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Giant *K*-doubling and in-plane/out-of-plane mixing in the asymmetric methyl-bending bands of CH_3SH

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ABSTRACT

In analyzing high-resolution spectra of the methyl-deformation bands of methyl mercaptan recorded at the Canadian Light Source synchrotron, we have encountered interesting interactions between certain levels of the ν_4 in-plane asymmetric CH_3-bending mode and its ν_{10} out-of-plane bending partner below. The origin of the $K = 0A$ ν_4 substate is just 0.2 cm^{-1} higher than that of the $K = 2A$ ν_{10} substate, while the $K = 0E$ ν_4 origin is only 0.035 cm^{-1} below the $K = 2E$ ν_{10} origin. These very close accidental near-degeneracies lead to substantial perturbations in the spectrum. For the former, the A^+/A^- asymmetry *K*-doublet coupling rules are such that the A^- component of the $2A$ ν_{10} doublet interacts and mixes strongly with the $0A^+$ ν_4 levels whereas the $2A^+$ component is unaffected. The $2A^-$ levels are pushed rapidly downwards by the coupling creating an extremely large apparent $K = 2A$ asymmetry splitting. We call this "giant *K*-doubling" by analogy with a comparable phenomenon seen for methanol. The $0A^+$ ν_4 state, in turn, is perturbed upward and passes through the descending $K = 1A^+$ ν_4 state between $J = 22$ and 23, leading to distinct local perturbations near the level-crossing. The $0E$ ν_4 and $2E$ ν_{10} coupling produces a correspondingly strong repulsion and mixing between those two substates, and gives rise to a forbidden $K = 0 \leftarrow 3E$ intermode sub-band in the spectrum via intensity borrowing.

1. Introduction

Methyl mercaptan is an important sulfur-bearing species, both in the terrestrial environment and in the interstellar medium. In our current program, we are conducting some of the first high-resolution studies of the infrared spectrum, employing synchrotron radiation at the Canadian Light Source in order to explore the torsion-rotation structure of the vibrational fundamentals. The most detailed previous investigation of the CH_3SH gas-phase spectrum was published nearly 50 years ago at moderate resolution by May and Page, who reliably established all of the vibrational band assignments [1]. Since then, there have been remarkably few works on the CH_3SH spectrum, with only the C-S stretching band studied at high resolution [2,3], some investigation of short regions of the C-H and S-H stretching bands for acquisition of spectral fingerprints to serve as biomarkers [4,5], and a recent study in the solid phase for astrophysical application [6]. In contrast, the ground-state microwave, THz and FIR spectra [7] have been extensively analyzed, providing a solid base of ground-state energies as foundation for assignment of the IR synchrotron spectra under investigation in our program.

In this paper we focus on unusual intermode coupling observed towards the low-*K* central region of the CH_3SH asymmetric methyl-bending fundamental bands. May and Page reported two strongly overlapped bands at 1453 and 1444 cm^{-1} in this region, and attributed them to the ν_4 in-plane A' and ν_{10} out-of-plane A'' methyl deformation modes, respectively, on the basis of the band profiles and intensities. At high resolution, we have found interesting perturbed behaviour for certain of the low-*K* sub-bands that we have traced to coupling between the in-plane and out-of-plane modes. Most notable is a "giant *K*-doubling" of the nominally $K = 2A$ ν_{10} substate, analogous in a number of respects to a similar phenomenon seen previously for CH_3OH [8]. Here, we describe our analysis, discuss the CH_3-bending term values and substate origin energies, and consider the form and magnitudes of the perturbations.

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2. Experimental aspects

For this study, synchrotron radiation at the Canadian Light Source Far-Infrared Beamline was employed to record the Fourier transform spectrum of CH_3SH in the range 1200–1700 cm^{-1}. The Far-IR beamline and its capabilities have been previously described elsewhere [9,10]. Briefly, the synchrotron infrared radiation is obtained from the bending magnet via a slotted mirror and focused through a diamond window. The light is then directed into the sample compartment of a Bruker IFS 125HR spectrometer via a 1.15 mm aperture and KBr beam splitter, using a series of flat and elliptical mirrors. In the present work, the bright infrared light, modulated by the interferometer, was then aligned through a 2-m multi-pass cell set to 72-m path containing 0.04 Torr of CH_3SH at 220.2 K, and finally recorded by a helium-cooled Ge:Cu detector. The reported spectrum is an average of 295 scans recorded at a resolution of 0.00096 cm^{-1} and a sampling rate of 80 kHz. Peakfinding was performed using the Bruker OPUS software. Wavenumbers retrieved for water lines in the spectrum were generally consistent with standard values to the order of ±0.0001 cm^{-1} with random scatter, hence further calibration was not considered necessary.

3. Notation and energy structure

The CH_3SH vibration-torsion-rotation energy levels can be labeled with a set of quantum numbers as $E(v_t\ TS\ K, J)_v$, where v_t is the torsional state, *TS* represents the *A* or *E* torsional symmetry species, and *K* is the axial *a*-projection of the overall rotational angular momentum *J*. The subscript *v* indicates the vibrational state and we will be concerned here with the ν_4 in-plane and ν_{10} out-of-plane asymmetric methyl-bending modes, which will also be denoted where convenient by the short-hand *ip* and *op*. Levels of *A* torsional symmetry with $K > 0$ can be split by molecular asymmetry, giving *K*-doublets with components labeled as A^+ or A^-. For *E* torsional symmetry with $|K| > 0$, we use a signed *K* quantum number to distinguish the two classes of *E* levels that are often alternatively denoted as E_1 ($K > 0$) or E_2 ($K < 0$). The basic terms in the molecular energy levels in a form relevant to the present work can be expressed as

$$E(v_t\ TS\ K,J)_v = E_{vib} + E_{tor}(v_t\ TS\ K)_v + B_{eff}\ J(J+1) + (A-B)_{eff}\ K^2 \quad (1)$$

where E_{vib} is the vibrational energy, E_{tor} is the torsional energy and B_{eff} and $(A–B)_{eff}$ are effective rotational constants for that vibrational state.

4. Spectral assignments and term values

Analysis and assignment of our spectra in the regions of the methyl-rocking and methyl-bending bands as well as the higher S-H and C-H stretching regions is ongoing, and these studies will be reported more fully in the near future. An interesting and unexpected feature of the analysis so far is that the pairs of states of *E* vibrational parentage, i.e. the methyl rocks and asymmetric bends and the asymmetric C-H stretches, tend to resemble the *l*-doublet pairs of degenerate perpendicular modes of a C_{3v} symmetric top, for which the $l = +1$ and $l = -1$ components would diverge linearly via *a*-type Coriolis coupling and the selection rule for angular momentum along the symmetry axis would be $\Delta(K - l) = 0, \pm3, \pm6 \ldots$ with only $\Delta K = \Delta l$ transitions being strongly allowed for the fundamental bands. In the present case, both $\Delta K = +1$ and $\Delta K = -1$ transitions are seen for each of the asymmetric methyl-bending bands but with a marked difference in intensity, with the $(K + 1) \leftarrow K$ sub-bands being much stronger than $(K - 1) \leftarrow K$ for the in-plane ν_4 mode ("$l = +1$") and the reverse for the ν_{10} mode ("$l = -1$").

The asymmetric methyl bending spectrum is complicated in the central low-*K* region where the two modes overlap, but confident assignments were possible through numerous ground-state combination difference (GSCD) relations. Initially, Loomis-Wood plots were used to locate series of related lines in the *P* and *R* branches, while a number of *Q* sub-branches were conspicuous in the spectrum as illustrated in the example of Fig. 1. These were entered into wavenumber difference tables in Excel spreadsheets, which permitted rapid extension of the sub-branches to higher *J*. With an "educated" guess for the assignment and *J*-numbering of a line series, the corresponding ground-state energies could be inserted into the spreadsheet, with GSCD columns then automatically generating predictions of related sub-branches and thereby quickly confirming or ruling out the proposed identification. Once assigned, a column of term values for the upper CH_3-bending substate was also generated by adding the appropriate ground-state energies to the observed wavenumbers, with the ground-state $J = K = 0$ A^+ $v_t = 0$ level taken as the zero reference for all states. For assigned sub-bands, the energy defects of closed combination loops were generally well within ±0.0003 cm^{-1}, apart from loops containing blended lines, hence the term values should be accurate to the order of ±0.0002 cm^{-1}. For each substate, the term values were fitted to a polynomial in powers of $J(J + 1)$, employing the Excel trendline function, in order to determine the hypothetical $J = 0$ substate origins. The resulting origins are presented in Table 1.

With the above approach, all of the low-*K* $v_t = 0$ sub-bands for the *A* and *E* torsional species of both in-plane and out-of-plane

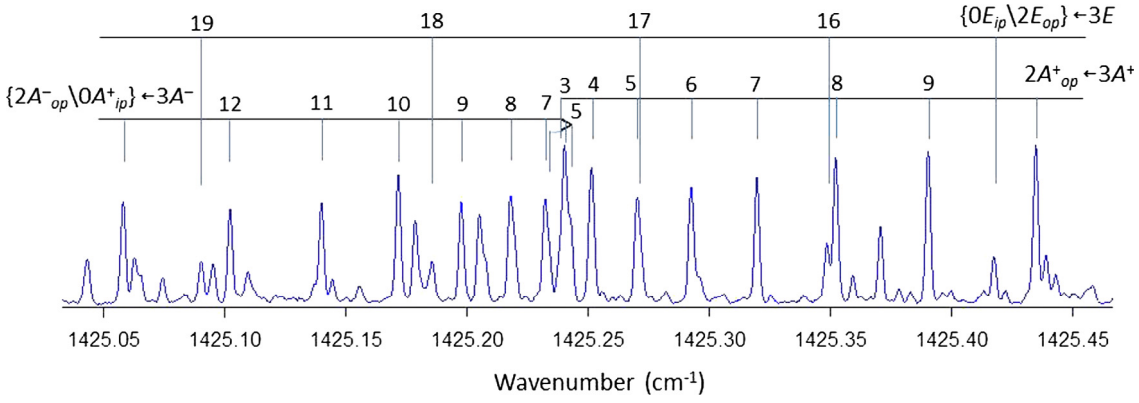

Fig. 1. *Q* branches in the asymmetric CH_3-bending spectrum of CH_3SH. Individual lines are labeled by *J*, and the transition levels are labeled by *K* and the torsional *A* or *E* symmetry. The *ip* and *op* subscripts denote the in-plane or out-of-plane CH_3 bending mode. The two upper states shown with braces are combinations of near-degenerate substates mixed by intermode coupling.

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