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Vibration–rotation–torsion analysis of the high resolution infrared spectrum of C_2H_6 between 1330 and 1610 cm^{-1}: The ν_6, ν_8, $\nu_4 + \nu_{12}$, $2\nu_4 + \nu_9$ interacting system and hot transitions from ν_4 to $\nu_4 + \nu_8$

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Abstract

The room temperature spectrum of ethane in the region of the ν_6 and ν_8 fundamentals, between 1330 and 1610 cm^{-1}, has been re-investigated at a resolution of 0.002 cm^{-1}. It is shown that the complex spectral structure with numerous strong local perturbations, which had hindered a global analysis of this region until now, is caused by a network of *l*-type resonances acting within the Fermi (or torsional-Coriolis) coupled system ν_8, $\nu_4 + \nu_{12}$. The *x*,*y*-Coriolis interaction between ν_6 and ν_8 and vibration–rotation interactions between ν_6 and $2\nu_4 + \nu_9$ also generate relevant effects on the spectrum. With an appropriate Hamiltonian model accounting for all these effects, we could fit 1814 upper state level energies belonging to ν_6, ν_8 and $\nu_4 + \nu_{12}$ with an overall RMS deviation better than 3.8×10^{-3} cm^{-1}. The determined values of the intrinsic torsional splittings in the different vibrational states are in agreement with the theoretical expectations. The intrinsic torsional splitting almost vanishes in ν_8, as in digermane and disilane; it is slightly larger in $\nu_4 + \nu_{12}$ than in ν_4, due to the decrease of the torsional barrier height with the excitation of ν_{12}. For the $2\nu_4 + \nu_9$ state, the determined values of the vibrational origin and torsional splittings are in good agreement with the large increase of the torsional barrier height expected with the excitation of the ν_9 mode.

Several hot transitions originating from the $v_4 = 1$ torsional state have been observed. An analysis of 294 line positions belonging to the $(\nu_4 + \nu_8) - \nu_4$ hot band has been performed, leading to a fit with a RMS deviation of 5.1×10^{-3} cm^{-1}. It is shown that a complex network of *l*-type resonances is also active in the $\nu_4 + \nu_8$, $2\nu_4 + \nu_{12}$ system.

Keywords: Ethane; Internal rotation; Planetary atmospheres; Titan; High resolution infrared spectra; Vibration–rotation interactions

1. Introduction

Ethane is a key molecule because of its highly symmetric geometry, with two coaxial identical internal rotors, and its peculiar large amplitude torsional dynamics. It is also of environmental and astrophysical interest. In fact, ethane is the second most abundant hydrocarbon in the Earth's atmosphere, and has been detected by infrared spectroscopy in comets [1] and in the atmospheres of the outer planets [2–4]. This justifies the great attention dedicated to the spectroscopy of this molecule. Nonetheless, a detailed high resolution rotational-torsional analysis of vibrational transitions of ethane could be performed only for the lowest infrared active fundamental ν_9, the asymmetric CH_3 rocking mode [5–9] centred around 821 cm^{-1}. Very recently Cooper and Moazzen-Ahmadi were able to complete a global fit analysis of the ν_9 band, together with the $(\nu_9 + \nu_4) - \nu_4$ hot band, the C—C stretching fundamental ν_3 near 994 cm^{-1} and the ν_4, $2\nu_4 - \nu_4$ and $3\nu_4$ torsional bands [10]. In all the other regions the complexity of

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the spectrum, with the occurrence of several resonances, has hindered so far a reliable detailed analysis.

The present contribution is concerned with the frequency analysis of the spectral region in which the ν_6 and ν_8 fundamentals occur. As Fig. 1 shows, such a band system is observed in spectra of the atmosphere of Titan [11,12]. Spectroscopic reference information is however rather limited in this range. Indeed, despite several attempts to analyze it, detailed below, this spectral region has not yet been fully understood. To the best of our knowledge, individual line intensities and broadening parameters have never been measured in this range, although some limited information on self-, N_2-, H_2- and air-broadening parameters has been obtained at lower energies (see [14] for a review of such measurements). Absorption cross sections of ethane diluted in one atmo-

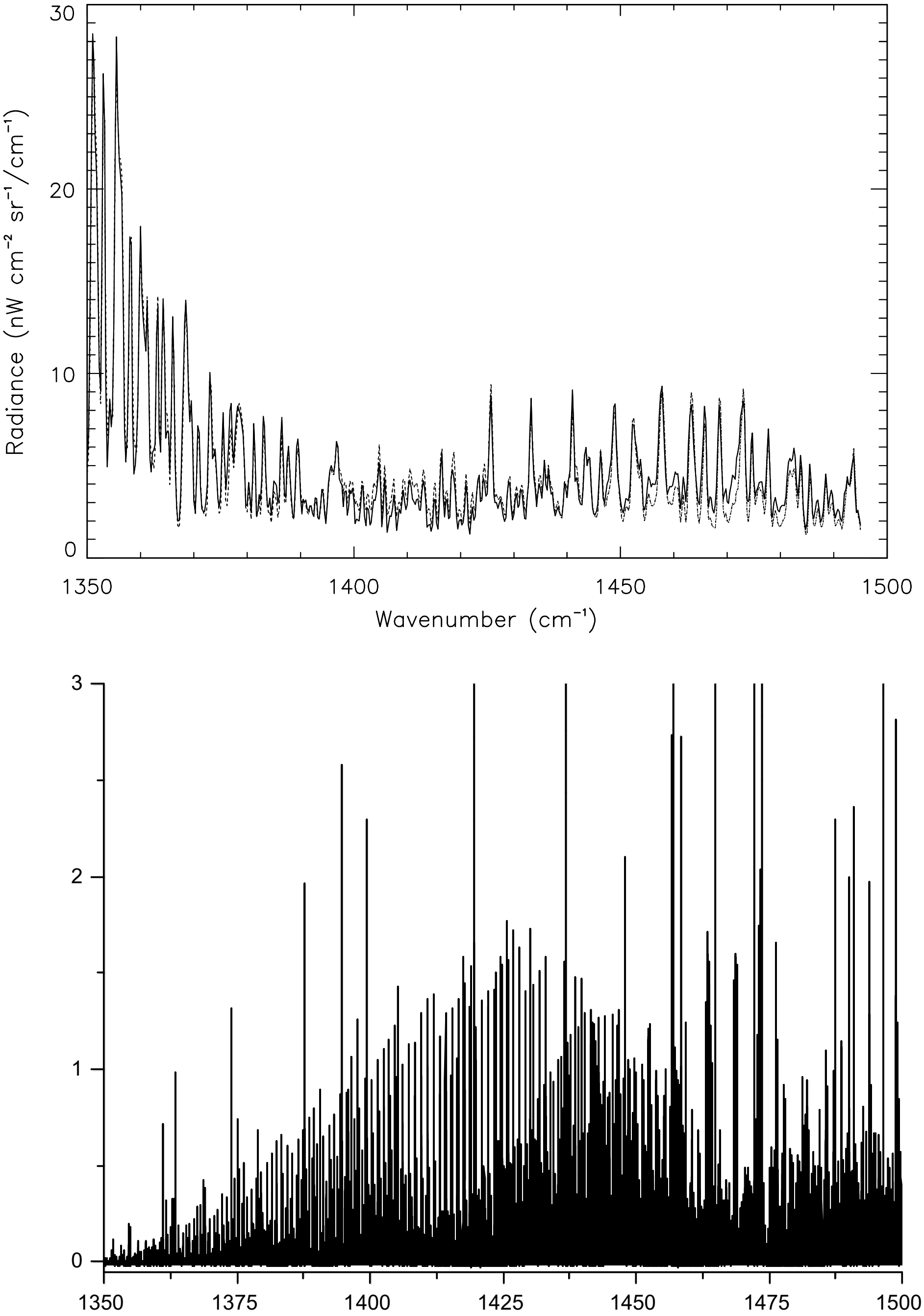

Fig. 1. (Top [11]) Solid line: Cassini CIRS spectrum of Titan at 0.5 cm^{-1} apodized resolution, produced by averaging 8780 individual spectra at low-latitude (15S-15N) and emission angle (0–15 degr) at a range of less than 3×10^5 km. Dotted line: synthetic spectral model including lines for CH_4 (HITRAN 2004 [13]) and C_2H_6 (JPL pseudo linelist). (Bottom) Laboratory high-resolution (0.002 cm^{-1}) Fourier transform absorption spectrum (spectrum S2 in Section 2: pressure = 0.11 mbar, path = 19.7 cm, room temperature) of the ν_6/ν_8 region of ethane; strong lines are due to residual water vapor present inside the evacuated instrument.