Journal of Molecular Spectroscopy 260 (2010) 77–83

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

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

The rotational spectrum of *tertiary*-butyl alcohol

E.A. Cohen [a,*], B.J. Drouin [a], E.A. Valenzuela [b,1], R.C. Woods [b], W. Caminati [c], A. Maris [c], S. Melandri [c]

[a] *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099, USA*
[b] *Department of Chemistry, University of Wisconsin, Madison, WI 53706-1322, USA*
[c] *Dipartimento di Chimica "G. Ciamician", dell'Università, Via Selmi 2, I-40126 Bologna, Italy*

ARTICLE INFO

Article history:
Received 21 October 2009
In revised form 16 November 2009
Available online 4 December 2009

Keywords:
tertiary-Butyl alcohol
Rotational spectrum
Internal rotation

ABSTRACT

The rotational spectrum of *tertiary*-butyl alcohol has been recorded in selected regions between 8 and 500 GHz. Early data from the University of Wisconsin in the 8–40 GHz region have been combined with recent measurements from the University of Bologna and the Jet Propulsion Laboratory in the millimeter and submillimeter wavelength regions. The spectrum was fit over a wide range of *J*'s and *K*'s using a common set of parameters for both the *A* and *E* states. This paper describes the initial assignment at Wisconsin and the final procedure used to assign and fit the higher rotational states. The resulting molecular constants and their interpretation are discussed.

1. Introduction

tertiary-Butyl alcohol (TBA) presents a particularly interesting internal rotation problem. It is a nearly spherical rotor with a moderately low barrier to internal rotation about the C–O bond. Effects due to internal rotation about the C–C bonds are not observable in the ground state. The *tert*-butyl symmetric internal top is nearly the entire molecule with the axis of internal rotation nearly coincident with the *c* axis in the *ac* plane as shown in Fig. 1.

The rotational spectrum of TBA was first reported by Valenzuela [1] as part of a study which also included *tert*-butyl mercaptan [2]. At that time, only the *E* state transitions between 8 and 40 GHz were fit using eight parameters and a data set which was limited by the available computing capability. The spectrum was again observed between 60 and 78 GHz in the Bologna laboratory as part of a study of the TBA-NH_3 complex [3]. In order to properly assign and predict the TBA spectrum in the higher frequency region, the original data set was refit using Pickett's SPFIT program [4]. Eventually, the predictions became sufficiently adequate to assign and fit spectra up to 500 GHz. At present 1539 features are fitted with a single set of parameters which describes both the *A* and *E* state spectra.

Although the primary purpose for the re-examination of this spectrum was to precisely predict previously unobserved features, this paper also reports some of the procedures used in the original assignment, the fitting method used, and the newly derived parameters. The parameters are compared with those derived from *ab initio* calculations and those of related compounds.

2. Experimental details

The data used in this analysis was obtained at the University of Wisconsin (UW) between 8 and 40 GHz with a Stark modulated spectrometer and data acquisition system described by Woods and Dixon [5], between 58 and 78 GHz at the University of Bologna (UB) with a free jet spectrometer described by Melandri et al. [6], and in selected regions between 160 and 508 GHz at the Jet Propulsion Laboratory (JPL) with a spectrometer utilizing a microwave synthesizer and amplifier–multiplier chains [8–10]. The sample in the UW experiment was cooled to a point below 273 K which was sufficient to enhance low *J* transitions while still maintaining sufficient vapor pressure for observation. The UB experiment utilized a jet cooled sample at 10 K. The JPL experiments were done at room temperature. Two μ_c, $J = 1 - 0$ transitions were measured with high accuracy at Bologna with a Fourier transform (FT), molecular beam spectrometer [11].

For the analysis, uncertainties of 100 kHz were assigned to the measurements below 40 GHz and above 200 GHz , 3 kHz to the two FT measurments, 20 kHz to most of the free jet measurements, and 50 kHz to the remaining lines.

3. The spectrum and its assignment

3.1. Initial assignment

The original work on TBA is reported in Ref. [1] and the procedure leading to the assignment is reviewed here.

The most striking features of the microwave spectrum of TBA in the traditional 8–40 GHz microwave region are the many strong lines with partially resolved first order Stark effects. These

---

* Corresponding author.
E-mail address: Edward.A.Cohen@jpl.nasa.gov (E.A. Cohen).
[1] Present address: 4901 Oakridge Dr. Midland, MI 48640, USA.

0022-2852/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2009.11.010

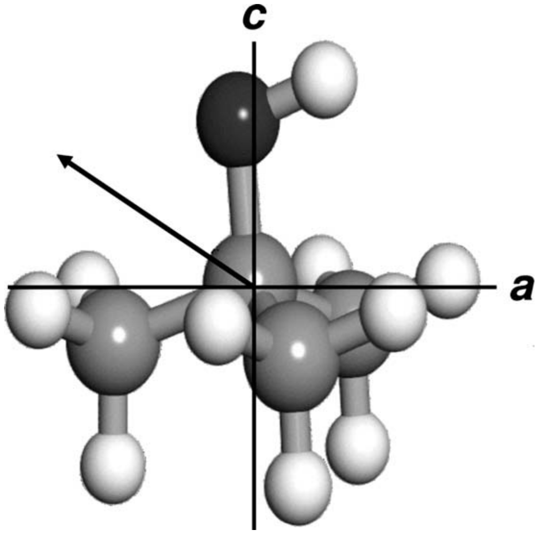

Fig. 1. *tert*-Butyl alcohol. The arrow shows the direction of the dipole moment with the tail positive.

provided the first clues which eventually led to the spectral assignment. In that region more than 200 strong lines showing partially resolved Stark effects of a first-order nature were eventually identified. Due to the complexity of the spectrum with consequent crowding of lines and the general weakness of the individual Stark lobes, the exact number of Stark lobes and therefore the J value for each line was difficult to determine. Some of these lines exhibited from 10 to 20 such Stark lobes. From the intensity patterns of the individual Stark components these lines were identified as R-branch transitions. The seemingly random pattern of these lines suggested that they were due to $\Delta K = \pm 1$ transitions allowed by the perpendicular component of the dipole moment, μ_a.

By counting Stark lobes for the resolved members of a transition within a given J family it proved possible to assign the J quantum numbers involved in the transitions to within ±2. From an examination of the spectra and by extrapolation of first differences, the last member of a family for which $K = J$ could be determined. The first sequences of transitions which were identified are shown in Fig. 2. These families are similar to the "b-type chains" of Lees and Baker [12] and the "τ-families" of Hershbach and Swalen [13]. With the five possible J assignments some of the transitions shown in Fig. 2 were fit to the six parameters characteristic of the IAM Hamiltonian using a nonlinear least squares fitting procedure [14]. Initial guesses were chosen from information extrapolated from the previously studied methanol [12] and *tert*-butyl mercaptan [2]. Although more than one of the possible J assignments gave equally good fits to the data, only the one shown in Fig. 2 gave reasonable values for the molecular parameters.

From the value of $(A + B)$ determined in this fitting procedure, we were able to locate the R-branch transitions due to changes in the parallel component of the dipole moment, μ_c. These confirmed the initial assignment since none of the other four possible choices yielded $(A + B)$ values in agreement with experiment. These R-parallel transitions were obscured by neighboring lines but we were able to confirm the 1–0 and some of the 2–1 transitions by their Stark effects. Another least squares fit to the expanded data along with double resonance experiments to locate Q-branch transitions served to further confirm the assignment. Ref. [1] reports 218 assigned transitions between 8 and 40 GHz.

3.2. Millimeter and submillimeter spectra

The available computational capability limited the analysis of the data in Ref. [1] to an eight parameter fit of selected E state transitions with $J \leqslant 15$. These parameters fit the selected transitions with an RMS of 2.05 MHz and were accurate enough to provide a new prediction using the program SPCAT [4]. Once this was done the energy level labels could be converted to those appropriate for SPFIT and most of the previously reported transitions could be accurately fit using higher order centrifugal and torsion–rotation parameters. The fitting procedure is similar to that employed for perchloric acid, $HClO_4$ [7]. The program SPFIT was run using symmetric rotor quantum number notation and what is referred to in the program description as "full projection ordering" to label the energy levels [4].

Both TBA and $HClO_4$ are near spherical rotors with moderately low barriers to internal rotation leading to energy ordering which is dominated by the K dependent solutions of the Mathieu equation. Fig. 3 shows the Mathieu energy for the torsional ground state of TBA as a function of K. The lower series is for states with $|K - \sigma| = 3n$, the center series is for states with $|K - \sigma| = 3n + 1$, and the top series is for states with $|K - \sigma| = 3n - 1$, where $\sigma = 0$ for A and ±1 for E states. The reduced energy $E - (A + B)J(J + 1)/2$ is plotted as a function of J in Fig. 4 for the A states. The E states show similar behavior but have not been plotted to avoid clutter. States with $K = 3n$ are seen to be at lower energy and interact only weakly at low K with $K = 3n \pm 1$ states. The $K = 3n \pm 1$ states interact more strongly with each other. For the E states, K is replaced by $K - \sigma$. This produces a characteristic pattern for the parallel μ_c transitions in which the $|K - \sigma| = 3n$ levels give rise at low K to a symmetric rotor like pattern at multiples of $A + B$ with a group of lines from the levels with $|K - \sigma| = 3n + 1$ to low frequency and another group with $|K - \sigma| = 3n - 1$ to high. At high J the spectrum becomes

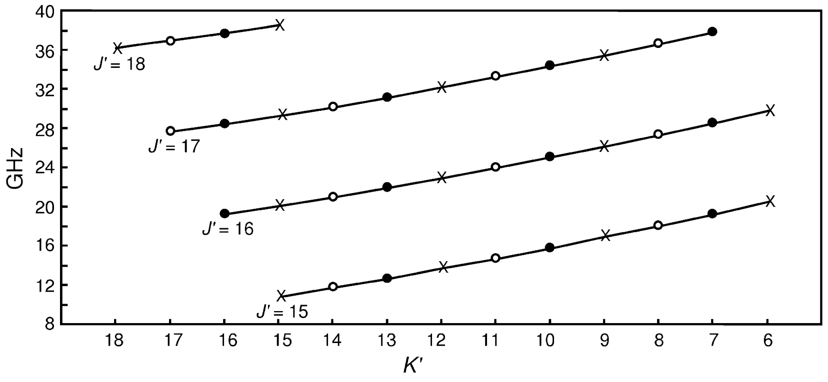

Fig. 2. Initially assigned sequences. The ×'s represent the A state, the ∘'s represent the E state with $K\sigma > 0$, and the •'s represent states with $K\sigma < 0$.