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Mid-infrared spectra of silane dispersed in solid neon

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ABSTRACT

We report mid-infrared spectra of silane dispersed in solid neon at relative concentrations 1:1000 and 1:5000, recorded with spectral resolution 0.15 cm⁻¹. Apart from major lines associated with internal vibrational motions of 28 SiH₄, 29 SiH₄ and 30 SiH₄ in fundamental modes ν_3 and ν_4 , several weak accompanying lines in each region become discernible at the resolution of our experimental measurements, and are tentatively associated with librational motions of silane molecules in the solid neon lattice. The wavenumbers associated with a few overtone and combination modes are also presented.

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1. Introduction

The mid-infrared absorption spectra of small tetrahedral molecules, such as methane and silane, dispersed in solid deposits of atomic noble gases have long been investigated for the purpose of obtaining an understanding of the motions of these molecules within an atomic lattice. Whether rotational motions accompany the vibrations was a matter of interest since the first recorded spectra, for comparison with spectra of H_2O for which essentially free rotation in both neon and argon has evolved as a definitive interpretation.

Our preceding exploration [1] of the infrared spectra of methane dispersed in solid argon or neon yielded no evidence for rotation, but numerous weak lines accompanied a major line associated with each active internal vibrational mode. For such pentatomic tetrahedral molecules of symmetry class T_{d} , only two active fundamental vibrational modes, both triply degenerate, are associated with intense spectral transitions in the mid-infrared region. Whether, or how, this degeneracy contributes to the multiple lines is unknown, but spectra of another tetrahedral molecular species might illuminate the origin of these lines and inspire theoretical investigations. For this reason we have taken

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advantage of the opportunity to record mid-infrared spectra of silane dispersed in solid neon at small concentrations. Here we report our analysis of these spectra and their implications about the motions of silane molecules isolated in solid neon.

2. Experiments

The experiments were performed at the photochemical end-station coupled to beamline BL 21A2 at Taiwan Light Source (TLS) in National Synchrotron Radiation Research Center (NSRRC); the apparatus was described previously [2]. A closed-cycle cryogenic refrigerator (Janis RDK-415) cooled a substrate KBr window to a minimum temperature 3.4 K. The cryo-chamber was evacuated with a turbomolecular pump backed in turn by a scroll pump; the pressure was typically less than 1.3 μ Pa before or after deposition. Infrared absorption spectra in transmission through the sample were recorded with an interferometric spectrometer (Bomem DA8, HgCdTe detector) to cover the spectral range 500–5000 cm⁻¹ at resolution 0.15 cm⁻¹ from 100 scans averaged with Hamming apodization in each case.

Samples of premixed gaseous silane and neon, in proportions 1:1000 or 1:5000, were deposited for 1.5–2 h on a target window at 3.4 K; infrared spectra were recorded after deposition of a sample, on raising the temperature of the sample to 9.0 \pm 0.1 K and on return to 3.4 K. The wavenumbers listed in Tables 1 and S1 were measured at the latter condition. The accuracy and reproducibility of wavenumbers of narrow infrared spectral features were 0.10 cm⁻¹.



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In a manifold designed for the purpose, we prepared gaseous mixtures of silane with Ne with conventional manometric techniques. SiH₄ (nominal purity 99%, Spectra Gases) and Ne (99.9995%, Matheson Gases) were used without further purification for the preparation of gaseous mixtures, but these mixtures were passed through a cold trap maintained at -80 °C before deposition on the KBr substrate.

3. Spectral analysis

Table S1 (in the Supplementary information) presents the wavenumbers of all observed lines in the infrared spectra of the specified samples of silane and neon. A few lines attributed to H₂O and CO₂ as vestigial impurities had minute intensities, not much greater than the noise level, like a few lines attributed to combination and overtone transitions that were barely discernible above the noise level but that were reproduced in all spectra. All other lines are attributed to silane in specified vibrational modes. For the most intense lines associated with fundamental vibrational modes v_3 and v_4 , the presence of isotopic species of Si in natural abundance – ²⁸Si 0.9223, ²⁹Si 0.0467, ³⁰Si 0.0309 - was readily deduced on comparison with the corresponding data for gaseous silane [3,4]. For the overtone or combination bands the signals were too weak for any pertinent lines of ²⁹SiH₄ and ³⁰SiH₄ to be expected to be detected. The relative intensities of the satellite lines due to 29 SiH₄ and 30 SiH₄ are greater than the nominal relative abundance because of severe saturation of the detector at the most intense lines of ²⁸SiH₄. For mode ν_4 , shown in Fig. 1, two lines are clearly visible for each isotopic variant, with mean shifts -0.43 ± 0.07 cm⁻¹ and $+0.06 \pm$ 0.04 cm^{-1} from the gaseous phase, such that the mean separation is

Table 1

Comparison of infrared spectral features of gaseous silane^a and silane in solid neon.

	mode	Gas	Ne	Shift, Δv
²⁸ SiH ₄	ν_4	913.47	913.02, 913.50	-0.45, +0.03
²⁹ SiH ₄		912.18	911.70, 912.23	-0.48, +0.05
³⁰ SiH ₄		910.98	910.61, 911.09	-0.37, +0.11
²⁸ SiH ₄	ν_3	2189.19	2191.89	+2.70
²⁹ SiH ₄		2187.63	2190.35	+2.72
³⁰ SiH ₄		2186.20	2088.94	+2.74
²⁸ SiH ₄	$\nu_2 + \nu_4$ $\nu_3 + \nu_4$ $\nu_2 + \nu_3$ $\nu_1 + \nu_3$	1892 3105 (3168) 4370	1880.15, 1881.11 3100.28, 3100.94 3155.48, 3156.14 4314.74, 4314.92	

^a For gaseous SiH₄ the sources of data are [3,4] and Physical Review (1935) 47, 828.



Fig. 1. Absorption of SiH₄ in solid neon (1:1000) at 3.4 K, after annealing at 9.0 K, in the region of fundamental mode v_4 ; the numbers indicate lines associated with ²⁸SiH₄, ²⁹SiH₄ and ³⁰SiH₄.



Fig. 2. Absorption of SiH₄ in solid neon (1:1000) at 3.4 K, after annealing at 9.0 K, in the region of fundamental mode ν_3 ; the numbers indicate lines associated with ²⁸SiH₄, ²⁹SiH₄ and ³⁰SiH₄.

 0.46 ± 0.02 cm⁻¹; these uncertainties are consistent with the reproducibility of our measurements of wavenumber. The relative intensities of the less intense lines are estimated to be roughly 0.5-0.7 of the more intense lines in each isotopic doublet, when account is taken of the underlying absorption tail due to the main line at 913.47 cm⁻¹. Although Fig. 2 for mode v_3 shows only one distinct line corresponding to each isotopic variant, with mean shift $+2.72 \pm 0.02$ cm⁻¹ from the gaseous phase, the line shapes are somewhat asymmetric, with an indication in each case of a second component, of relative intensity perhaps 0.5–0.7, at ~ 0.1 cm^{-1} greater wavenumber; as this difference is less than the spectral resolution in these experiments, 0.15 cm⁻¹, these values are rough estimates. The intensities of all lines associated with combination or overtone modes, of which the wavenumbers are listed in Tables 1 and S1, are much smaller than for the two fundamental modes that are active in infrared absorption; the listed wavenumbers hence apply strictly to ²⁸SiH₄.

The most remarkable feature of these spectra of silane in solid neon is the presence of two sequences of weak but narrow lines near 916 cm⁻¹, discernible in Fig. 1 and enlarged in Figs. 3 and 4; one sequence appears on either side of the major absorption associated with mode v_4 . These lines become developed on annealing the sample, deposited about 3.4 K, at 9.0 K, with the temperature maintained at that point for 10 min plus the time required to scan the spectrum. These



Fig. 3. Absorption of SiH₄ in solid neon (red, upper curve 1:1000, shifted upward by 0.04 absorbance unit for clarity; black lower curve 1:5000) at 3.4 K, after annealing at 9.0 K, in the region of fundamental mode v_4 below the band centre.



Fig. 4. Absorption of SiH₄ in solid neon (red upper curve 1:1000, shifted upward by 0.04 absorbance unit for clarity; black, lower curve 1:5000) at 3.4 K, after annealing at 9.0 K, in the region of fundamental mode v_4 above the band centre.

lines remain on cooling to 3.4 K; the pattern is nearly unaffected by the temperature change. The same pattern is reproducible both in separate experiments at the same minute proportion of silane in neon, 1:1000, and at an even smaller proportion, 1:5000. The lines are hence an artefact of neither interference phenomena nor the thickness of the sample, but must be an intrinsic property of the molecules of silane isolated in solid neon. Separate from the doublets of the isotopic variants in the intense lines between 910 and 914 cm⁻¹, these two weak sequences of narrow features appear from 900 to 907 cm⁻¹ and from 915 to 919 cm⁻¹. As the central features have wavenumbers nearly identical with the centres of the vibration-rotational bands for v_4 in the gaseous phase, it is tempting to associate these features with internal molecular motions in vibrational modes, i.e. deformation of H₂Si angles, in the free molecule. The weak sequences of lines imply states of the silane molecule in its neon lattice environment involving combinations of the deformational vibration with other motions. The fact that these sequences are independent of both temperature, from 3.4 K to 9.0 K, and concentration under the conditions of great dilution in our experiments, and that the widths of the lines are limited by our spectral resolution, seems to exclude an attribution to aggregates, such as $(SiH_4)_2$, within the neon lattice after the annealing operation.

The sequence of at least six significant lines from 901 to 906 cm⁻¹ implies a sequence of states of spectral terms from 7 to 12 cm^{-1} associated with the ground vibrational state of the SiH₄ molecule, whereas the sequence of at least seven significant lines from 914.5 to 918.5 cm⁻¹ implies a sequence of states between 1 and 5 cm⁻¹ associated with the vibrationally excited state associated with mode v_4 . The differences with the major feature at 913.47 cm^{-1} are +1.38, +1.96, +2.32, +3.04, +3.28, +4.22, +4.76, and -7.17, -7.87, -8.28, -9.47 cm⁻¹. In either case the sequence of states seems to terminate abruptly. What is abundantly clear, consistent with preceding conclusions [5] for silane dispersed in solid argon, is that these subsidiary features are not due to free molecular rotation, for which the lines in P- and Rbranches of a band of a gaseous sample have intervals about 5 cm⁻¹ [3,4]; direct experimental evidence in droplets of helium at 0.37 K proves the existence of free rotation there [6]. A symmetry change [7] is likewise unable to explain these weak satellite lines. A possible explanation is hence merely a librational motion [8], which is a reciprocating motion of a type that occurs when free rotation is restricted or constrained by adjacent atoms in the lattice.

The fewer and broader subsidiary lines beside the principal line associated with mode ν_3 about 2192 cm⁻¹, shown in Fig. 2, are readily attributed to rapid non-radiative decay of the associated molecular states; the widths of the lines in this region are about 0.5 cm⁻¹ or more, in contrast with lines in the ν_4 region of which the width is limited by the



Fig. 5. Infrared absorption [1] of ¹²CH₄ in solid neon (1:1000) at 3.4 K at the centre of the spectral pattern associated with fundamental mode v_4 ; the spectral resolution is 0.04 cm⁻¹.

spectral resolution, 0.15 cm⁻¹. The differences with the major feature at 2191.89 cm⁻¹ are +3.39, +4.17, +7.42, and -4.60, -5.54, -5.77, -6.50 cm⁻¹. These differences are dissimilar to the differences for v_4 above.

A comparison with the mid-infrared spectrum of methane dispersed in solid neon [1] might be meaningful because both methane and silane have tetrahedral molecular structures of quasi-spherical shape and exhibit no rotational fine structure; apart from silane being somewhat larger than methane and having isotopic variants due to ²⁹Si and ³⁰Si that contribute spectral lines near the centres of regions containing lines associated with fundamental modes v_3 and v_4 of ²⁸SiH₄, methane and silane are nearly isomorphous. For ¹²CH₄ the subsidiary structure on either side of the principal line associated with both modes v_3 and v_4 occurs within a much smaller range, about 2 cm⁻¹, than for silane. Similarly to silane, however, the widths of lines associated with mode v_3 are significantly greater than those of lines associated with mode v_4 . Instead of only a doublet with the weaker component at greater wavenumber for mode ν_4 of ²⁸SiH₄, for ¹²CH₄ Fig. 5 [1] shows a sequence of at least five lines of decreasing wavenumber and slowly decreasing intensity; the relative intensities of these lines is insensitive to temperature during an annealing operation. It appears that the differences between the spectra of CH₄ and SiH₄ are much greater than the similarities, despite the comparable molecular structures and similar sizes. How the motions of CH₄ and SiH₄ molecules in a neon lattice differ also depends on the nature of the sites occupied by these molecules.

4. Discussion

In the early days of the recording of mid-infrared spectra, by means of spectrometers with a prism to disperse the radiation, of samples of molecules in solid deposits of noble gases, a single spectral feature or line could generally be simply associated with each active vibrational mode of the dispersed molecules. When spectral resolution was improved through dispersion with a diffraction grating, multiplets became discernible instead of single lines per vibrational mode. In the case of H₂CO this additional structure was attributed to multiple trapping sites in the lattice of the dispersant argon [9]. In other cases [10] it became practicable to associate the subsidiary lines with aggregates of the pertinent molecules, such as dimers or trimers, generally at ratios of order 1:100 - 200 of guest molecules to host atoms. Several lines of SiH₄ dispersed in solid N₂ [10] were attributed to dimers on the basis of their dependence on concentration, but the present Figs. 2 and 3 show little or no effect of concentration at the small ratios 1:1000 and 1:5000 of silane to neon in our experiments. Another previous report [11] of infrared absorption spectra of silane in solid neon specified the

spectral resolution in those experiments to be $0.5-1.0 \text{ cm}^{-1}$; a comparison of those spectra with the present figures (Figs. 1–4) demonstrates that the interpretation of those experiments was hampered by the poor resolution in relation to the width of spectral lines, to the point that some conclusions of that work are questionable. For small molecules such as H₂O, spectral lines were also associated with a nearly free rotation of molecules within a, likely, substitutional site in the lattice, such as we observe for the vestigial H₂O impurity in the present samples. As the accessible spectral resolution increased further, many lines appeared to be associated with a particular vibrational mode, such as for silane in the present work, or for methane [1] previously. In this case no association with transitions between the rotational states of the free molecule is practicable because the intervals between adjacent spectral features are much less than their pertinent rotational intervals.

If the effective size of the guest molecules is larger than the effective size of the atoms that constitute the lattice, the nature of the sites, which can hence not be substitutional, in the atomic lattice occupied by the individual molecules is unknown, and likely unknowable; even after an annealing operation, such as what we practised for our samples of silane in neon, varied conformations of neon atoms around a particular silane molecule likely occur. Under these conditions a meaningful calculation of the subsidiary structure is impracticable. Infrared spectra of a single neon atom associated with a silane molecule in a gaseous sample subjected to an expansion jet [12,13] demonstrate an intermolecular interaction described as a van der Waals complex, but in a neon lattice a silane molecule likely has 12 or more intimately adjacent atoms that are involved in van der Waals interactions and that prevent free molecular rotation.

Our conjecture of librational motions of a guest molecule [8] associated with a particular internal vibrational mode seems the most likely explanation of the several weak lines near the line or lines associated with internal vibrational modes. The small spectral shifts, such as -0.27 or +0.06 cm⁻¹ for v_4 or even +2.72 cm⁻¹ for v_3 of silane in solid neon, from the band centres in the gaseous phase [3,4] would seem to indicate that the surrounding neon atoms affect only slightly the internal molecular vibrational motions. Such circumstances would seem to facilitate various accompanying librational motions.

5. Conclusion

The mid-infrared spectra of silane dispersed in solid neon exhibit several weak lines on either side of each major line associated with internal vibrational modes ν_3 and ν_4 . Librational motions of the molecules constrained by the neon environment are suggested to encompass these effects.

Supplementary data to this article can be found online at https://doi. org/10.1016/j.saa.2019.117838.

Author contributions

J.F. Ogilvie: Conceptualization, Supervision, Formal analysis, Writing.

- S.-L. Chou: Investigation, Method, Formal analysis.
- J.-I. Lo: Investigation, Methodology, Formal analysis.
- Y.-C. Peng: Investigation, Methodology, Formal analysis.
- B.-M. Cheng: Supervision, Resources, Funding acquisition, Writing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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