Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Spectroscopy 243 (2007) 168–181
Journal of MOLECULAR SPECTROSCOPY
www.elsevier.com/locate/jms

Rotation–torsion–vibration term-value mapping for CH_3OH: Torsion-mediated doorways and corridors for intermode population transfer

R.M. Lees [a,*], Li-Hong Xu [a], J.W.C. Johns [b], B.P. Winnewisser [c,d], M. Lock [d]

[a] *Centre for Laser, Atomic and Molecular Sciences (CLAMS) and Department of Physical Sciences, University of New Brunswick, Saint John, NB, Canada E2L 4L5*
[b] *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ont., Canada K1A 0R6*
[c] *Department of Physics, The Ohio State University, 174 W. 18th Avenue, Columbus, OH 43210, USA*
[d] *Physikalisch-Chemisches Institut, Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany*

Received 24 December 2006; in revised form 5 February 2007
Available online 15 February 2007

Abstract

Fourier transform infrared spectra of CH_3OH from 930–1650 cm^{-1} have been analyzed to reveal details of the rotation–torsion–vibration energy manifold of the CO-stretching, CH_3-rocking, OH-bending and CH_3-deformation modes and their torsional combination states. Mapping of the upper-state term values as a function of the rotational quantum number J has shown the locations of numerous substate crossing resonances that give rise to J-localized spectral perturbations and substate mixing and thereby create "doorways" for collision-induced population transfer among the different modes. Other near-degenerate substates are more globally mixed over a wide range of J, corresponding to "corridors" of doorways. Where both partner substates in a doorway resonance have been identified, the perturbations have been analyzed to find estimates of the interaction matrix elements and the degree of mixing between the coupled states. Many of the resonances are between substates of differing torsional quantum number, highlighting the importance of torsion in generating the doorway channels and enhancing intermode vibrational population transfer.

Keywords: Methanol; Infrared spectra; Vibrational modes; Internal rotation; Rotation–torsion–vibration term values; Perturbations; Local resonances; Avoided crossings; State mixing; Torsion-mediated vibrational coupling; Energy transfer; IVR

1. Introduction

An important question about thermal equilibration in gases is how molecules transfer from one vibrational state to another. An interesting possible route for intermode transfer is via molecular "doorways" created by mixing between near-degenerate levels of two different modes. As illustrated schematically in Fig. 1, a molecule arrives in a mixed state collisionally from Mode A on one side of the doorway, and then departs via collisional transfer into the partner Mode B on the other side of the door. To explore such a mechanism, one needs a good map of the excited state energy levels in order to locate the possible mixed doorway states. That is the subject of the present paper.

In our program, we have been analyzing rotationally resolved Fourier transform infrared (FTIR) spectra of CH_3OH in the 930–1650 cm^{-1} region to investigate the rotation–torsion–vibration (R–T–V) energy manifold of the CO-stretching, CH_3-rocking, OH-bending and CH_3-deformation vibrational modes along with their torsional combinations [1–7]. By mapping the upper-state term values as a function of the J-rotational quantum number, we obtain a vivid and detailed picture of the energy structure that exposes a network of local resonances and near

---

[*] Corresponding author. Fax: +1 506 648 5948.
E-mail address: lees@unb.ca (R.M. Lees).

0022-2852/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2007.02.008

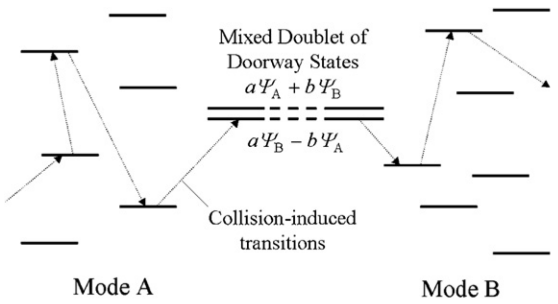

Fig. 1. Scheme for collisional intermode population transfer via a hybridized doublet of "doorway" states. A molecule enters one of the mixed pair of doorway states via a collision-induced transition from Mode A on the left, then leaves on the other side of the door into Mode B on the right. The probability of transfer depends on the mixing ratio $|b/a|^2$.

degeneracies interlinking the different modes and giving rise to a variety of spectral perturbations. Modeling of the perturbed energies can give the interaction matrix elements and the degree of mixing between the coupled states. Many of the resonances are between substates of differing torsional quantum number, highlighting the importance of torsion in generating the doorway channels and enhancing intermode vibrational population transfer.

Torsional substructure was first observed in a methanol vibrational band by Woods [8] in his investigation of the ν_8 CO-stretching fundamental of CH_3OH in the classic program of methanol studies by Dennison and coworkers (see [9], for example, and references cited therein). Since then, the CO stretch has been explored in great detail by a variety of high-resolution techniques, and studies have also been extended to other vibrational modes and isotopic species. Results up to 1995 for CH_3OH were reviewed in a monograph by Moruzzi et al. [10], and a number of further studies have since been reported (see [1–7] and [11–17] for example, plus references therein). In their book, in addition to extensive tables of rotation–torsion energies for the ground vibrational state, Moruzzi et al. also presented term values for many excited ν_8 CO-stretching substates as well as several substates of the ν_7 in-plane CH_3-rocking mode [10].

Torsion-mediated J-localized coupling was first seen for methanol by Mukhopadhyay et al. [18] and involved a crossing resonance within the ground vibrational state of the $^{13}CH_3OH$ isotopic species. Further $^{13}CH_3OH$ ground-state resonances and mixings among torsion–rotation substates were recently reported by Moraes et al. [19]. In excited vibrational states, localized resonances have been found for the ν_{11} out-of-plane CH_3 rock [1], the ν_4 asymmetric in-plane CH_3 bend [2] and the $2\nu_8$ CO-stretching overtone [5] for normal CH_3OH, as well as the ν_8 CO-stretching and ν_7 in-plane CH_3-rocking modes of the $^{13}CH_3OH$ [20–22] and $CH_3{}^{18}OH$ [23] isotopomers. A number of substate crossings were clearly revealed in plots of the excited-state energies as a function of J in [5] and [22] and were of material help in establishing and confirming the identities of the interacting partner levels.

In the current phase of our program, we are exploring maps of J-reduced R–T–V term values derived from CH_3OH subbands from 930 to 1650 cm^{-1} for which the lower rotation–torsion states have been assigned. As noted in [7], although the torsion–vibration identities of the upper states of a number of the subbands are not yet clearly established, the positions of the upper energy levels can still be accurately determined by adding known ground-state energies [10] to the observed transition wavenumbers. Mapping of these upper term values then gives an informative picture of the locations of the local resonances and near-degeneracies occurring among the various torsion–vibration substates, and adds considerable insight into some of the spectral puzzles that have been encountered. In a number of instances where an otherwise well-behaved subband had been observed to vanish suddenly in the spectrum, the energy map now reveals a substate crossing lying just beyond that point, accounting for the problem in following the assignments to higher J.

In the present paper, we discuss the term value mapping for $^{12}CH_3{}^{16}OH$ and give several illustrations of the R–T–V energy manifold and the patterns of intermode resonances. We present a list of doorway local resonances together with results for the J-localized perturbations near the crossing points of the interacting partner substates, as well as a listing of more global corridor interactions that mix near-degenerate substates over a broad range of J. Where both partners in the resonance have been identified and mapped, we have employed simple two-state interaction models to estimate the magnitude of the coupling matrix elements and the degree of mixing of the coupled levels. A major outcome of the work is a set of three Excel files, deposited as Supplementary material, that contain compilations of the upper-state term values and term value maps for A and E torsional symmetries plus a listing ordered by wavenumber of all transitions that have been assigned to date.

2. Experimental details

This work was based on several CH_3OH room temperature FTIR spectral recordings obtained at a resolution of 0.002 cm^{-1} at different pressures and path lengths to optimize different spectral features, employing the modified DA3.002 Bomem FTIR spectrometer at the National Research Council of Canada in Ottawa and the Bruker IFS120 instrument at Giessen. The spectra have been described previously in [6] and [7] and the reader is referred to those reports for more specific details. In the linelist in the Supplementary data, the transmittances are labeled as OttA for the NRC spectrum recorded at 13.5 Pa pressure and 2.0 m path, as OttB for the NRC spectrum at 100 Pa pressure and 2.0 m path, and as Gies for the Giessen spectrum recorded at 25 Pa pressure and 16.3 m path [7]. Recent precise sub-Doppler CO_2-laser/microwave-sideband Lamb-dip measurements for CH_3OH [12–14,17,24] showed that our earlier calibration in the 10 μm region [6] should be updated by dividing the reported wavenumbers