Journal of Quantitative Spectroscopy & Radiative Transfer 129 (2013) 316–323

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt


Journal of
Quantitative
Spectroscopy &
Radiative
Transfer

The $\nu_{12}+\nu_6-\nu_6$ and $\nu_{11}-\nu_{12}$ bands of $^{12}CH_3{}^{13}CH_3$: A frequency analysis including data from the four lowest vibrational states

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ARTICLE INFO

Article history:
Received 6 April 2013
Received in revised form
7 July 2013
Accepted 9 July 2013
Available online 25 July 2013

Keywords:
Ethane
Infrared spectra
Vibrational bands
Coriolis coupling
Fermi coupling
Planetary data analysis

ABSTRACT

High-resolution infrared spectra of the $\nu_{12}+\nu_6-\nu_6$ (around 820 cm^{-1}) and $\nu_{11}-\nu_{12}$ (around 370 cm^{-1}) bands of $^{12}CH_3{}^{13}CH_3$ were measured. Frequencies from these bands together with data from the ν_{12} and ν_5 fundamentals and the torsional bands were analyzed in a 4-state fit to determine the torsion mediated Coriolis and Fermi interactions. As compared to normal ethane this lower symmetry isotopologue shows more complicated vibrational couplings. The combined data set includes more than 6800 frequencies and was fitted to within experimental accuracy using a 78-parameter Hamiltonian. The first determination of molecular parameters for the ν_{11} state of $^{12}CH_3{}^{13}CH_3$ has been made and using this Hamiltonian we provide lower state energies and partition functions between 100 and 320 K in increment of 10 K for planetary data analysis.

1. Introduction

Methane is an important constituent of the atmosphere of giant planets and their moons. Methane decomposition in the upper atmosphere initiates a series of reactions producing ethane and other compounds. Polymerization of some of these compounds leads to various materials around which ethane and other gases apparently condense and then fall to the surface. This methane cycle in planetary atmospheres is not completely understood and one important question that needs to be answered is how methane is continually replenished in these atmospheres.

Ethane is the second most abundant hydrocarbon after methane in planetary atmospheres. It plays an important role as a tracer for constraining the models for chemical and dynamical processes [1–7] . Photochemistry of CH_4 in the upper atmosphere converts it to more complex hydrocarbons, including ethane (C_2H_6), acetylene (C_2H_2), propane (C_3H_8) and benzene (C_6H_6). Voyager and Cassini have measured spectra of ethane in planetary atmospheres. The very prominent ν_9 vibrational fundamental around 820 cm^{-1} and the band system around 1400 cm^{-1} are mostly used for abundance measurements. The band systems in ethane are indeed very wide and affect the neighboring spectral regions. For example, the spectrum of C_2H_2 occurring in the spectral region between 720 and 760 cm^{-1} overlaps with that of ethane and cannot be properly analyzed until a thorough understanding of line parameters for ethane is obtained. Laboratory measurements of ethane and $^{12}CH_3{}^{13}CH_3$, which also has bands in the same spectral regions, are therefore required to interpret planetary spectra.

We have carried out a systematic study of the four lowest vibrational states of ethane. Here, we have reported several frequency studies for ethane including data from ν_4 (torsional fundamental), $2\nu_4-\nu_4$ (first torsional hot band), $3\nu_4$ (a torsional overtone), ν_9 (IR active lowest degenerate fundamental), ν_3(Raman active lowest non-degenerate fundamental), $\nu_9+\nu_4-\nu_4$ (the hot band associated with the ν_9 fundamental) and the difference band $\nu_{12}-\nu_9$ [8–12]. In this paper, we present an analogous 4-state frequency analysis for $^{12}CH_3{}^{13}CH_3$ by adding frequencies from

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http://dx.doi.org/10.1016/j.jqsrt.2013.07.009

$\nu_{12}+\nu_6-\nu_6$ and $\nu_{11}-\nu_{12}$ bands to two previously reported studies which included data from ν_6 (torsional fundamental), $2\nu_6-\nu_6$ (first torsional hot band), $3\nu_6$ (a torsional overtone), ν_{12} (IR active lowest degenerate fundamental) and ν_5 (Raman active lowest non-degenerate fundamental) bands [13,14] . Although, the bands studied in [13,14] bear a close resemblance to those of normal ethane, $\nu_{12}+\nu_6-\nu_6$ and $\nu_{11}-\nu_{12}$ show significant differences with their analogs in ethane. For example, some rotational series in $(\nu_{11}=1,\nu_6=0)$ are perturbed by the torsional stack of ground vibrational state (gs) and $\nu_{12}+\nu_6-\nu_6$ exhibits torsional tripling of transitions (analogous to methyl silane) rather than doubling as is the case for normal ethane. These differences can be attributed to lower symmetry of $^{12}CH_3{}^{13}CH_3$ and the fact that ρ, which is the ratio of the moment of inertia of $^{12}CH_3$ to the moment of inertia of $^{12}CH_3{}^{13}CH_3$ about the symmetry axis, is not exactly 1/2.

2. Spectra and analysis

2.1. Torsional bands

The experimental details for the far-infrared torsional spectrum of $^{12}CH_3{}^{13}CH_3$ are given in Ref. [13]. The torsional fundamental and the torsional hot band show doubling of transitions due to internal rotation and have close resemblance to their counterparts in normal ethane. This is because for $v_6=0$, 1, and 2 two of the three torsional sublevels are accidently degenerate. The degenerate levels are $\sigma=\pm1$ with $K=3m$, $\sigma=0$ and +1 with $K=3m+1$, or $\sigma=0$ and -1 with $K=3m+2$, where the integer $m\geq0$. In ethane, on the other hand, $\sigma=0$, 1, 2 and 3, but only $K+\sigma=$ even are populated.

Frequencies from the torsional bands can be analyzed using a 1-state Hamiltonian whose parameters would be effective and contain nonresonant contributions from Coriolis and Fermi couplings with other vibrational states. In such analysis ρ can be fixed at 1/2. Arrows a and b in Fig. 1 represent data from the torsional fundamental and the first torsional hot band, respectively. Fig. 1 also illustrates the hindering potential for the gs, ν_{12}, ν_5 and ν_{11} fundamentals. For each vibrational state, torsional levels labeled by v_6 are shown for $J=K=0$.

The torsion–rotation parameters for the 1-state analysis are also given in Ref. [13]. A two step program whose detailed description is given in Ref. [15] was used to calculate the torsion–rotation energies. In the first step the torsional energies were calculated using the truncated basis given by

$$|v_6,\sigma\rangle=\frac{1}{\sqrt{2}}\sum_{k_s=-10}^{+10}A^{v_6}_{3k_s+\sigma}e^{i(3k_s+\sigma)\alpha}$$

where α is the torsional angle. The expansion coefficients $A^{v_6}_{3k_s+\sigma}$ were then used to calculate the matrix elements of the torsional operators. In the second step the lowest 9 torsional states were used to calculate the total energy. This 9×9 matrix is shown as the first diagonal block in Fig. 2.

2.2. The ν_{12} fundamental

The experimental conditions for the ν_{12} fundamental of $^{12}CH_3{}^{13}CH_3$ are given in Ref. [13]. Like the ν_9 fundamental of ethane, the ν_{12} band of $^{12}CH_3{}^{13}CH_3$ exhibits doubling of rovibrational lines due to internal rotation with the same spin statistical weight ratios. This is 4:1 with the weaker component being $\sigma=-1$ for $K=3m+1$, or $\sigma=+1$ for $K=3m+2$ and 2:1 when $K=3m$ with the strongest component being $\sigma=0$. See Figs. 5 and 6 in Ref. [13]. The σ-splitting in ν_{12} band, whose intrinsic value is about 0.002 cm^{-1} and arises from the difference in the values of the barrier heights between the gs and $\nu_{12}=1$, is an excellent indicator of perturbations in this band. Fig. 1 indicates that the observed state $(\nu_{12}=1,\nu_6=0)$ is close to the dark state $(gs,v_6=3)$ and if K-dependent terms in the energy expression are considered, it can be shown (see the discussion below and Ref. [13]) that the P branch doublets in ν_{12} experience noticeable but differing upward energy shifts because of large torsional splittings in the dark state. There is an eventual energy crossing at $(K=18,\sigma=0)$ which allows for observation of a perturbation allowed rotational series in the $3\nu_6$ overtone [14]. Arrows c and f in Fig. 1 represent data from the ν_{12} fundamental and $3\nu_6$ overtone, respectively.

The parameters obtained from the frequency analysis of a 2-state fit are given in Ref. [13]. The two step program was also used to calculate the energies for gs and $\nu_{12}=1$. In the first step the torsional energies and matrix elements of the torsional operators for each of the two states as well as Coriolis-type coupling terms between the states were calculated. In the second step the lowest 9 torsional states were used to calculate the total energy. As shown in Fig. 2, the Hamiltonian matrix for the 2-state analysis includes the first three diagonal blocks and the vibrational couplings (the three off-diagonal blocks).

2.3. The ν_5 fundamental

The experimental details for the ν_5 fundamental of $^{12}CH_3{}^{13}CH_3$ are given in Ref. [14]. This band which corresponds to the C–C stretching fundamental is Raman active, represented in Fig. 1 as arrow e. It has been analyzed with the data discussed in Sections 2.1 and 2.2 using a 3-state fit [14]. As for ethane [10], it was found that one torsional component of $(\nu_5=1,\nu_6=0)$ is perturbed by the dark state $(gs,\nu_6=4)$ and this interaction was successfully modeled by Fermi-type couplings which reduced the required number of terms in the Fourier expansion of the torsional potential for the ground vibrational state from three (in the 2-state fit) to only the term in the barrier height.

The parameters for the 3-state fit which were obtained using the two step program are given in Ref. [14]. The Hamiltonian matrix in this case consists of the first four blocks and the vibrational coupling (the four off-diagonal blocks) as shown in Fig. 2. No coupling between $v_{12}=1$ and $v_5=1$ was required.

2.4. The $\nu_{12}+\nu_6-\nu_6$ band

The hot bands $\nu_{12}+\nu_6-\nu_6$ and $\nu_{12}+2\nu_6-2\nu_6$ occur in the same spectral region as the ν_{12} band. Even at the low