Internal rotation in halogenated toluenes: Rotational spectrum of 2,3-difluorotoluene

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ABSTRACT

The microwave rotational spectrum of 2,3-difluorotoluene has been studied by pulsed supersonic jet using Fourier transform microwave spectroscopy. The tunneling splitting due to the methyl internal rotation in the ground torsional state could be unambiguously identified and the three-fold (V_3) potential barrier hindering the internal rotation of the methyl top was determined as 2518.70(15) J/mol. The ground-state rotational parameters for the parent and seven ^{13}C isotopic species in natural abundance were determined with high accuracy, including all quartic centrifugal distortion constants. The molecular structure was derived using the substitution (r_s) method. From the rotational constants of the different isotopic species the r_s structure as well as the r_0 structure was determined. Supporting ab initio (MP2) and DFT (B3LYP) calculations provided comparative values for the potential barrier and molecular parameters.

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1. Introduction

Microwave spectroscopy is a unique technique and has placed a vital role in the studies of internal rotation problems and molecular interactions [1]. The high (sub-Doppler) resolution and the sensitivity of Fourier transform technique studied on molecular jets make this method unmatched by other experimental spectroscopic techniques [2–5]. Despite a considerable increase of studies in the last decades, some types of internal rotation problems have received less attention than desirable. In particular, low internal rotation barriers, like those of methylated toluenes, may produce large (even on the GHz scale) torsional splittings, adding difficulty to the assignment and interpretation of the rotational spectrum of these molecules [6–27]. In cases of high symmetry, the presence of six-fold potential barriers requires group theoretically appropriate treatments for a meaningful comparison between different molecules [6]. A global view of the molecular forces controlling the torsional motion of these molecules can only be adequately modeled if we provide a systematic set of experimental torsional barriers.

The structure and intramolecular interactions in toluene and substituted toluenes were subject of interest for a considerably long time. Toluene has a methyl group attached to a C_{2v}-symmetric planar benzene ring, such that the V_3 potential term vanishes and only a tiny V_6 potential barrier remains, determined as 13.832068(3) cal/mol (57.873372(13) J/mol) from the splitting of the lines belonging to |±m| = 3n states (with n being positive integer) [7–13]. However, when substituents are introduced on toluene, the symmetry may reduce and a V_3 potential barrier appears predominantly as in the case of ortho-chlorotoluene [20–24]. The barrier height may change considerably depending on the number and relative position of the substituents. Thus, in ortho-fluorotoluene the V_3 potential was found to be 649.3 cal/mol (2716.7 J/mol) [14] whereas in meta-fluorotoluene it is 45.3 cal/mol (189.5 J/mol) [10]. However, in para-flurotoluene the V_6 potential becomes the leading term again and the value obtained is only 13.638 cal/mol (57.061 J/mol) [8,15,26]. The microwave spectra of ortho-chlorotoluene were investigated earlier and the potential barrier obtained for CH_3 torsion in ortho-chlorotoluene is 5642(5) J/mol [20,23,24]. The microwave spectra of the dihalogenated toluenes 2,4-, 2,5-, 2,6- and 3,5-difluorotoluenes were studied by us earlier [6,28,29] and the potential barriers were determined in these isomers. We have now extended these investigations to 2,3-diflurotoluene $C_7H_6F_2$ (Fig. 3), as part of a detailed internal rotation and structural study of substituted toluenes. No microwave study on this molecule was reported earlier. In this study we have employed Fourier transform microwave spectroscopy (FT-MW) on a molecular supersonic jet-expansion, largely

benefiting from the higher resolution of this technique. Seven ^{13}C isotopologues of the molecule were also observed in natural abundance, resulting in an accurate structure of the carbon skeleton.

The experimental methods have been described elsewhere [30–33]. The coaxial adiabatic jet expansion simultaneously reduces the collisional as well as Doppler line-width and the molecules experience a strong rovibrational cooling, depopulating all but the lowest-lying rovibrational levels, and thereby efficiently simplifying the observed spectrum. We have also conducted *ab initio* calculations on the molecule aiding the assignment and to test the predictive value of the theoretical data against the experiment.

2. Experiment

Commercial samples of 2,3-diflurotoluene obtained from Alfa-Aesar GmbH were used without further purification. The spectra were taken on a pulsed supersonic jet Fourier transform microwave spectrometer in Hannover, using the coaxially oriented beam and resonator arrangement (COBRA) [30–33] described before. The principal advantage in the COBRA arrangement is the longer transit time of the molecular jet, which can be exploited for Stark effect experiments if necessary, rather than using external electrode plates, the spherical reflectors forming the resonator are utilized as high-voltage electrodes (Coaxially Aligned Electrodes for Stark effect Applied in Resonators, CAESAR) [33]. The substance was kept in a small reservoir at the nozzle orifice, using neon or helium as carrier gas (stagnation pressures of 1–2 bar). The spectra were measured in the frequency range 5–25 GHz. All frequency measurements were referenced to a GPS-disciplined rubidium frequency standard and unblended lines have an estimated uncertainty of <1 kHz. Lines separated less than ~5 kHz are not resolved.

2.1. Rotational spectrum and internal rotation barrier

Ab initio predictions were used to obtain estimates of the rotational parameters, electric dipole moments and the torsional potential function for the parent species and seven isotopologues. Number of lines were then initially observed and identified in the frequency region 10–16 GHz, as exemplified in Fig. 1. However, in order to rationalize the spectrum some considerations should be given on the torsional fine structure. The internal rotation governed by V_3 barrier splits the three-fold degeneracy of the ground vibrational state (v = 0) in two (A, E) C_3-symmetry components. Initially the A-symmetry series of lines was successfully fitted to an asymmetric rotor pattern for the parent and for its isotopologues by the program SPFIT written by Pickett [34]. The potential barrier obtained from DFT and *ab initio* calculations were used to obtain a theoretical prediction of the E-symmetry internal rotation component and could be easily identified first for the parent and of its isotopologues later on. An illustrative typical torsional splitting is shown in Fig. 1.

The rotational lines measured and their assignments are given in the Supplementary Material (Tables S1–S8). In order to fit the internal rotation splitting we have employed the program XIAM2 written by Hartwig [35,36].

The Hamiltonian employed for the asymmetric rotor in presence of a symmetric internal rotor can be written as

$$H = H_{rr} + H_{cd} + H_{ir} + H_{ird} \qquad (1)$$

where the standard rigid frame-rigid top Hamiltonian is given by [4,34–37]

$$H_{rr} + H_{ir} = AP_a^2 + BP_b^2 + CP_c^2 + F\pi_\alpha^2 + V(\alpha) \qquad (2)$$

which contains the rotational constants of the molecule (A, B, C) and the reduced rotational constant F of the methyl top. The components of the total angular momentum are denoted as P_g and refer to the principal inertia axes g = a,b,c. Specifically, $\pi_\alpha = P_\alpha – \rho_a P_a – \rho_b P_b$ contains the angular momentum P_α of the methyl top with $\rho_g = \lambda_g I_\alpha / I_g$ (g = a,b), the moment of inertia I_α of the methyl top, the structural moments of inertia I_g components of the molecule and the direction cosines λ_g between the internal rotation axis i and the respective inertial axes (in case of 2,3-difluorotoluene: $\lambda_a = \cos \delta$, $\lambda_b = \sin \delta$, $\delta = \angle$(a,i); $\lambda_c = 0$ by symmetry).
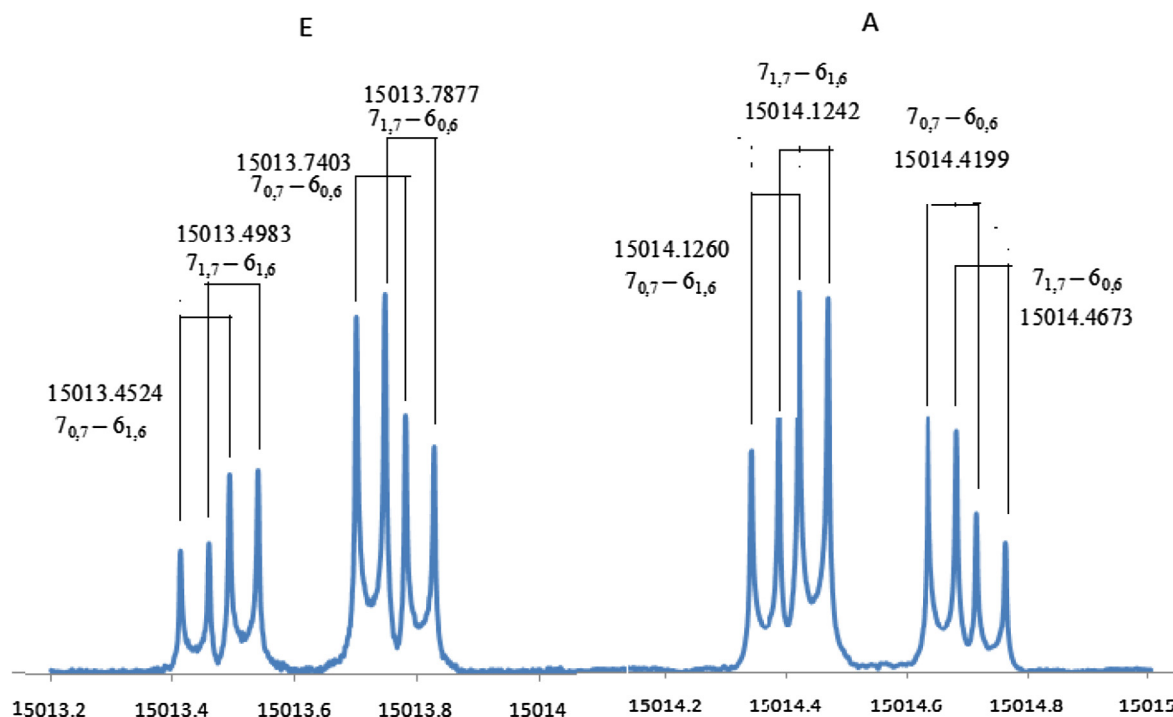

Fig. 1. (A–E) splitting and K splitting in the J′-J = 7–6 rotational transitions of 2,3-difluorotoluene.