

Vibrational properties of β -KSiH₃ and β -RbSiH₃: a combined Raman and inelastic neutron scattering study

Janos Mink,^{a,b} Yuan-Chih Lin,^c Maths Karlsson,^c Carin Österberg,^c Terrence J. Udovic,^d Henrik Fahlquist^e and Ulrich Häussermann^{e*}

The hydrogen storage materials ASiH₃ (A = K and Rb) represent complex metal hydrides built from metal cations and pyramidal SiH₃[−] ions. At room temperature, SiH₃[−] moieties are randomly oriented because of dynamical disorder (α -modifications). At temperatures below 200 K, ASiH₃ exist as ordered low-temperature (β) modifications. The vibrational properties of β -ASiH₃ were characterized by a combination of Raman spectroscopy and inelastic neutron scattering. Internal modes of SiH₃[−] are observed in the spectral range 1800–1900 cm^{−1} (stretching modes) and 890–1000 cm^{−1} (bending modes). External modes are observed below 500 cm^{−1}. Specifically, SiH₃[−] librations are between 300–450 cm^{−1} and 270–400 cm^{−1} for A = K and Rb, respectively, SiH₃[−] translations are between 95 and 160 cm^{−1}, K⁺ translations are in the range 60–100 cm^{−1} and Rb⁺ translations in the range 50–70 cm^{−1}. The red-shift of libration modes for A = Rb is associated with a 15–30% reduction of the libration force constants of SiH₃[−] ions in β -RbSiH₃. This correlates with a lower temperature for the β - α order-disorder phase transition (278 vs 298 K). Libration modes become significantly anharmonic with increasing temperature but are maintained up to at least 200 K. The vibrational properties of ASiH₃ compare well to those of alkali metal borohydrides ABH₄ (A = Na–Cs). Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: complex metal hydrides; alkali metal silanides; inelastic neutron scattering; libration modes; order-disorder phase transition

Introduction

Recently, it was shown that the silicide-silanide systems ASi–ASiH₃ (A = K, Rb and Cs) possess excellent thermodynamic characteristics for reversible hydrogen absorption, and the phenomenon has been attributed to an unusually low entropy variation.^[1,2] The silanides ASiH₃ exist as low- and high-temperature forms with crystal structures that consist of alkali metal ions and pyramidal silyl SiH₃[−] anions. The high-temperature (α) phase is the product of the ASi hydrogen absorption process and corresponds to a NaCl-type arrangement of alkali metal and randomly oriented, dynamically disordered, SiH₃[−] moieties.^[3] From spectroscopic and neutron diffraction studies, it was established that silyl anions possess the ideal C_{3v} symmetry in NaCl type α -ASiH₃. The Si–H distance is 1.52 Å, and the H–Si–H angle is 92.2°.^[4]

At temperatures below 200 K, ASiH₃ adopts an ordered low-temperature (β) modification. β -KSiH₃ crystallizes with the orthorhombic space group *Pnma*.^[5] Silyl groups possess a local C_s symmetry, which implies two different Si–H distances and H–Si–H bond angles (Fig. 1a). Distances and angles appear slightly elongated compared with C_{3v}-SiH₃[−] in the α -forms.^[4] The β -modifications of RbSiH₃ and CsSiH₃ crystallize with the monoclinic *P2₁/m* KClO₃ structure.^[2] The crystal symmetry lowering with respect to β -KSiH₃ does not affect the local symmetry of the silyl anions and their coordination by counter cations. This coordination is shown in Fig. 1b. The polyhedron defined by the seven A⁺ cations encapsulating SiH₃[−] corresponds to a mono-capped trigonal prism, which can be considered as a common building block of both the orthorhombic and monoclinic β -structures.^[2] In the two structures,

mono-capped trigonal prisms are linked differently. As a consequence, the coordination of A⁺ by silyl groups is different (Fig 1c, d).

In a previous study, we characterized the structural and vibrational properties of silyl SiH₃[−] anions in KSiH₃ and RbSiH₃.^[4] In this work, we present the analysis of external (lattice) modes, i.e. librations and translations, of the low temperature β -forms based on Raman spectroscopy and inelastic neutron scattering (INS).

* Correspondence to: Ulrich Häussermann, Department of Materials and Environmental Chemistry, Stockholm University, SE-10691 Stockholm, Sweden. E-mail: Ulrich.Haussermann@mmk.su.se

a Research Center of Natural Sciences, Hungarian Academy of Sciences, P.O. Box 77, H-1525, Budapest, Hungary

b Research Institute of Chemical and Process Engineering, Faculty of Information Technology, University of Pannonia, P.O. Box 158, H-8201, Veszprém, Hungary

c Department of Physics, Chalmers University of Technology, SE-41296, Gothenburg, Sweden

d NIST Center for Neutron Research, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, Maryland, 20899-6102, USA

e Department of Materials and Environmental Chemistry, Stockholm University, SE-10691, Stockholm, Sweden

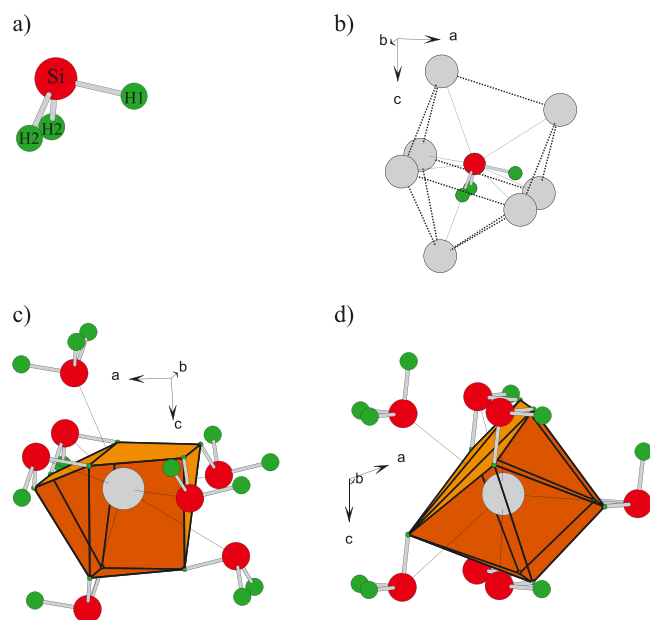


Figure 1. Structure features of β -AsiH₃. Green, red and gray circles denote H, Si and A atoms, respectively. (a) The silyl anion with C_{3v} symmetry possesses one short (Si–H1) and two long (Si–H2) distances. (b) Coordination environment of silyl anions: The coordination polyhedron of A^+ around a SiH_3^- moiety corresponds to a mono-capped trigonal prism. (c) Coordination environment of the A^+ ions in orthorhombic β -KSiH₃ (left) and monoclinic β -RbSiH₃ (right). The orange polyhedra indicate the nearest-neighbor coordination by 9 H atoms stemming from six silyl groups. A seventh silyl ion is coordinated via the Si lone pair.

Methods

Synthesis

The silanides α -KSiH₃ and α -RbSiH₃ (α -AsiH₃) and deuterides α -KSiD₃ and α -RbSiD₃ (α -ASiD₃) were synthesized as described in detail in Ref. 4.

Raman spectroscopy

Powder samples were sealed in 0.3-mm lithium borate (Lindemann glass) capillaries. Raman spectra were measured at 300, 200 and 100 K on a Dilor XY-800 triple grating spectrometer with double subtractive configuration.^[6] The instrument is equipped with an 800 mm focal length spectrograph and a liquid nitrogen cooled (−70 °C), back thinned CCD detector. Capillaries were placed in a Linkam temperature stage.^[6] A cooling rate of 3 K/min was applied, and the capillaries were equilibrated for 10 min after having reached the target temperature. Samples were excited with a Ar⁺/Kr⁺ laser (647 nm). The input power of the laser was locked at 13 mW, which approximately corresponds to 0.90 mW output power under the microscope with the $\times 40$ objective lens. Data covering the spectral range 30–4000 cm^{-1} were collected in 18 spectral windows using an 1800 grooves/mm grating. The exposure time for each window was 120 s, and the number of accumulations was 10. Spectral windows were subsequently merged. Raman spectra were processed and evaluated with the GRAMS/AI (7.02) spectroscopy software suite.^[7] Normal coordinate calculations were performed by means of the Wilson's **GF** matrix method. Force constants were obtained by optimizing the vibrational frequencies using a symmetrized valence force field. For the calculations the

PC-based program package developed by J. Mink and L. Mink was used.^[8]

Neutron scattering

For INS spectroscopy the hydride samples were loaded into an aluminum sample holder under a He atmosphere. The sample holder was subsequently sealed and mounted in a cryostat. The spectra of the two hydrides were measured at 4 K on the filter-analyzer neutron spectrometer instrument at the NIST Center for Neutron Research using the PG(002) monochromator for accessing the neutron energy loss range from 10 to 30 meV and the Cu(220) monochromator for 30 to 200 meV. 20'–20' collimations were used before and after the monochromators. The instrumental resolution is $\sim 10\text{ cm}^{-1}$ fwhm. (Note, that there are INS instruments (e.g. TOSCA at ISIS and VISION at SNS), which provide considerably higher resolution.) Data were corrected for the fast-neutron backgrounds.

Computation

Density functional theory (DFT) calculations were performed to assist the assignment of modes in the experimental spectra. In particular, the QUANTUM-ESPRESSO package was used to calculate and to analyze the symmetry of phonons at the center of the Brillouin zone.^[9] The crystal structures of orthorhombic β -KSiH₃ and monoclinic β -RbSiH₃ were relaxed with respect to volume, lattice parameters and atomic positions. Forces were converged to better than $10^{-3}\text{ eV/\AA}$. An electronic Monkhorst–Pack k -point grid of $6 \times 6 \times 6$ was used with a 65 Hartree planewave kinetic energy cutoff.^[10] The Perdew–Burke–Erzerhof exchange–correlation was used with norm-conserving pseudopotentials set according to Goedecker, Tetter and Hutter.^[11,12]

Results and discussion

Overall features of AsiH₃ spectra

Figure 2 shows the Raman spectra of KSiH₃ and RbSiH₃ at 300, 200 and 100 K. The spectrum at 300 K corresponds to cubic α -AsiH₃ and contains only bands that are associated with the internal modes of the SiH_3^- complex anion. For a pyramidal SiH_3^- anion with C_{3v} symmetry, one expects two symmetric (A_1) and two asymmetric (E) vibrations. The four vibrations are Raman active. The strong bands near 1900 and 900 cm^{-1} correspond to the symmetric stretch and bend (umbrella) vibration, respectively.^[4] A recent quasi-elastic neutron scattering study revealed pronounced rotational dynamics of the SiH_3^- ions in AsiH₃.^[3] In the Raman spectra, dynamical disorder expresses in drastically widened lines. The fwhm of the symmetric stretch is about 100 cm^{-1} and that of the symmetric bend is around 40 cm^{-1} . Dynamic disorder also explains that the bands of the less intense asymmetric (E) modes are barely noticeable in the spectra of α -AsiH₃.

The orthorhombic and monoclinic unit cells of β -KSiH₃ and β -RbSiH₃ contain four and two formula units, respectively. Hence, there are 24 and 12 internal mode vibrations, respectively. According to factor group analysis (Table 1), 12 modes are Raman-active for the orthorhombic ($Pnma$) case and 6 modes for the monoclinic ($P2_1/m$) case.^[13] Half of each accounts for stretches and bends. Broad bands in the room-temperature spectra become narrow and distinct lines at low temperatures. Especially the bands of the asymmetric degenerate modes, which are barely discernible in

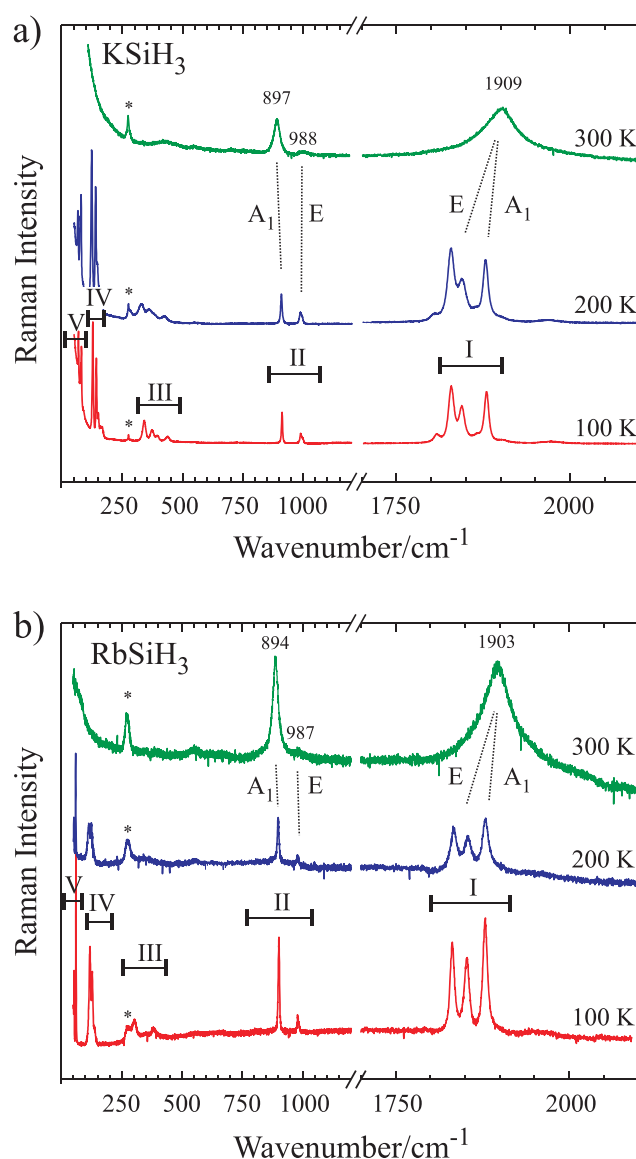


Figure 2. Raman spectra of KSiH₃ (a) and RbSiH₃ (b) at 300, 200 and 100 K. The relation between internal modes (A₁ symmetric stretch and bend, E asymmetric stretch and bend) when going from the disordered α to the ordered β form is indicated. The Roman letters denote different sections in the spectrum; I = Si–H stretches, II = Si–H bends, III = SiH₃ librations, IV = SiH₃ translations, V = A translations. The asterisk at 270 cm^{−1} marks a band of unknown origin.

the spectra of the α -forms, are clearly visible in the low-temperature spectra. The asymmetric (E) modes are split into two components as a consequence of the symmetry lowering of the SiH₃[−] anion from

C_{3v} in the disordered modification to C_s in the ordered low-temperature structures.^[4] Furthermore, in contrast with the room-temperature spectra, the low-temperature ones clearly show bands of external (lattice) modes, which are located below 500 cm^{−1}. Libration (torsion) modes of SiH₃[−] moieties occur in a range between 270 and 450 cm^{−1}. There are 12 and 6 for β -KSiH₃ and RbSiH₃, respectively (cf. Table 1). Half of each is Raman-active. Further, translation modes of SiH₃[−] moieties occur between 95 and 160 cm^{−1}. Again there are 12 and 6 for β -KSiH₃ and RbSiH₃, respectively (half of each is Raman-active). Lastly, the translation modes of the cations are found between 60 and 100 cm^{−1} for K⁺ (9, of which six are Raman-active) and between 50 and 70 cm^{−1} for Rb⁺ (3, all Raman active), see Table 1. In conclusion, the spectra of ASiH₃ represent textbook examples for complex anion salts with clearly separated vibrational regions, stretching and bending modes of the anion, libration modes of the anion, translation modes of the anion and cation. See Fig. 2.

Comparison of Raman and INS spectra

The INS provides complementary aspects to Raman spectroscopy.^[13,14] In INS – unlike optical spectroscopy – the intensity does not depend on electronic properties such as dipole moment or polarizability. Thus, there are no symmetry-based selection rules, and all modes are allowed. Furthermore, the intensity of modes is proportional to the amplitude of motion (displacement) and the total scattering cross section of atoms involved. Compared with all other elements, the total cross section of hydrogen is extremely large. Thus, vibrations involving H displacements will dominate the INS spectrum. Additionally, because of their larger amplitudes of motion, bending and libration modes will generally attain a higher intensity than stretching modes and translations.

The complementarity of Raman and INS spectra for ASiH₃ is clearly revealed in Fig. 3. In the Raman spectra, the translation modes have highest intensity, whereas librations and bending modes are pronounced in the INS spectra. With respect to the bending modes, the asymmetric ones are more intense than the symmetric ones in the INS spectra. The broad distribution of neutron scattering intensity in the region 600 to 800 cm^{−1} is attributed to overtone bands of libration modes. Tail-like features on the blue side of libration and bending bands, especially recognizable in the KSiH₃ spectrum, are attributed to combinations with translation modes (i.e. phonon wings). The INS spectrum also suggests that the RbSiH₃ sample contained RbH (NaCl structure) as an impurity. This has not been noticeable in the Raman spectrum.

Although there are no selection rules, the INS spectra are not sufficiently resolved to reveal all modes. When focusing on the bending modes (900–1000 cm^{−1} range), there should be 12/6 in total for KSiH₃/RbSiH₃. 6/3 are Raman-active. The split of the asymmetric mode – which is degenerate for the C_{3v}-SiH₃[−] ion – is seen as a

Table 1. Compilation of optical modes for β -KSiH₃ and β -RbSiH₃ according to factor group analysis (Ra = Raman-active, IR = IR-active)^[13]

Modes	β -KSiH ₃ (Pnma, D _{2h})	β -RbSiH ₃ (P2 ₁ /m, C _{2h})
	A _g , B _{1g} , B _{2g} , B _{3g} = Ra, B _{1u} , B _{2u} , B _{3u} = IR, A _u = inactive	A _g , B _g = Ra, A _u , B _u = IR
Stretching	12 = 2A _g + B _{1g} + 2B _{2g} + B _{3g} + A _u + 2B _{1u} + B _{2u} + 2B _{3u}	6 = 2A _g + B _g + A _u + 2B _u
Bending	12 = 2A _g + B _{1g} + 2B _{2g} + B _{3g} + A _u + 2B _{1u} + B _{2u} + 2B _{3u}	6 = 2A _g + B _g + A _u + 2B _u
Libration	12 = A _g + 2B _{1g} + 2B _{2g} + B _{3g} + 2A _u + B _{1u} + 2B _{2u} + B _{3u}	6 = A _g + 2B _g + 2A _u + B _u
SiH ₃ [−] translation	12 = 2A _g + B _{1g} + 2B _{2g} + B _{3g} + A _u + 2B _{1u} + B _{2u} + 2B _{3u}	6 = 2A _g + B _g + A _u + 2B _u
A ⁺ translation	9 = 2A _g + B _{1g} + 2B _{2g} + B _{3g} + A _u + B _{1u} + B _{3u}	3 = 2A _g + B _g

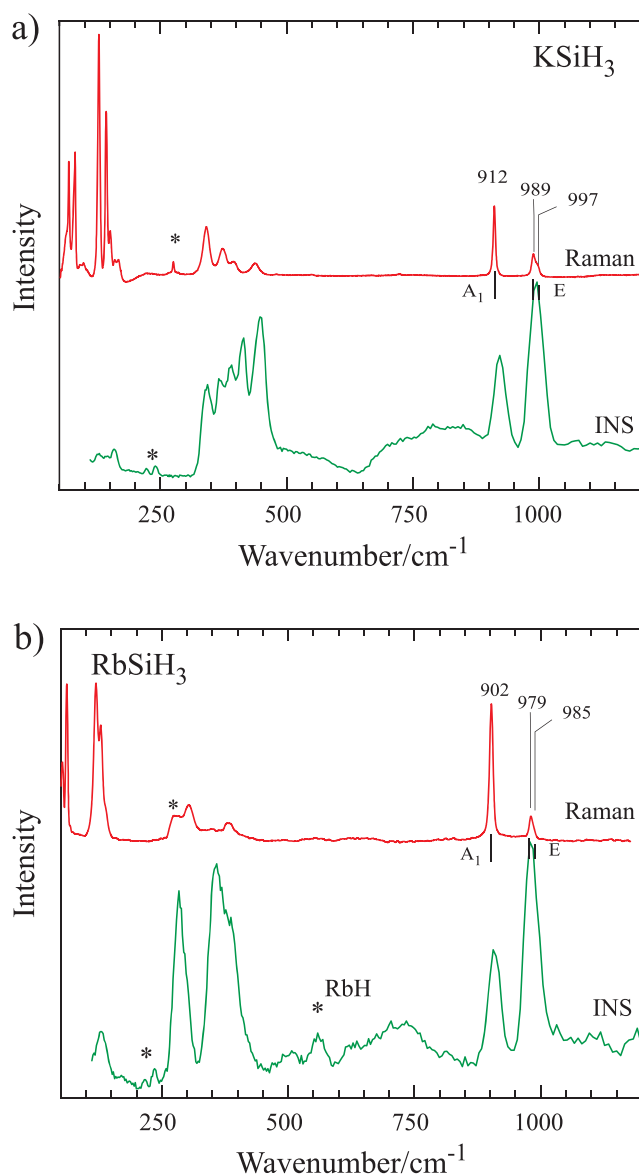


Figure 3. Comparison of Raman spectra (recorded at 100 K) and INS spectra (measured at 4 K) for KSiH₃ (a) and RbSiH₃ (b). For the INS spectra, the asterisks mark a possible impurity (RbH) and spurious ghost peaks due to the presence of some $\lambda/2$ incident neutron contamination from the PG (002) monochromator. For the Raman spectra, the asterisk marks a band of unknown origin (cf. Fig. 2).

shoulder in the Raman spectra. However, a further split of modes in the KSiH₃ spectrum due to correlation splitting is not detectable.^[4] In the INS spectra, the bending modes are only seen as two broad bands, centered around 1000 cm⁻¹ (the asymmetric ones) and around 930 cm⁻¹ (the symmetric ones). When analyzing the second derivative of the neutron scattering intensity, possibly three modes at 987, 980 and 968 cm⁻¹ may be resolved in the region of the asymmetric bends and three modes at 919, 912 and 905 cm⁻¹ in the region of the symmetric (umbrella) ones (cf. Fig. 4). Their assignment, however, is ambiguous. Likewise, a similar analysis for RbSiH₃ may yield the location of four modes, two associated with asymmetric bends (at 996 and 975 cm⁻¹) and two associated with symmetric ones (at 913 and 902 cm⁻¹).

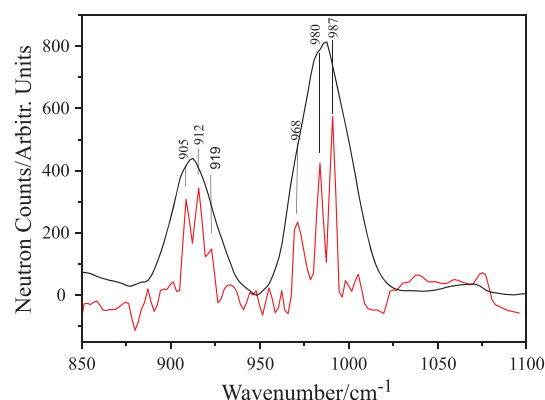


Figure 4. Second derivative of the INS spectrum of KSiH₃ (red line) in the range of the SiH₃ bending modes, revealing possibly the location of six bands.

Analysis of libration modes

The libration modes are in the range 300–450 and 270–400 cm⁻¹ for KSiH₃ and RbSiH₃, respectively. There are 12 modes for *Pnma* β -KSiH₃ and 6 for *P2₁/m* RbSiH₃. Their distribution according to factor group analysis is given in Table 1. Figure 5 depicts the Raman and INS spectra for the spectral region of the libration modes. Their location and assignment is compiled in Tables 2 and 3.

The spectral range of librations looks clearly different for KSiH₃ and RbSiH₃ because of their different crystal structures. For KSiH₃, six Raman-active modes are expected. Four well-developed bands are seen at 438, 395, 373 and 341 cm⁻¹, which are very close to the DFT calculated bands at 440, 397, 369 and 341 cm⁻¹, respectively. The two missing bands (DFT calculated at 433 and 375 cm⁻¹) may be identified as shoulders to the bands with maxima at 438 and 373 cm⁻¹ when analyzing the second derivative of the Raman spectrum (Fig. 6a and Table 2). These bands may then be interpreted as overlapping modes at 440/433 and 375/369 cm⁻¹, respectively. The librational part of the INS spectrum of KSiH₃ exhibits five well-defined bands at 440, 405, 381, 358 and 335 cm⁻¹. Three other bands at 443, 400, 373 and 311 cm⁻¹ may be obtained by analyzing its second derivative. The six Raman bands were used to assign the six 'g' modes among the 12 librational modes. The nine INS bands were assigned to the closest DFT-calculated wavenumbers (Table 2).

Figure 6b shows the spectral range of librations for β -KSiD₃. Although slightly distorted from their ideal *C_{3v}* symmetry, both SiH₃⁻ and SiD₃⁻ correspond to symmetric top rotors with two different principal moments of inertia, i.e. one along the *C₃*(*z*) rotational axis (*I_A*) and two (*I_B* = *I_C*) along axes perpendicular to *C₃*(*z*). The libration modes correlate with the inverse of the moments of inertia (*I*⁻¹), and the isotope shifts can be predicted as $\nu/\nu^* = (I^*/I)^{1/2}$, where ν and *I* are the libration frequency and moment of inertia for SiH₃⁻ and ν^* and *I*^{*} analogously for SiD₃⁻. The moments of inertia *I_A* (*I_B* = *I_C*) are 5.0863 (4.5260) and 10.1649 (8.6946) amu Å² for SiH₃⁻ and SiD₃⁻, respectively, using a Si–H bond length of 1.552 Å and a H–Si–H angle of 92.7° (which are the average geometrical parameters of *C_s*-SiH₃⁻ in β -ASiH₃^[2,4]). Therefore, the isotope shift of librations around the *C₃*(*z*) axis (*R_z*' rotation) can be estimated as $\nu/\nu^* = 1.414$. The corresponding value for the *R_x*, *R_y* rotations using *I_B* and *I_B*^{*} is very close, $\nu/\nu^* = 1.386$. The bands at 317, 312, 278, 271, 259 and 247 cm⁻¹ in the Raman spectrum of β -KSiD₃ (Table 2) correspond to isotope shifts of 1.381, 1.391, 1.421, 1.391, 1.440 and 1.381, respectively. Thus, a clear assignment of Raman active librations from their

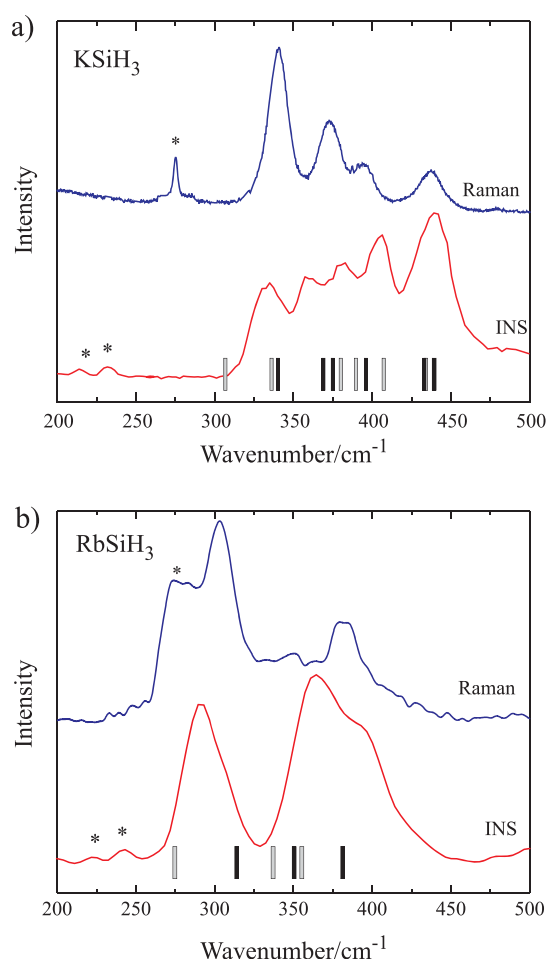


Figure 5. Comparison of Raman spectra (recorded at 100 K) and INS spectra (measured at 4 K) in the spectral range of the libration modes for KSiH_3 (a) and RbSiH_3 (b). Asterisks are explained in the legend of Fig. 3. Bars at the bottom of each spectrum correspond to DFT-calculated values. (Values for RbSiH_3 are scaled.) Black and gray distinguish 'g' and 'u' modes, respectively.

isotope shift is not possible. According to factor group analysis, modes with respect to rotation around the different axes distribute as follows: $R_z = A_g + B_{2g} + B_{1u} + B_{3u}$; $R_x = R_y = B_{1g} + B_{3g} + A_u + B_{2u}$.^[13] That is, the set of four R_x and R_y librations fall in the same symmetry species, and we do not attempt to distinguish them in our mode analysis. According to the DFT calculations, R_x and R_y librations attain higher wavenumbers than the R_z ones (Table 2). The strongest intensity band at 341 cm^{-1} is assigned to the A_g R_z libration. The conclusion $R_x, R_y > R_z$ follows, of course, also from the moments of inertia I_B (I_C) and I_A . According to the aforementioned values, the estimated wavenumber ratio R_x/R_z is ~ 1.060 for SiH_3^- and ~ 1.081 for SiD_3^- . Thus, when averaging the R_x and R_y modes for SiH_3^- (402 cm^{-1}), one expects R_z at 379 cm^{-1} (observed 341 cm^{-1}). (The corresponding DFT-calculated values are at 407 and 351 cm^{-1} , respectively.)

A similar analysis was performed for $\beta\text{-RbSiH}_3/\text{RbSiD}_3$ (Table 3). It is interesting to note that the libration modes of SiH_3^- in RbSiH_3 are strongly red-shifted compared with KSiH_3 . Three Raman bands at 382 , 350 and 303 cm^{-1} were assigned to three 'g' modes and four INS features at 392 , 355 , 302 and 283 cm^{-1} were distributed between 'g' and 'u' modes. For their assignment, we follow again the principle $R_x/R_y > R_z$. The averaged librational wavenumbers

Table 2. Proposed assignment of Raman and INS spectra of KSiH_3 and KSiD_3 in the spectral range of external modes

KSiH_3 Raman	INS ^c	DFT ^e	KSiD_3 Raman	Assignment ^d
438 (170) ^a	443	440 B_{1g}	317 (110)	R_x, R_y
	440	434 B_{2u}		R_x, R_y
434 (150) sh	433 sh	433 B_{3g}	312 (100) sh	R_x, R_y
	405	408 A_u		R_x, R_y
395 (215)	405	397 B_{1g}	278 (300)	R_x, R_y
	400 sh	390 B_{2u}		R_x, R_y
	381	382 A_u		R_x, R_y
377 (300) sh	373	375 B_{2g}	271 (300)	R_z
373 (400)	373	369 B_{3g}	259 (300) sh	R_x, R_y
341 (700)	358	341 A_g	247 (300)	R_z
	335	337 B_{1u}		R_z
	311	307 B_{3u}		R_z
159 (300)	155	156 B_{2g}	146 (480)	Transl SiH_3
151 (630)	152	155 A_g	146 (480)	Transl SiH_3
142 (2250)	142	148 B_{2g}	138 (1120)	Transl SiH_3
	134	132 B_{1u}		Transl SiH_3
	128	127 B_{3u}		Transl SiH_3
128 (3300)	128	127 B_{1g}	125 (1420)	Transl SiH_3
128 (3300)	124	121 A_g	125 (1420)	Transl SiH_3
119 (900) sh		119 B_{3g}	125 (1420)	Transl SiH_3
	117	119 B_{1u}		Transl SiH_3
97 (150)		113 B_{2g}	[94] ^b	Transl K
		111 B_{2u}		Transl SiH_3
		108 B_{3u}		Transl SiH_3
		96 A_u		Transl SiH_3
90 (190)		88 B_{2g}	[88]	Transl K
		87 B_{1u}		Transl K
		81 A_u		Transl K
81 (1700)		75 A_g	80 (1140)	Transl K
77 (1000) sh		75 B_{3g}	77 (700)	Transl K
		67 B_{3u}		Transl K
68 (1500)		67 B_{1g}	67 (500)	Transl K
62 (580) sh ^b		62 A_g	[61]	Transl K

^aIn parentheses are the relative experimental intensities of the Raman lines (counts).

^bIn square brackets are the predicted values of missing experimental wavenumbers. For calculations see text.

^cBand separation was observed on the basis of second derivative spectra.

^d R_z libration mode of rotation around the C_3 symmetry axis, R_x, R_y are rotational motions perpendicular to this axis.

^eDFT calculation using the QUANTUM-ESPRESSO code.^[9]

are 360 and 293 cm^{-1} for R_x, R_y and R_z rotations, respectively. These values are considerably lower compared with KSiH_3 (by $30\text{--}60\text{ cm}^{-1}$). Accordingly, the libration force constants of SiH_3^- ions in $\beta\text{-RbSiH}_3$ are about $15\text{--}30\%$ smaller. In other words, the libration modes of SiH_3^- moieties are less restricted in the $\beta\text{-RbSiH}_3$ structure (or the potential for the torsional vibration is softer). Note that the DFT-calculated wavenumbers for the translations and especially librations of $\beta\text{-RbSiH}_3$ are largely overestimated. This is a consequence of a rather large underestimation in the calculated equilibrium volume (by about 8%), which is attributed to shortcomings of the Rb norm-conserving pseudopotential in describing this system.

Table 3. Proposed assignment of Raman and INS spectra of RbSiH₃ and RbSiD₃ in the spectral range of external modes

RbSiH ₃			RbSiD ₃	Assignment ^c
Raman	INS ^b	DFT ^e	Raman	
382 (200) ^a	382	573 B _g	283 (400)	R _{xx} R _{yy}
	353	530 A _u		R _{xx} R _{yy}
350 (200)	353	521 B _g	253 (170)	R _{xx} R _{yy}
	353	505 A _u		R _{xx} R _{yy}
303 (380)	302	467 A _g	222 (650)	R _z
	281	409 B _u		R _z
139 (330) sh	143	201 A _g	136 (180)	Transl SiH ₃
129 (1150)	132	184 A _g	125 (600)	Transl SiH ₃
		174 B _u		Transl SiH ₃
119 (1620)	115	159 B _g	117 (740)	Transl SiH ₃
		139 A _u		Transl SiH ₃
		134 B _u		Transl SiH ₃
69 (130) sh		74 A _g	[68] ^f	Transl Rb
62 (1550)		70 A _g	61 (1100)	Transl Rb
54 (770)		50 B _g	53 (600)	Transl Rb

^aIn parentheses are the relative experimental intensities of the Raman lines.
^bBand separation was observed on the basis of second derivative spectra.
^cR_z libration mode of rotation around the C₃ symmetry axis, R_{xx}R_{yy} are rotational motions perpendicular to this axis.
^dVery weak shoulder (sh) bands were obtained at 103 and 47 cm⁻¹ based on second derivative features.
^eDFT calculation using the QUANTUM-ESPRESSO code.^[9]
^fIn square brackets are the predicted values of missing experimental wavenumbers.

The order–disorder (β -to- α) transition for RbSiH₃ occurs at 278 K upon heating.^[3] Because of the dynamical disorder of the α phase, it is expected that increasing temperature influences the librations of the β phase decisively. Figure 7 compares INS spectra obtained at 4, 125, 145 and 175 K and the Raman spectrum recorded at 200 K. From the Raman spectrum, it is clear that libration bands are maintained at 200 K. In the 4 K INS spectrum, two broad bands with maxima at about 355 and 280 cm⁻¹ envelope the R_{xx}R_{yy} and R_z modes, respectively. With increasing temperature, the intensity of these bands decreases. Additionally, when going from 4 to 175 K, one notices a red-shift of about 5 and 10 cm⁻¹ for the R_{xx}R_{yy} and R_z bands, respectively. The latter band broadens significantly and develops two maxima with increasing temperature. The softening of the librations due to anharmonicity translates to a force constant lowering of 3–5% (R_{xx}R_{yy}) and 8–10% (R_z), cf. Table 3. The Raman spectrum at 200 K exhibits good agreement with the 175 K INS spectrum. The R_z band at around 275 cm⁻¹, which is assigned to an A_g mode, overlaps with a feature at 270 cm⁻¹ of unknown origin (cf. Fig. 2b). Compared with the Raman spectrum at 100 K (Table 3), the R_z band is red-shifted by more than 25 cm⁻¹, which suggests a stronger anharmonic weakening of the libration force constants than indicated from the INS spectra.

Analysis of translation modes

The translation modes of SiH₃⁻ anions are between 95 and 160 cm⁻¹ for both KSiH₃ and RbSiH₃. K⁺ and Rb⁺ translation modes are in the range 60–100 and 50–70 cm⁻¹ for KSiH₃ and RbSiH₃,

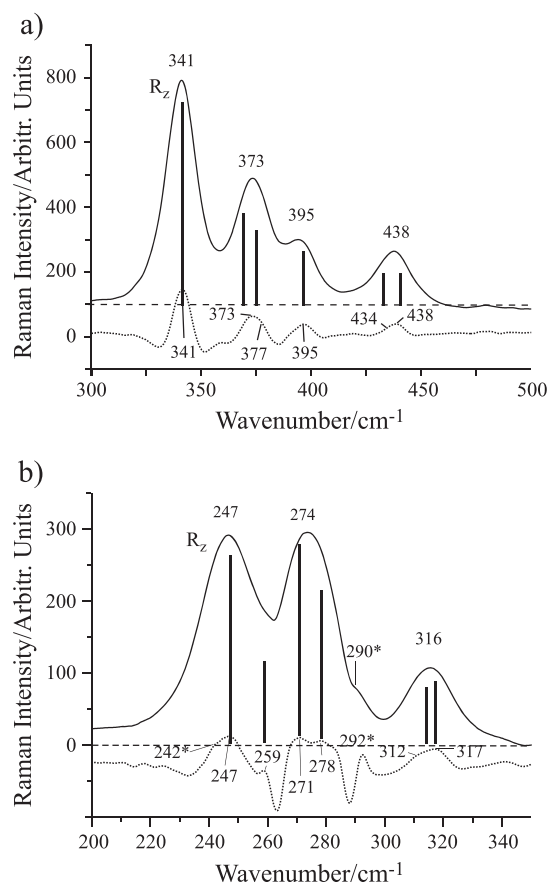


Figure 6. Analysis of Raman-active libration modes of KSiH₃. (a) Comparison of the experimental spectrum at 100 K (upper trace) with DFT-calculated wavenumbers (bars). The second derivative spectrum (multiplied by 100) is shown as lower trace. (b) Raman spectrum of KSiD₃ at 100 K in the spectral range of the libration modes of SiD₃⁻. The bars are calculated modes from applying the isotope shift $v/v^* = (m^*/m)^{1/2}$ to the DFT computed modes for KSiH₃. Asterisks mark an artifact from the subtraction of laser plasma lines.

respectively. Their distribution according to factor group analysis is given in Table 1. Figure 8 depicts the Raman spectra of ASiH₃ and ASiD₃ and INS spectra of ASiH₃ for the spectral region of the

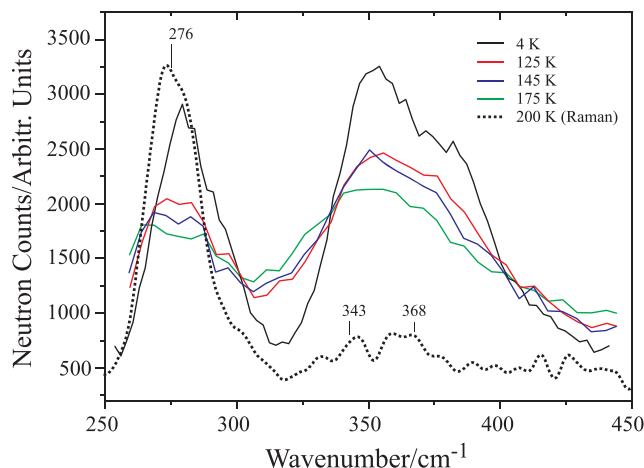


Figure 7. Evolution of the β -RbSiH₃ libration bands with temperature. INS spectra measured at 4, 125, 145 and 175 K are compared with a Raman spectrum recorded at 200 K.

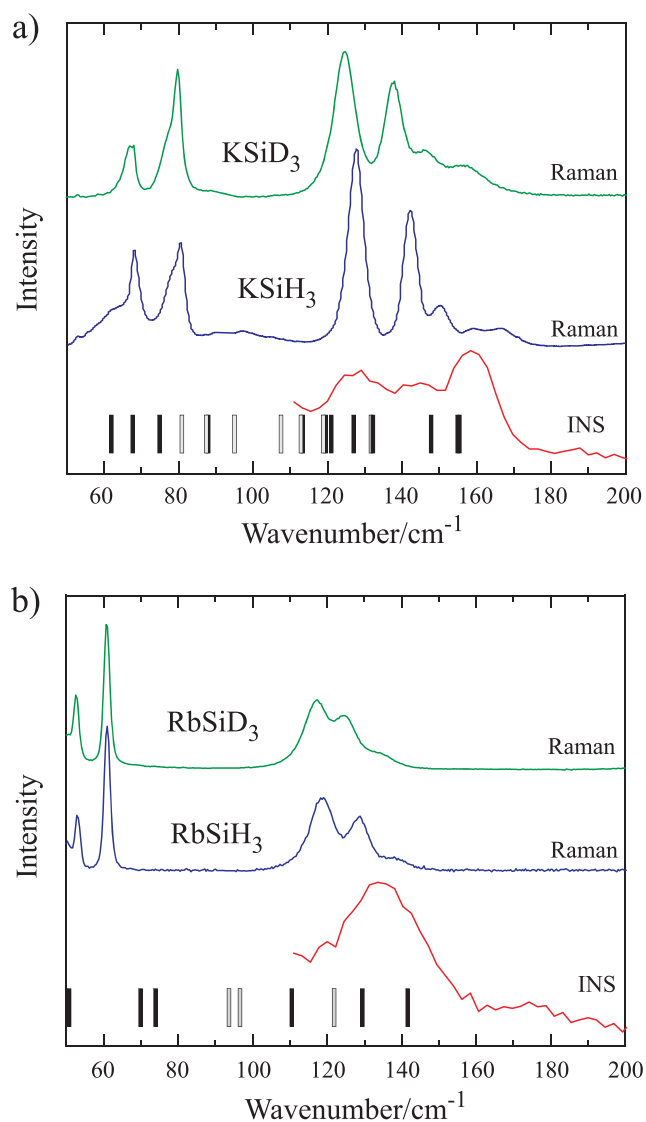


Figure 8. Comparison of Raman spectra (recorded at 100 K) and INS spectra (measured at 4 K) in the spectral range of the translation modes for KSiH₃/KSiD₃ (a) and RbSiH₃/RbSiD₃ (b). Only the Raman spectra show translation modes of cations (below 100 cm⁻¹). Bars at the bottom of each spectrum correspond to DFT-calculated values. (Values for RbSiH₃ are scaled.) Black and gray distinguish 'g' and 'u' modes, respectively. Fig. 1.

translation modes. Their location and assignment is compiled in Tables 2 and 3. The INS spectra were truncated at ~110 cm⁻¹ because at lower wavenumbers they mainly show $\lambda/2$ wavelength contamination from the PG monochromator. We note that the translation modes are preferably analyzed from the Raman spectra where they are present as lines with high intensity. Additionally in the Raman spectra, SiH₃⁻ translations are clearly separated from librations and A⁺ translations.

There are six Raman active SiH₃⁻ translations expected for KSiH₃. Five bands can be discerned in the spectrum shown in Fig. 8a. Those were assigned according to the closest lying DFT calculated wavenumbers (Table 2). Six INS features were obtained by analyzing the second derivative spectrum. For RbSiH₃, three of the six SiH₃⁻ translational modes are Raman active. In the spectrum shown in Fig. 8b, two well-defined lines at 129 and 119 cm⁻¹ and one weak shoulder at 139 cm⁻¹ can be seen. Their assignment is included in Table 3. Band deconvolution of the broad INS feature near

130 cm⁻¹ yielded three components at 143, 132 and 115 cm⁻¹. Similarly to libration modes, the translations of SiH₃⁻ and SiD₃⁻ anions are red-shifted (by 2–5 cm⁻¹) in the Rb salts as compared with the K salts. The translational modes of SiH₃⁻ and SiD₃⁻ anions should follow the mass effect of the square roots of G/G^* (where $G = (1/C^+ + 1/A^-)$), which is 1.025 for the pair KSiH₃ and KSiD₃, and 1.034 for the pair RbSiH₃ and RbSiD₃. These isotope shifts are well supported by the experimental observations (for the K salts, ratios are between 1.024 and 1.029, and for the Rb salts between 1.017 and 1.032).

Translational modes of K⁺ are between 60 and 120 cm⁻¹. From nine optically active cation translations, six are Raman-active (Tables 1 and 2). They all can be extracted from the second derivative Raman spectrum and match the DFT-calculated wavenumbers well (cf. Table 2). For RbSiH₃, there are only three Rb⁺ translations, which are all Raman active. Their red-shift compared with the K⁺ ones is primarily due to the increased mass (Table 3). However, the experimental ratios of $\nu(K)/\nu(Rb)$ of 1.224 and 1.323 are slightly larger than 1.147, which is the value predicted from a simplified G matrix. Thus, the A⁺ translation force constant in RbSiH₃ appears weaker than in KSiH₃. An approximate A⁺ translational force constant (f) can be calculated from the averaged translation modes, 77 and 61 cm⁻¹ for KSiH₃ and RbSiH₃, respectively. We obtain $f(K^+) = 0.061$ N cm⁻¹ and $f(Rb^+) = 0.050$ N cm⁻¹.

Conclusions

The vibrational properties of the recently structurally characterized low-temperature (β) modifications of KSiH₃ and RbSiH₃^[2] were investigated by a combination of Raman spectroscopy and INS. Their crystal structure consists of metal cations and pyramidal SiH₃⁻ ions. The spectra of ASiH₃ represent textbook examples for complex anion salts with clearly separated vibrational regions. Internal modes of SiH₃⁻ are observed in the spectral range 1800–1900 (stretching modes) and 890–1000 cm⁻¹ (bending modes). External modes are observed below 500 cm⁻¹. Specifically, SiH₃⁻ librations are between 300–450 and 270–400 cm⁻¹ for A = K and Rb, respectively, SiH₃⁻ translations are between 95 and 160 cm⁻¹, K⁺ translations are in a range 60–100 cm⁻¹ and Rb⁺ translations in a range 50–70 cm⁻¹. The red-shift of libration modes for A = Rb is associated with a 15–30% reduction of the libration force constants of SiH₃⁻ ions in β -RbSiH₃. This correlates with a lower temperature for the β - α order-disorder phase transition (278 vs 298 K).^[3] The vibrational properties of the silanides ASiH₃ relate remarkably well to those of borohydrides ABH₄ (A = Na–Cs). The ABH₄ systems also adopt an average NaCl structure at room temperature with dynamically disordered BH₄⁻ ions and undergo disorder-order phase transitions upon cooling.^[15] The transition temperatures decrease from 190 to 27 K when going from Na to Cs, which correlates with a red-shift of the libration band.^[15,16] Libration bands for ABH₄ are in a range 270–320 cm⁻¹. This is at somewhat lower wavenumbers compared with ASiH₃ – which again correlates with a lower temperature for the ABH₄ phase transition – yet librations are still well separated from translations.

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