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Long-path infrared spectra of SiH_4–Ar, –Kr, and –*para*-H_2 van der Waals complexes in the 2190 cm^{-1} region

A.R.W. McKellar *

Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ont., Canada K1A 0R6

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Abstract

Infrared spectra of SiH_4–Ar, SiH_4–Kr, and SiH_4–*para*-H_2 van der Waals molecules are observed in the region of the ν_4 fundamental band of silane by means of long-path (84–180 m), low temperature (95 K) equilibrium gas cell FTIR spectroscopy. The observed spectral features mostly correspond to unresolved Q-branches. For SiH_4–Ar, some of these features are the same as those previously analyzed at high-resolution in a supersonic jet study by Randall et al. [J. Chem. Phys. 100 (1994) 7051], while others are higher K-value transitions that were not populated in the jet. The positions of these new transitions can be predicted very well by the parameters of Randall et al. For SiH_4–Kr, which has not been studied previously, 15 Q-branch feature are assigned and fitted to obtain a preliminary set of parameters. For SiH_4–*para*-H_2 a single prominent feature is observed and assigned as the ${}^{R}Q_0(J)$ branch with A symmetry correlating with the SiH_4 monomer $R(0)$ transition. The SiH_4–Kr and SiH_4–*para*-H_2 results should be useful as a basis for future high-resolution studies of these complexes.

Keywords: infrared spectrum; van der Waals complexes; weakly-bound molecules; silane complexes; intermolecular forces

1. Introduction

Van der Waals complexes containing spherical top molecules pose special challenges for high-resolution spectroscopists due to symmetry and internal rotation effects. The most fundamental of these, the methane—rare gas complexes, have been the subject of a pioneering series of studies by Gisbert Winnewisser and co-workers, starting in 1996 with CH_4–Ar [1–5] and continuing with CH_4–Kr [2,5,6], CH_4–Ne [7], and CH_4–*para*-H_2 [6,8] (*para*-H_2 behaves almost like a rare gas atom in this context—see below). Winewisser's studies of CH_4 containing complexes have focused on the region of the ν_4 fundamental band around 1300 cm^{-1}. There has also been work on infrared spectra of CH_4–Ar accompanying the ν_3 band around 3020 cm^{-1}, starting with unassigned observations [9] and progressing to a detailed comparison of experiment and ab initio theory [10,11]. Interestingly, the microwave spectrum of CH_4–Ar seems to be very difficult to detect, even though a detailed study of CH_4–Kr has been reported [12].

Around 1990, a number of more strongly bound methane complexes were originally studied in the microwave region by Legon and co-workers [13–16] and by Ohshima and Endo [17], including CH_4–HCN, –HF, –HCl, and –HBr. Subsequently, extensive far-infrared [18] and microwave [19] studies of CH_4–H_2O were reported. More recently, other methane-containing van der Waals complexes studied in the infrared or microwave region have included CH_4–CO [20,21], CH_4–OCS [22], and CH_4–O_3 [23].

Of course, methane is not the only spherical top molecule. The effects of partially hindered internal rotation in XY_4-rare gas complexes were first explored in detail by Howard and co-workers in a series of papers on the infrared spectra of SiH_4–Ar [24,25] and SiH_4–Ne [26,27]. It turned out that there is a significantly greater degree of angular anisotropy in the former case than in the latter, so that different angular momentum coupling schemes are appropriate. SiH_4–Ne is closer to the free internal rotation limit, and the Coriolis model developed [26] for it was subsequently applied to CH_4-rare gas complexes [5,7,8], which are also relatively close to this limit.

The present paper reports some long-path equilibrium gas cell studies of SiH_4–Ar, –Kr, and –*para*-H_2 complexes obtained in the 2190 cm^{-1} region of the ν_3 fundamental band of SiH_4, the same region as the earlier supersonic jet

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* Corresponding author. Tel.: +1 613 990 0736; fax: +1 613 991 2648.
E-mail address: robert.mckellar@nrc-cnrc.gc.ca.

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studies [24–27]. Comparing the two experiments (equilibrium gas cell vs. supersonic jet), the former has a much higher rotational temperature (~95 vs. 0.5–5 K) so that many more quantum states of the complex are populated and the spectrum is more dense and complicated. As well, in the equilibrium cell experiment, the spectral resolution is lower, so that individual transitions of the complex are not resolved in the present case, and unwanted interference from monomer (SiH_4) lines in the spectrum is much more serious. Altogether, jet spectra are usually superior and one might ask whether there is any point in the equilibrium cell experiments. The answer is that the results reported here supplement the more powerful supersonic jet results in two ways. First, if the jet spectrum has already been analyzed (as in the case of SiH_4–Ar), then the cell spectrum can add information on previously inaccessible higher energy states. Second, if the jet spectrum has not previously been studied (as in the case of SiH_4–Kr and –*para*-H_2), then the cell spectrum provides a useful starting point for further research. This is especially true since a wide-band survey is easier in the cell experiment (using a Fourier transform spectrometer) than in the jet experiment (using a tunable laser).

2. Experimental details

The spectra were recorded using previously described [9,28] 3.5 m and 5 m low temperature gas cells coupled to a Bomem DA3.002 Fourier transform spectrometer. The cells were cooled to temperatures around 95 K with a Philips PGH-105 cryogenerator system and used for total absorption paths of 84 or 180 m. *para*-H_2 was prepared by liquefying normal hydrogen in the presence of a chrome-alumina catalyst for about 15 min.

Silane is surprisingly volatile, with a vapor pressure of about 1 Torr at 94 K. This is favorable for the present experiment since we want the lowest possible temperature in order to form more van der Waals complexes. Also favorable is the fact that the SiH_4 ν_3 band is rather strong. The experiments were conducted by first recording the spectrum of pure SiH_4 at a pressure of about 0.5 Torr. Then about 5 Torr of Ar, Kr, or *para*-H_2 was added, and the spectrum of the mixture was recorded. As an example, the upper trace in Fig. 1 shows a spectrum of pure SiH_4 at 0.47 Torr and 93 K, while the lower trace shows the same SiH_4 sample after the addition of 4.6 Torr of Ar. This is a small portion of the SiH_4 ν_3 band located between the band origin (2189.19 cm^{-1}) and the $R(0)$ transition (2194.79 cm^{-1}). Even at this temperature and pressure, the pure SiH_4 spectrum already shows a huge number of silane monomer lines, ranging from weak to extremely strong and completely saturated. The addition of Ar causes a large drop in overall intensity, mostly due to the effect of additional pressure broadening in the wings of the stronger lines in this region.

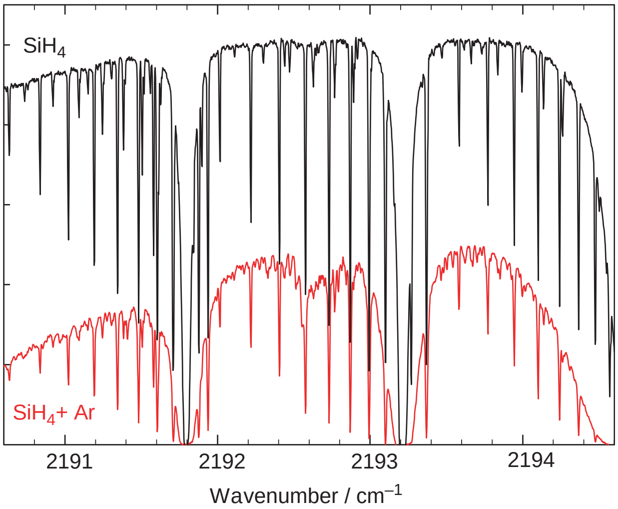

Fig. 1. Raw spectra of SiH_4 (upper trace) and SiH_4+Ar (lower trace) near the origin of the ν_3 fundamental band of SiH_4. SiH_4 pressure = 0.47 Torr; Ar pressure = 4.6 Torr; temperature = 93 K; path = 180 m; spectral resolution = 0.005 cm^{-1} (apodized).

Rather than search for features due to SiH_4–Ar complexes directly in these raw spectra, we first ‘flattened’ each spectrum by drawing (on the computer) a local background with which to ratio the spectrum. These backgrounds were, of course, artificial and somewhat arbitrary, but they could generally be drawn quite reliably except in regions of low intensity near very strong absorption lines. The ‘flattening’ process results in spectra plotted in terms of a sort of ‘local transmittance,’ such as those shown for SiH_4–Ar in Fig. 2.

3. SiH_4–Ar results

In searching through Fig. 2 for features due to SiH_4–Ar complexes, we are looking for shaded regions between the upper (pure SiH_4) and lower (SiH_4+Ar) traces of ‘local transmittance.’ A clear example of such a feature is found in the upper panel of Fig. 2 at about 2174.11 cm^{-1}. Each very strong SiH_4 line tends to have a shaded region around it, but these are not real SiH_4–Ar features—they are simply due to the breakdown of the ‘flattening’ process when the real transmittance become small near a strong line. Those features that we judged to be ‘real’ ones due to SiH_4–Ar complexes are indicated by arrows in Fig. 2. Some of these are fairly obvious and localized, like 2174.11 or 2198.08 cm^{-1}. Another, around 2192.6 cm^{-1} is quite obvious and strong, but not so localized. Others, which may not be so evident in Fig. 2 were judged to be real upon close examination. The observed positions of these features are listed in the first column of Table 1.

The most likely sources of detectable features in our partly-resolved spectrum are regions where many individual vibration–rotation transitions occur close together; that is Q-branches (and, possibly, P- or R-branch heads). We expect Q-branches from perpendicular subbands ($\Delta K = \pm 1$), as well as from parallel subbands ($\Delta K = 0$) with $K > 0$. The infrared spectrum of SiH_4–Ar has been studied at high-resolution in a supersonic jet by Randall et al. [25]. Not surprisingly, we find that three of our observed features correspond closely to three of their reported perpendicular subband origins, as shown in the second column of Table 1. These previous values [25] are, of course, more accurate than ours since they are based on high-resolution line-by-line fits. Note that the origins given