High resolution infrared spectrum and global analysis of v_5, v_{12}, and $v_{12} + v_6 - v_6$ in CH$_3$SiH$_3$

L. Borvayeh [a], I. Ozier [b,*], A. Bauder [c], N. Moazzen-Ahmadi [a]

[a] Department of Physics and Astronomy, University of Calgary, 2500 University Drive NW, Calgary, Alta., Canada T2N 1N4
[b] Department of Physics and Astronomy, University of British Columbia, 6224 Agricultural Road, Vancouver, BC, Canada V6T 1Z1
[c] Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8093 Zürich, Switzerland

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ABSTRACT

The vibration–torsion–rotation spectrum of CH$_3$SiH$_3$ has been measured from 470 to 725 cm^{-1} at near-Doppler resolution. The full-width at half - maximum of the lines observed near 600 cm^{-1} was 0.0011 cm^{-1}. The spectra were obtained using a Bruker IFS 125 HR Fourier transform spectrometer with the broadband source radiation being supplied from the synchrotron emission of the storage ring at the Canadian Light Source. Three vibrational bands were investigated: the lowest lying perpendicular fundamental v_{12} centred near 524 cm^{-1}, the lowest lying parallel fundamental v_5 near 703 cm^{-1}, and the torsional hot band $v_{12} + v_6 - v_6$ near 534 cm^{-1}. For v_{12} and v_5, the resolution and sensitivity are much improved over those in earlier studies, with many of the torsional multiplets now being resolved even in the cases where the upper levels are unperturbed. The primary motivation for the present work was the hot band, here reported for the first time, where the dependence of the silyl rock in v_{12} on the torsional motion is much more pronounced. In addition, for the vibrational ground state (gs), two "forbidden" high torsional overtones $v_6 = 3 \leftarrow 0$ and $5 \leftarrow 0$ have been observed that become allowed through resonant mixing of the upper states with v_{12} and v_5, respectively. In each case, two (K, σ) series have been measured where the mixing is largest. Here $\sigma = 0, 1, -1$ labels the torsional sub-levels. Using the Fourier transform waveguide spectrometer at E. T. H., the three σ-components of the ($J = 1 \leftarrow 0$) transition in $v_{12} + v_6$ were observed, and a series of direct l-doubling transitions in $v_{12} + v_6$ were measured for $\sigma = 0$. In a global fit, all the new data have been analysed along with the frequencies for other transitions obtained in earlier investigations. The analysis takes into account the relevant interactions among the torsional stacks of levels in the gs, v_{12}, and v_5. These include the previously known (gs, v_{12}) Coriolis-like and (gs, v_5) Fermi-like interactions along with a higher order (v_{12}, v_5) Coriolis-like coupling introduced here. This last is responsible for the strong perturbation of the v_5 series with $K = 10, 11$, and 12, and of the corresponding hot band series. A good fit to 9282 frequencies including 7942 new measurements was obtained both with the Free Rotor model in which the torsion is classified as a rotation, and with the High Barrier model in which the torsion is classified as a vibration. The Hamiltonian is discussed with emphasis on the new terms required for treating $v_{12} + v_6 - v_6$.

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1. Introduction

Vibration–torsion–rotation interactions in symmetric tops with a single torsional degree of freedom have been studied previously in detail [1]. The current work addresses two new challenges concerning the Hamiltonian for an excited degenerate mode. The first deals with the matrix elements diagonal in the vibrational quantum numbers and how these must be modified as excited torsional levels in the degenerate state are added to the analysis. The second challenge deals with the torsion-mediated interactions between the lowest degenerate and non-degenerate modes. Previous work

has shown that Coriolis and Fermi interactions between stacks of torsional levels in different vibration modes can create highly mixed gateway states, which can greatly accelerate intramolecular vibrational energy redistribution. By investigating the vibration–torsion–rotation Hamiltonian in levels with both skeletal and torsional quanta excited, further insight can be obtained into the energy redistribution pathways and into large amplitude motion in general.

Methyl silane has become the prototype polar molecule in this class. The energy level system previously probed for CH$_3$SiH$_3$ is shown schematically in Fig. 1, along with the potential hindering the internal rotation. This potential has three equivalent wells, but only one is shown for each skeletal vibrational state in order to simplify the diagram. For each value of the principal torsional
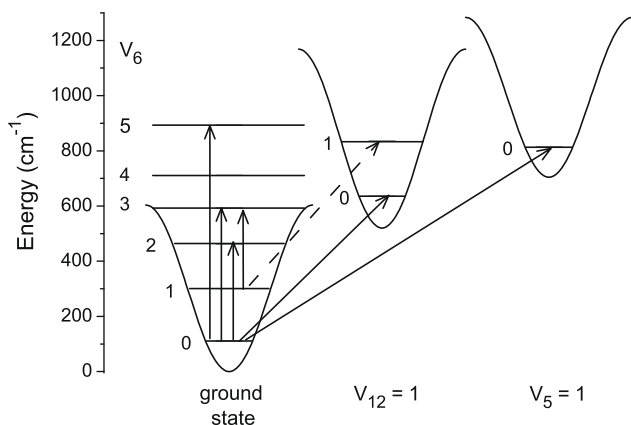
* Corresponding author. Fax: +1 604 822 5324.
  E-mail address: iozier@phas.ubc.ca (I. Ozier).

Fig. 1. Hindering potential and energy level diagram for the ground state (gs), v_{12}, and v_5. For each vibrational state, the potential has three equivalent wells, but only one is shown for simplicity. The energy levels are shown for $J = 3$, $G = 2$, $\sigma = 0$. For v_{12}, the l_{12}-dependence of the energy has been suppressed, again for simplicity. Only the levels of the torsional mode v_6 of direct interest here have been included. The arrows indicate the infrared bands included in the data set. In the present work, the hot band $v_{12} + v_6 - v_6$ (dashed diagonal arrow) has been reported for the first time at high resolution. The fundamentals v_{12} and v_5 (solid diagonal arrows) have been re-measured with higher resolution and sensitivity, as have been the perturbation-allowed gs torsional bands $3v_6$ and $5v_6$ (vertical arrows).

quantum number v_6, there are three torsional sub-levels labelled with the quantum number $\sigma = -1, 0, +1$. However, for simplicity, Fig. 1 shows the energies only for $\sigma = 0$. As an example, the states with $(J = 3, G = 2)$ have been selected, where $G = K - l_{12}$. The infrared components of the previously existing data set are indicated by the solid arrows in Fig. 1. Not surprisingly, most of the previous measurements have been on the lower energy states [1]. In the ground vibrational state (gs), internal rotor levels with $v_6 \leqslant 5$ have been investigated, as indicated by the vertical arrows in Fig. 1. The perpendicular fundamental v_{12} near 524 cm^{-1} has been measured for $v_6 = 0$, along with the parallel fundamental v_5 near 703 cm^{-1}, again for $v_6 = 0$; see the solid diagonal arrows in Fig. 1. The highest resolution used in these earlier infrared studies is 0.0045 cm^{-1}.

In the present work, the spectral region from 470 to 725 cm^{-1} has been measured with Fourier transform infrared spectroscopy at near Doppler-limited resolution. In order to detect weak lines, a long absorption path of 8 m was used. To improve the sensitivity, the source radiation was provided by the broadband emission from the third-generation synchrotron at the Canadian Light Source at the University of Saskatchewan. The v_{12} and v_5 bands have been re-measured. In each case, the new data extend the maximum value of J from 25 to 35 and the maximum value of G from 9 to 15. Two new perturbation allowed torsional series in the gs have been observed involving large changes in v_6. For $v_6 = 3 \leftarrow 0$, the series with $(K, \sigma) = (8, 0)$ was detected; this becomes allowed through the Coriolis-like resonance between $(v_{12} = 0, l_{12} = 0, v_6 = 3)$ and $(v_{12} = 1, l_{12} = -1, v_6 = 0)$. For $v_6 = 5 \leftarrow 0$, the series with $(K, \sigma) = (2, -1)$ has been measured; this becomes allowed through the Fermi-like resonance between $(v_5 = 0, v_6 = 5)$ and $(v_5 = 1, v_6 = 0)$. However, the initial motivation for the current investigation was to obtain the hot band $v_{12} + v_6 - v_6$ centred near *534* cm^{-1}, illustrated by the dashed arrow in Fig. 1. In previous work on v_5 [2], a near degeneracy was detected between $(v_6 = 0)$ levels in v_5 and $(v_6 = 1)$ levels in v_{12} for the K sub-bands of v_5 with $K = 10, 11, 12$. The v_5 data with $K \geqslant 10$ could not be properly analysed primarily because no information on the hot band $v_{12} + v_6 - v_6$ was then available. Using the present measurements, v_5 lines with $(K, \sigma) = (11, +1)$ were identified on both sides of a level crossing which occurs with the J-value in v_5 between *29* and *30*. The leading term in the resonant interaction is shown to be the tor-

sion-mediated Coriolis-like coupling. In addition to the infrared study, the Fourier transform microwave investigation at the Eidgenössische Technische Hochschule reported in Ref. [3] has been extended. The three σ-components of the $(J = 1 \leftarrow 0)$ transition in the level $v_{12} + v_6$ have been measured, along with nine direct l-doubling transitions for $\sigma = 0$ in $v_{12} + v_6$. These microwave lines were observed during the earlier study, but could not be identified at that time. With the current model, these 12 frequencies could be conclusively identified with ease, thus providing an excellent check on the fits obtained.

The data analysis was carried out using two models that differed in the treatment of the Hamiltonian coupling the torsional stacks of levels in non-degenerate and degenerate skeletal vibrational states. In the High Barrier (HB) treatment [1,4] of the interaction terms $\mathbf{H}^{v_6}(gs, v_{12})$ and $\mathbf{H}^{v_6}(v_5, v_{12})$, the torsional motion is classified as a vibration. In the Free Rotor (FR) approach [1,5], the torsional motion is classified as a rotation. Although some systematic effects remain, a good fit was obtained in both cases. The quality of the fit was better for the FR model, but the differences in the fit characteristics were not large enough to draw any definite conclusions about the relative merits of the HB and FR treatments.

Two closely related studies have been recently reported for different isotopomers of ethane. For CH$_3$CD$_3$ [6], a three state analysis of the torsional stacks of levels in the gs, v_{12}, and v_5 has been carried out. No data on the hot band $v_{12} + v_6 - v_6$ were available. However, a local resonance was observed in the $(K = 7)$ lines of v_5. This was shown to arise from a $(\Delta G = \pm 3)$ interaction between $(K = 7)$ levels in $(v_5 = 1, v_6 = 0)$ and $(K = 5)$ levels in $(v_{12} = 1, l_{12} = 1, v_6 = 1)$. Associated perturbation-allowed transitions were identified in the combination band $v_{12} + v_6$, but not included in the fit. For CH$_3$CH$_3$, the symmetry is higher, both simplifying the Hamiltonian and restricting the data set to infrared transitions. A four state analysis was carried out [7,8], involving the gs and one non-degenerate mode v_3, as well as two degenerate modes v_9 and v_{12}. Four resonant interactions between torsional stacks in the different skeletal modes were identified, including two that involve levels in v_9 with one quantum of torsion v_4 excited.

2. Theoretical background

The methods used to model the frequencies have been reviewed recently [1]. The formation of the Hamiltonian operator, the form of the free rotor basis functions, and the derivation of the matrix elements have been discussed in detail, along with the notation and the calculational procedures used. Here only a brief summary will be given discussing the new terms which have been introduced into the Hamiltonian and specifying the options selected in the theoretical treatment. A three state $(gs/v_{12}/v_5)$ analysis is developed using the principal axis method (PAM) [9], but the hybrid model [1,10] is adopted in which the PAM torsional angular momentum $\mathbf{J}_\alpha$ is replaced by its hybrid counterpart $\tilde{\mathbf{J}}_\alpha \equiv (\mathbf{J}_\alpha - \rho \mathbf{J}_z)$ simply by re-grouping the operators. In lowest order, the structural parameter ρ is the ratio of the moment of inertia about the symmetry axis of the methyl top to the corresponding moment of the entire molecule. The Hamiltonian matrix is diagonalized using the one-step procedure [1,2].

The effective vibration–torsion–rotation Hamiltonian $\mathbf{H}^{eff}_{VTR}$ for the torsional stacks of levels in the gs, v_{12}, and v_5 is given in Table 1. The index i listed in the first column labels each operator $\mathcal{O}_i$ and its associated molecular parameter X_i (or ΔX_i). The rows in Table 1 are divided into six groups. The first three characterize the matrix elements diagonal in v_{12} and v_5, while the last three groups characterize the matrix elements that couple one torsional stack to another. To construct $\mathbf{H}^{eff}_{VTR}$, all the terms $X_i \mathcal{O}_i$ are formed and summed over i, with three types of special cases being taken into