spectrum for SiH_5^+ from 3650 to 3740 cm^{-1} obtained by using ion trap vibrational predissociation spectroscopy. Of the interesting features observed in the spectrum are rotation-vibration transitions of the H-H stretching mode in SiH_5^+.

2. EXPERIMENTAL DETAILS

The experimental apparatus used in this work has been described previously.[15,16] Briefly, the siliconium ions were produced from a high pressure corona discharge source and subsequent supersonic expansion through a 75 µm nozzle. The corona discharge was maintained in 200 torr of gas mixture with ultrahigh purity (UHP) H_2, UHP He, and UHP SiH_4 in a 50,000:5,000:1 ratio, flowing past a 1.0 kV potential from the discharge tip of the needle to the source body maintained at 350 V above ground. The discharge currents under these conditions were around 30 µA. The temperature of the source body was maintained at approximately -10°C by heating the source body in contact with a liquid nitrogen trap. Typical pressures in the source chamber were around 2×10^{-5} torr during the experiment. To prevent the acceleration of ions in the higher pressure region which causes internal excitation and dissociation of the ion clusters via collisions with the background gas, the potential of the skimmer was maintained within 0.3 V of that of the source body.

After the skimmer, the ion beam entered a second differential pumping region containing collimating and focusing lenses. The pressure in this region was typically an order of magnitude lower than that of the source region. The beam was directed into a 60° sector magnet mass analyzer through a third differentially pumped region maintained at 2×10^{-8} torr.

The mass-selected beam was then bent 90° in a dc quadrupole field, decelerated to less than 0.5 eV, and focused into a rf octapole ion trap through an entrance aperture lens. The ions were usually trapped here for 18 msec per cycle for the interaction with the IR lasers. Usually 1,000 ions were trapped per cycle, which is not enough to allow direct measurement of photon absorption.

The trapped, mass-selected clusters were then vibrationally excited by a pulsed, tunable infrared laser. A Quanta-Ray IR WEX was used as a tunable infrared light source. The infrared wavelength was generated in a $LiNbO_3$ crystal that takes the difference frequency between a Lambda Physics pulsed dye laser (Model FL3002E) and the 1.06 µm fundamental of a Continuum Nd-YAG laser. The IR resolution was 0.2 cm^{-1}, the pulse duration was 6 nsec with a 20 Hz repetition rate, and the laser power was 2-3 mJ/pulse in the 3300-4200 cm^{-1} region.

Because of the large binding energy of SiH_5^+ (17.8 kcal/mole),[3,17] the absorption of one

photon from the tunable IR laser could not cause the vibrational predissociation of SiH_5^+. In this case, a line tunable cw CO_2 laser (MPB Technologies, 5W @10.6 μm) was used to drive the SiH_5^+ ions excited by the tunable IR laser over the dissociation threshold through the absorption of multiple CO_2 laser photons, as the schematic is shown in Fig. 1. Typical irradiation time of the CO_2 laser at 10.6 μm and 5W was about 16 msec after the tunable IR pulse. After the CO_2 laser irradiation, the potential on the exit aperture was lowered to extract ions of all masses from the trap. These ions were filtered by a quadrupole mass spectrometer tuned to pass only the SiH_3^+ daughter ions for the SiH_5^+ parent ions. In this work, the observation of the SiH_3^+ signal as a function of laser frequency was a measure of the infrared absorption of SiH_5^+.

Daughter ions were counted with a Daly ion detector[18] for each laser shot. Background daughter ions resulting from both the multiphoton dissociation (MPD) by the CO_2 laser irradiation alone and the decay of metastable parent ions in the rf ion trap were monitored in a separate cycle with the tunable IR laser off at each wavelength and subtracted from the laser on signal. The laser power was monitored at each data point, and spectra were normalized for the power of the tunable infrared laser assuming a simple linear power dependence. For a typical experiment, signals were averaged for about 2,000 laser shots at each wavelength from 3650 to 3750 cm^{-1}, where only infrared absorption of SiH_5^+ was found in the frequency range of 3300-4200 cm^{-1} scanned in this work.

In this experiment, it was seen that the composition of ions in the beam was strongly dependent on the H_2/He/SiH_4 mixing ratio, the discharge current, the source temperature and the source pressure. The ratio of SiH_4:He:H_2 used in this work was 1:5,000:50,000. An increase of the concentration of SiH_4 in the gas mixture resulted in an increase in the formation of the larger siliconium ions, namely $Si_xH_y^+$($x \geq 2$). The discharge current was kept as low as possible to reduce the internal excitation of the ions. In the mass spectra under these source conditions, the SiH_5^+ ions (m/e=33) showed a maximum intensity among the several mass peaks observed. Fig. 2 shows the mass spectrum obtained with the 200 torr source pressure, - 10°C source temperature and 30 μA discharge current for a gas mixture of SiH_4:He:H_2=1:5,000:50,000.

3. GROUP THEORETICAL TREATMENT[19,20]

Ab initio calculation[8] predicted that the siliconium ion, SiH_5^+, has a free internal rotation of H_2 around the A-axis, as shown in Fig. 3. In order to treat this problem, it is required to use the complete nuclear permutation inversion (CNPI) group theory, instead of the point group theory. We label the H atoms 1 through 5 as shown in Fig. 3. The size of the CNPI group is $5! \times 2 = 240$ for the permutations and inversions of the five H atoms in SiH_5^+. Since the scrambling of the H atoms via the in-plane wagging of the 3c2e bond observed for CH_5^+, responsible for the total scrambling of the five H atoms, was predicted to be strongly hindered in SiH_5^+ ($\Delta E=26.8$ kcal/mole),[8] the size of the feasible permutation inversion operations, i.e the size of the molecular symmetry (MS) group, is reduced to $3 \times 2 \times 2 = 12$, G_{12} group, consisted of the exchanges of H1, H2, and H3 atoms, and H4 and H5 atoms, respectively, and the inversions through the origin of the molecule-fixed axes. The elements of the G_{12} MS group, isomorphic with the D_{3h} point group, are listed in the character table shown in Table A1 of the Appendix. In the character table, the equivalent rotations for the G_{12} symmetry operations are also listed in the bottom of Table A1, following the Bunker's idea.[20] The R_α^β means the rotation by the angle β around the α axis. The (θ,ϕ,χ), shown in Table A1, are Euler angles to define the molecule-fixed coordinates (x,y,z) with respect to the space-fixed coordinates (X,Y,Z), and their transformation properties under G_{12} group are also listed in the table. In addition, the transformation properties of ρ, the torsional angle for the internal rotation of H_2, are listed in Table A1. In the Table, the primes and double primes indicate the character with respect to the element (45).

According to the exclusion principle, if a symmetry element has the sole effect of permuting the positions and spins of identical particles, then it must multiply the wavefunction by the factor $\Pi(-1)^p$, where the product is over all sets of identical particles of half-odd spin and p denotes the parity of the permutation which the symmetry element induces in a typical set. Therefore, the overall wavefunction of SiH_5^+ must belong to one or other irreducible representations A_1'' or A_2'', which are antisymmetric with respect to the (45) and (123)(45), and symmetric with respect to the (123) elements.

Table A2 shows the characters of the reducible representations generated by the five

proton spin functions consisted of the SiH_3 and H_2 groups, resulted from the free internal rotation, but no scrambling via the in-plane wagging motion. As the irreducible representations are also shown in the last column of Table A2, the possible spin states are the direct products of ($4A_1'$, $2E'$) and ($3A_1'$, $1A_1''$).

Turning to the rotational problem, SiH_5^+ is predicted to be a near prolate top with the ab initio rotational constants A=2.522 cm^{-1}, B=1.691 cm^{-1}, and C=1.644 cm^{-1} for the global minimum energy structure shown in Fig. 3. The zero order rotational Hamiltonian of SiH_5^+ is that of an asymmetric top, and the asymmetric rotor species can be deduced from the equivalent rotations given in Table A1. The results, as shown in Table A3, are A_1', A_2', A_1'' and A_2'' for K_aK_c = ee, eo, oe, and oo, respectively, where K_a and K_c indicate the prolate and oblate levels, respectively with which the level correlates ($K_a = |k_a|$ and $K_c = |k_c|$), and e and o means even and odd numbers, respectively.

For the free internal rotation, the eigenfunctions and eigenvalues are given by

$$\Phi_{tor} = \exp(ik_i\rho)$$

and

$$E_{tor} = Dk_i^2$$

where $k_i = 0, \pm1, \pm2,...$ and D is the internal rotational constant of the H_2-SiH_3 about the A-axis ($D_{ab} \approx 58.5$ cm^{-1}). The symmetry species of the torsional wavefunctions is shown in Table A4.

Now we are in a position to calculate the nuclear spin statistical weights of the rotational states in any vibration and internal rotation states. For the ground vibrational and internal rotational states of the totally symmetric A_1' symmetry, the direct product of the proton spin symmetry species of SiH_3 and H_2, and the rotational symmetry species, must belong to A_1'' or A_2'' symmetries, i.e.

$$(4A_1', 2E') \times (3A_1', 1A_1'') \times (A_1', A_2'', E', E'') \supseteq A_1'' \text{ or } A_2''$$

As a result, the nuclear spin statistical weights of the rotational states of SiH_5^+ are shown in the parentheses of Table A3, i.e.

$$A_1'(4) \quad A_1''(12) \quad A_2'(4) \quad A_2''(12).$$

The same procedure can be used to determine the nuclear spin statistical weights of the rotational states in the excited vibration and internal rotation states, by incorporating their symmetry species into the direct product described above.

4. RESULTS AND ANALYSIS

Fig. 4A shows the infrared spectrum of the siliconium ion SiH_5^+, taken with 0.2 cm^{-1} resolution from 3650 to 3740 cm^{-1}. In the spectrum, clear P, Q, and R-rotational branches were observed, indicating the A-type transition of an asymmetric top. The average spacing of the adjacent rotational lines in the P and R-branches was ~3.3·cm^{-1}, very close to the (B+C) (=3.335 cm^{-1}) for the minimum energy structure of SiH_5^+ predicted by the ab initio calculation (A=2.522, B=1.691, C=1.644 cm^{-1}).[8]

Since the rotational lines are clearly resolved in the spectrum, they were able to fit with the A-type rotational transitions of an asymmetric top using the Watson S-type asymmetric top rotational hamiltonian.[21] Since the individual J, K_a, K_c states are not resolved in the spectrum, the following approximations were made in the analysis. In the fit, each J, K_a, K_c rotational transition was represented by a Lorentzian function with certain bandwidth, and its center and height were determined by calculating the frequencies and intensities for the A-type transitions from the individual J, K_a, K_c states, with the Boltzmann factors and the nuclear spin statistical weights for G_{12} MS group, $A_1'(4)$, $A_1''(12)$, $A_2'(4)$, and $A_2''(12)$, taken into account. The resulting Lorentzian functions for each J value were added to give the final line shape, and the frequency at the maximum was compared with the observed frequency for each J quantum number. As a preliminary fit, the ground state A rotational constant was fixed at 2.519 cm^{-1}, the effective A rotational constant which was calculated from the ab initio structures of SiH_5^+, with the free internal rotation of H_2--SiH_3^+ taken into account. In addition, the centrifugal distortion terms were entirely ignored in the fit since the number of rotational lines resolved in the spectrum (16 lines) were not enough to determine those terms. Therefore, the six parameters, i.e. ground state B, C, excited state A, B, C constants, and the band origin were used to fit the 16 lines. As shown in Table 1, the ground state B, C constants were determined to be 1.689 (0.003), 1.639 (0.003) cm^{-1}, the excited state A, B, C constants were 2.537 (0.008), 1.692 (0.002), 1.636 (0.004) cm^{-1}, respectively, and the band origin was 3693.97 (0.06) cm^{-1}. Note that the numbers in parentheses are single standard deviations calculated from the fit. The observed and calculated frequencies for the J rotational quantum numbers are listed in Table 2, along with the differences of the two frequencies. A complete agreement was found between the experimental results and

the theoretical predictions for the ground state B and C rotational constants. This result strongly suggests that SiH_5^+ can be described as a complex of SiH_3^+ and H_2 , and the internal rotation of $H_2\text{--}SiH_3^+$ is likely to be free. Unlike CH_5^+, the scrambling through the C_{2v} transition state does not occur in SiH_5^+.

Fig. 4B shows a simulated spectrum obtained with the rotational constants determined from the fit, the Lorentzian bandwidth of 0.15 cm^{-1}, and the rotational temperature at 90°K. The intensity distribution in the P and R-branches of the simulated spectrum was different from that of the observed spectrum, as shown in Fig. 4A and 4B. A close examination of the observed spectrum reveals that the intensity distribution of the observed spectrum is well correlated with the upper state J's, rather than the lower state J's. For example, both the P and R-branches of the observed spectrum have maximum intensities at the upper state J=6, and then decrease slowly in intensity as the upper state J increases, as shown Fig. 4A. In addition, the intensity alternation for the upper state J≤5 is similar for both P and R-branches. This result indicates that the multiphoton process induced by the CO_2 laser (see Fig. 1), which drives the vib-rotationally excited SiH_5^+ ions over the dissociation threshold, could influence the observed vibrational predissociation spectrum. This arises because since SiH_5^+ is small, the initial IR excitation leads to a discrete rather than quasicontinuum region. In fact, the density of states for SiH_5^+ at the energy of one IR photon from the tunable laser ($\sim$3700 cm^{-1}) was calculated to be far below the quasicontinuum threshold, as shown in Table 3, so that multiphoton processes are likely to occur in the discrete states, rather than in the quasicontinuum states. Previously, the multiphoton process in the discrete states was known to depend strongly upon the intermediate vibration-rotational states involved in the process.[22]

In spite of the errors involved in determining the frequencies used in the fit from neglecting both the multiphoton process and the high order terms such as centrifugal distortions, the results of the preliminary fit would be still valid within the accuracy of the observed rotational line width since the observed lines are sharply resolved. Therefore, we conclude that the siliconium ion SiH_5^+ possesses the structure predicted by the ab initio calculation, which can be described as a complex between SiH_3^+ and a freely internally rotating H_2 groups. Unlike the carbonium ion CH_5^+, the siliconium ion SiH_5^+ does not scramble through the C_{2v} transition state, and the 3c2e bond is highly localized. A complete analysis of the observed IR spectrum with

the multiphoton process taken into account is now on progress.

ACKNOWLEDGEMENT

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Table 1. Parameters for the ground and excited states of the H-H stretching mode in SiH_5^+, derived from a least squares fit to 16 lines. Single standard deviations are given in parenthesis. Units are in cm^{-1}.

Parameter	Ground	Excited
A	2.519[a]	2.537(0.008)
B	1.689(0.003)	1.692(0.002)
C	1.639(0.003)	1.636(0.004)
Band origin	3693.97(0.06)	

[a]The ground A constant was determined from ab initio results for SiH_5^+ with a free internal rotation, and was fixed in the fit.

Table 2. Observed and calculated rotational transitions in the H-H stretching mode of SiH_5^+. Units are in cm^{-1}.

Lower J	Upper J	Obs.[a]	Calc.[b]	Obs.- Calc.
11	10	3657.60	3657.49	0.11
10	9	3660.85	3660.82	0.03
9	8	3664.05	3664.12	- 0.07
8	7	3667.48	3667.50	- 0.02
7	6	3670.70	3670.79	- 0.09
6	5	3673.95	3674.10	- 0.15
5	4	-	3677.42	-
4	3	3680.60	3680.71	- 0.11
3	2	-	3684.05	-
2	1	-	3687.34	-
1	0	-	3690.63	-
Q-branch	Q-branch	3694.25	3694.19	0.06
0	1	-	3697.31	-
1	2	3700.70	3700.64	0.06
2	3	3704.15	3703.98	0.17
3	4	-	3707.36	-
4	5	3710.65	3710.74	- 0.09
5	6	3714.23	3714.12	0.11
6	7	3717.45	3717.50	- 0.05
7	8	3720.85	3720.84	0.01
8	9	3724.15	3724.18	- 0.03
9	10	3727.45	3727.55	- 0.10
10	11	-	3730.89	-

[a]The transitions marked by "-" were not resolved in the spectrum.
[b]These frequecnies were determined at the maximum of the rotational band contour, constructed from the transitions of all the K_a, K_c quantum numbers for each J. Each J, K_a, K_c transition was represented by a Lorentzian line shape function with 0.15 cm^{-1} FWHM.

Table 3. Density of states for SiH_5^+ calculated as a function of internal energy using the Witten-Rabinovich equation. The torsional mode was considered as a free internal rotation, and was not included in this calculation.

$$\underline{\rho(E) \text{ per } cm^{-1}}$$

Energy	3500 cm^{-1}	5000 cm^{-1}	7000 cm^{-1}
$\rho(E)$	0.40	2.03	11.6

†The vibrational frequencies used in this calculation were obtained by scaling the ab initio harmonic frequencies at TZ2P CCSD (ref. 8), by the ratio of the observed and calculated H-H stretching frequencies. The results are 3694, 2201, 2194, 937, 874, 867, 822, 666, 604, and 588 cm^{-1}.

FIGURE CAPTIONS

Fig. 1 Schematic of the two color IR multiphoton process used in this experiment. The H-H stretching mode of SiH_5^+ was excited first by the pulsed and tunable IR laser, then the cw CO_2 laser pumped the vibrationally excited ions over the dissociation threshold.

Fig. 2 Mass spectrum showing the siliconium ions, SiH_5^+ and SiH_7^+. The mixing ratio SiH_4:He:H_2 was 1:5,000:50,000, and source pressure, the source temperature, and the discharge current were 200 torr, -10°C, and 30μA, respectively.

Fig. 3 Structure of SiH_5^+, predicted by ab initio calculation (ref. 8).

Fig. 4 (A) Infrared spectrum of the H-H stretching mode in SiH_5^+, showing clear features for the A-type vibration-rotation transitions. (B) Simulated spectrum of the A-type transitions with the rotational constants determined from the fit, a Lorentzian line width of 0.15 cm^{-1}, and the rotational temperature at 90°K. Note the assignments of J quantum numbers for the lower and upper states.

Fig. 1

INTENSITY(arb.)
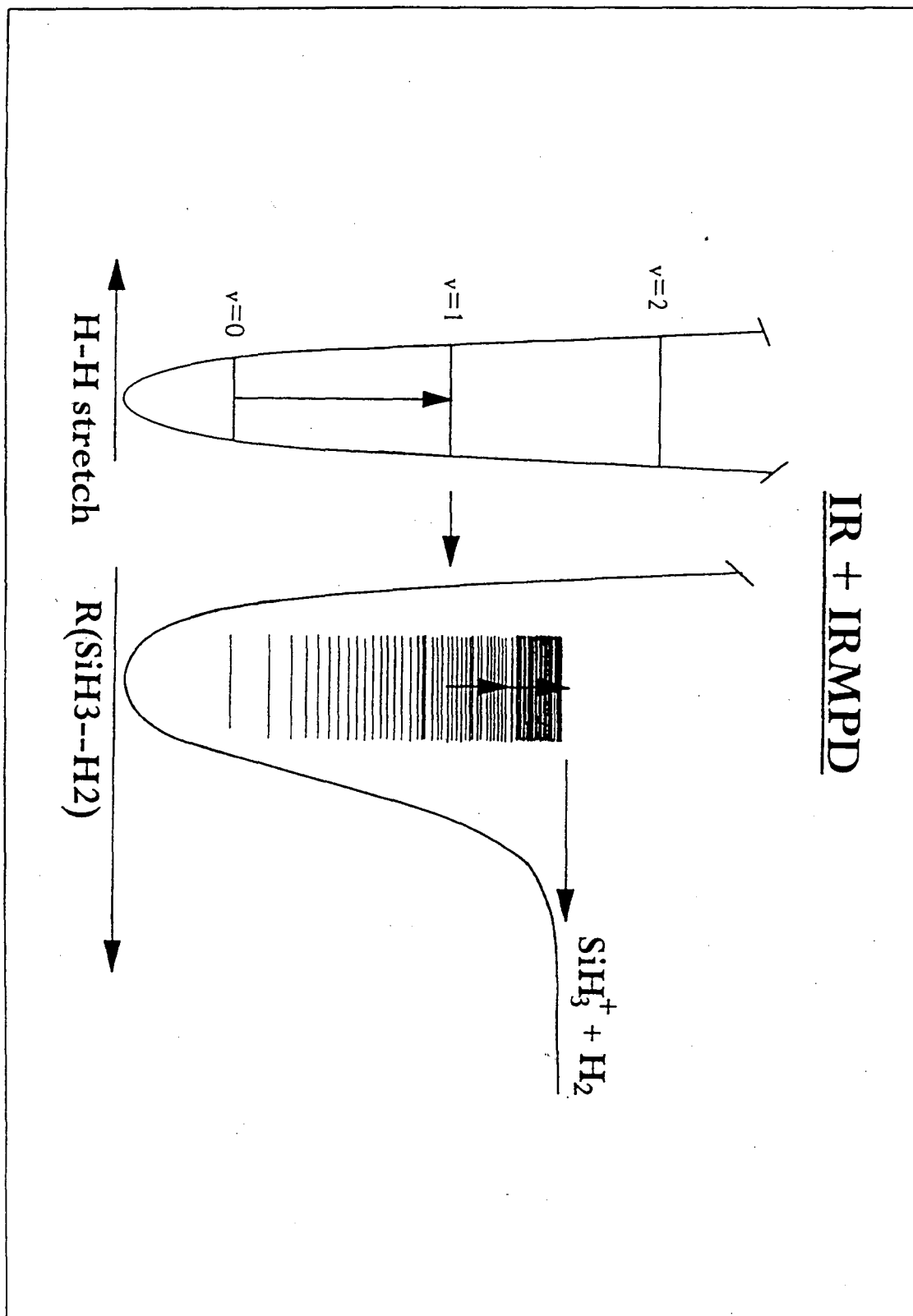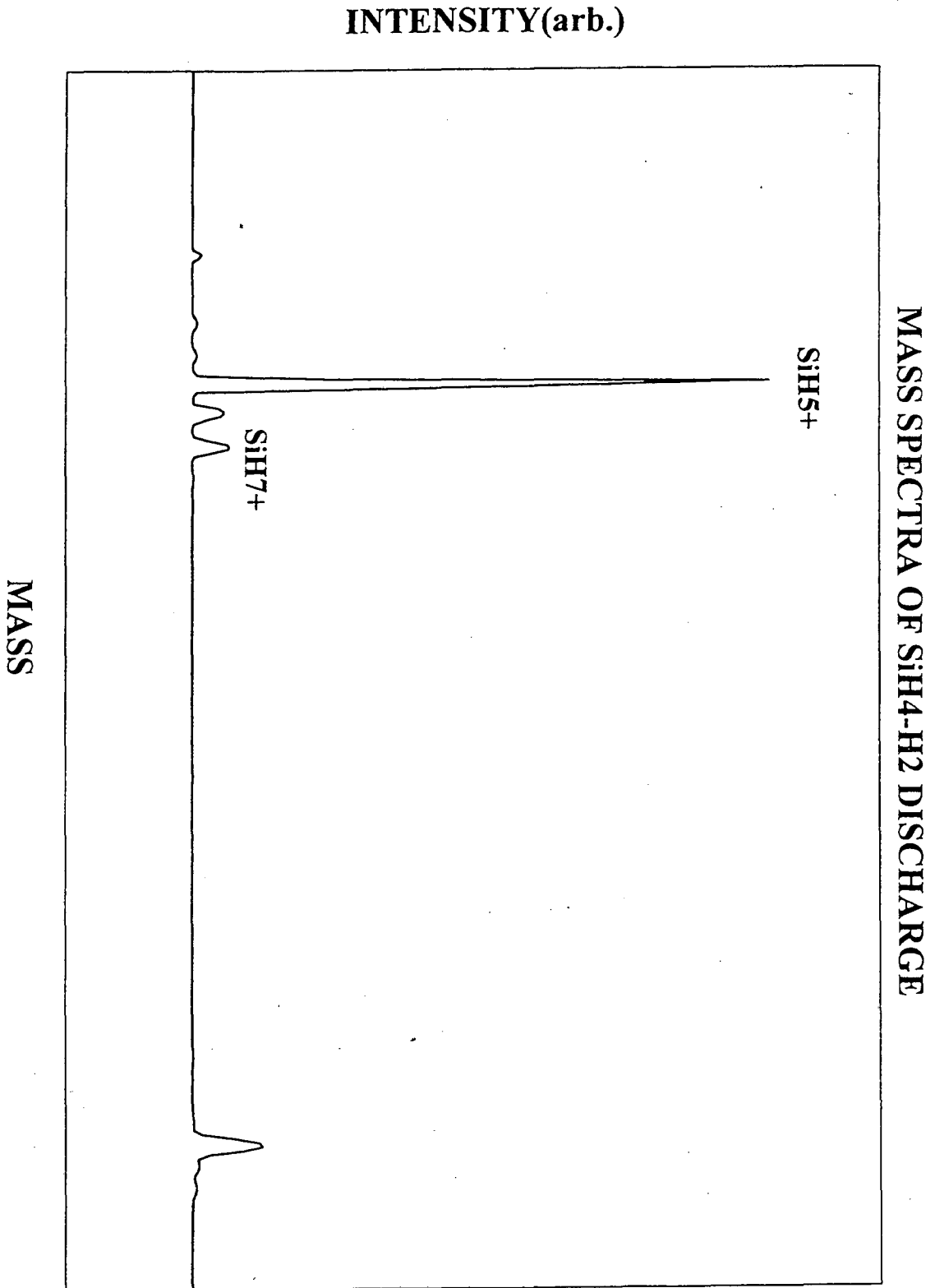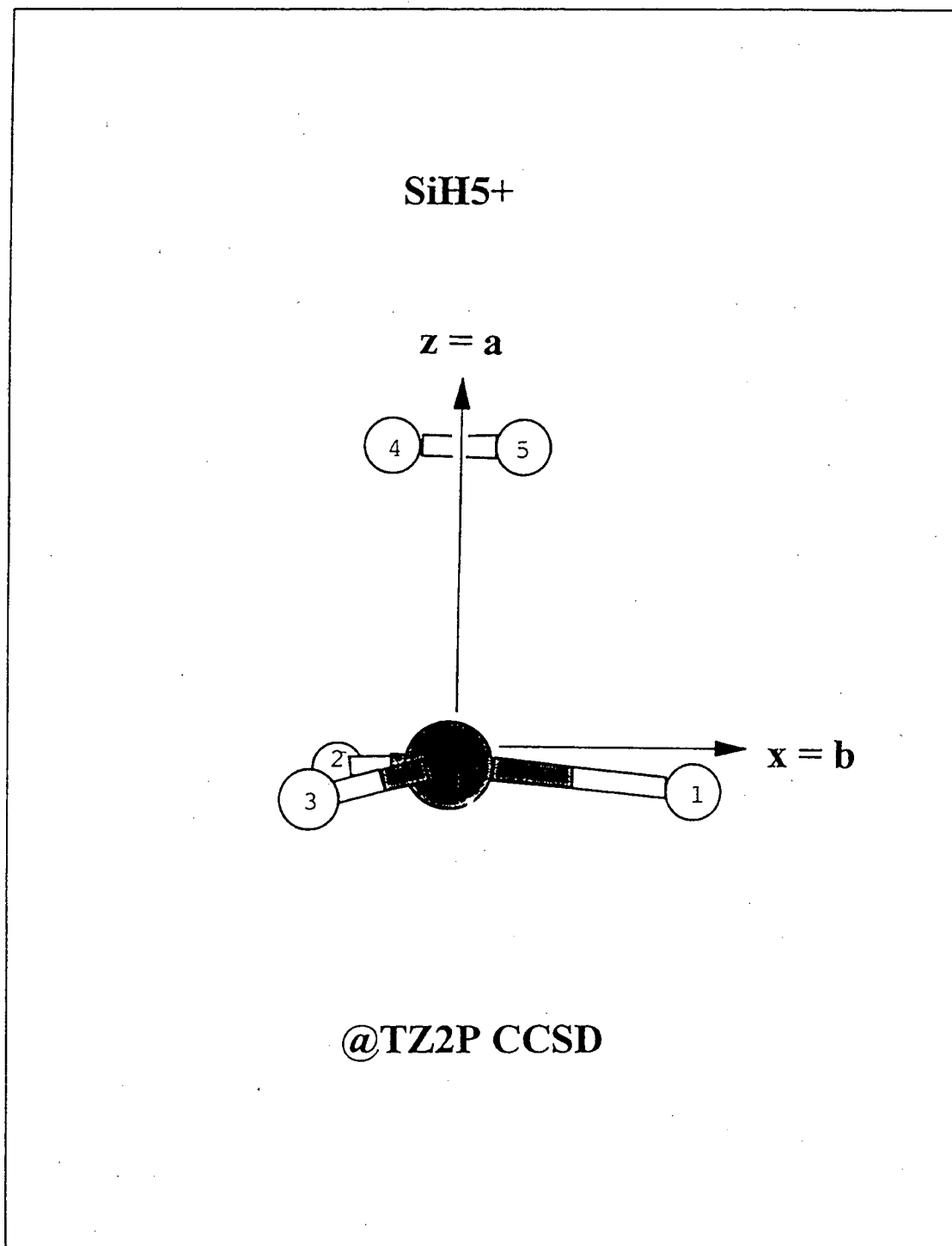
MASS

MASS SPECTRA OF SiH4-H2 DISCHARGE

SiH5+

SiH7+

Fig. 2

Fig. 3

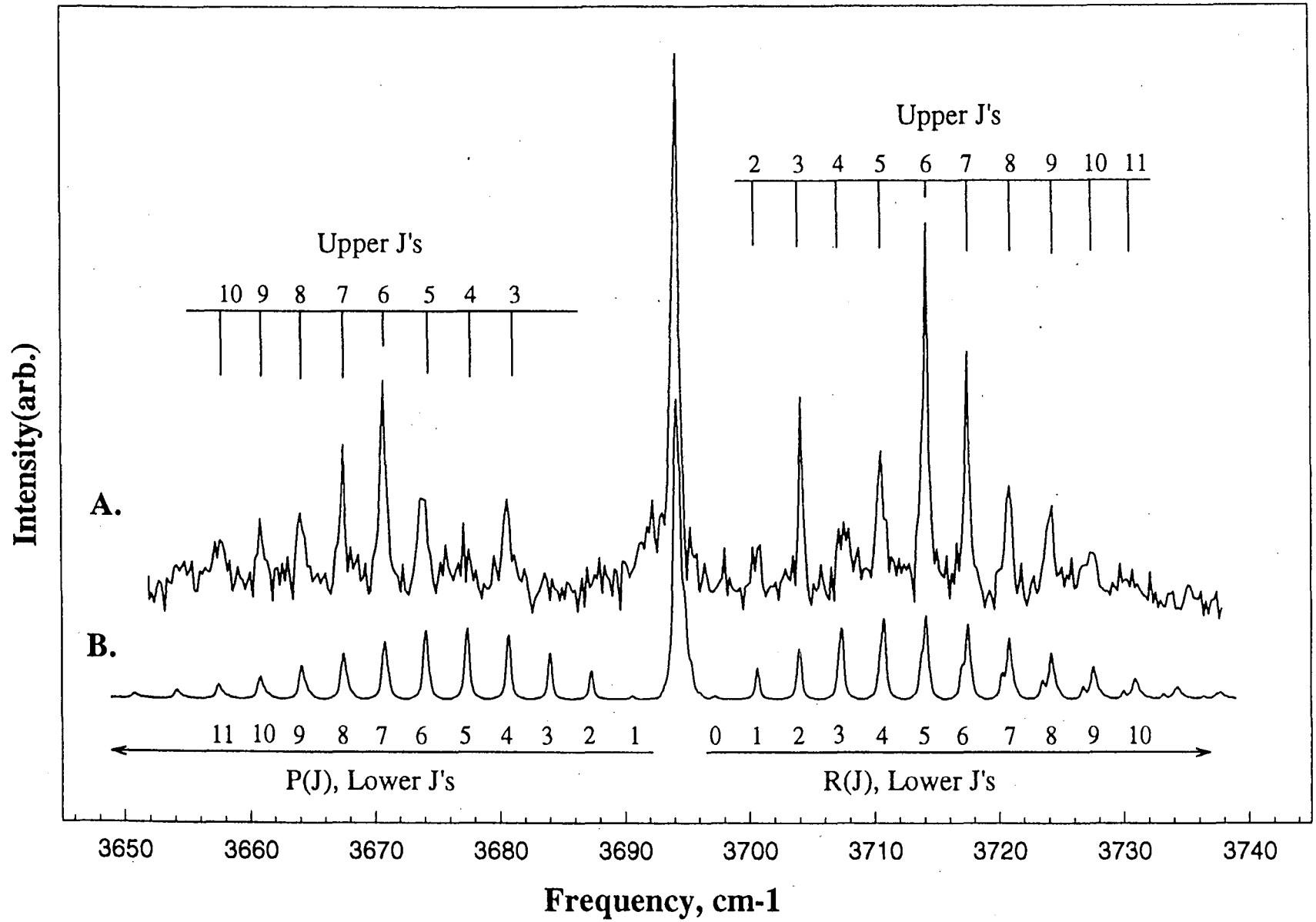Fig. 4

APPENDIX

Results of the group theoretical treatment of SiH_5^+ using G_{12} molecular symmetry (MS) group are listed below. The numbering of the H atoms is shown in Fig. 3.

Table A1. Character table of the G_{12} group for SiH_5^+

G_{12}	E	(123) (132)	(23)[*] (31)[*] (12)[*]	(45)	(123)(45) (132)(45)	(23)(45)[*] (31)(45)[*] (12)(45)[*]
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0
Equiv. Rotation	R^0	R^0	R_c^π	R_a^π	R_a^π	R_b^π
θ,ϕ,χ [a]	θ,ϕ,χ	θ,ϕ,χ	$\pi-\theta,\pi+\phi,\ \pi-\chi$	$\theta,\phi,\pi+\chi$	$\theta,\phi,\pi+\chi$	$\pi-\theta,\pi+\phi,2\pi-\chi$
ρ [b]	ρ	$\rho-2\pi/3$	$2\pi-\rho$	$\rho+\pi$	$\rho+\pi/3$	$\pi-\rho$

[a] θ,ϕ,χ are the Euler angles to define the molecule-fixed coordinates (x,y,z) with respect to the space-fixed coordinates (X,Y,Z).
[b] ρ defines the torsional angle for the internal rotation of H_2--SiH_3^+.

Table A2. The characters of the reducible representations generated by the proton spin functions of SiH_5^+ in the G_{12} group.

G_{12}	E	(123)	$(23)^*$	(45)	(123)(45)	$(23)(45)^*$	Γ_{nspin}
$\alpha_1\alpha_2\alpha_3(1)^a$	1	1	1	1	1	1	A_1'
$\alpha_1\alpha_2\beta_3(3)$	3	0	1	3	0	1	$A_1'+E'$
$\alpha_1\beta_2\beta_3(3)$	3	0	1	3	0	1	$A_1'+E'$
$\beta_1\beta_2\beta_3(1)$	1	1	1	1	1	1	A_1'
$\alpha_4\alpha_5(1)$	1	1	1	1	1	1	A_1'
$\alpha_4\beta_5(2)$	2	2	2	0	0	0	$A_1'+A_1''$
$\beta_4\beta_5(1)$	1	1	1	1	1	1	A_1'

[a]The number in the parenthesis is the number of the possible combinations of α,β spin functions.

Table A3. Symmetry species of asymmetric top rotational wavefunctions of SiH_5^+ in the group G_{12}.

K_aK_c	Γ_{rot} [a]
ee	$A_1'(4)$
eo	$A_2'(4)$
oe	$A_1''(12)$
oo	$A_2''(12)$

[a]The numbers in parentheses are the nuclear spin statistical weights for the ground vibrational and torsional states.

Table A4. Symmetry species of torsional wavefunctions, $\exp(ik_i\rho)$, of SiH_5^+ in the G_{12} group.

K_i [a]	Γ_{tor}
0	A_1'
$6m\pm1$	E''
$6m\pm2$	E'
$6m\pm3$	$A_1''+A_2''$
$6m\pm6$	$A_1'+A_2'$

[a]$K_i = |k_i| > 0$, and m is a nonnegative integer.