

Microwave study of internal rotation in *para*-Tolualdehyde: local versus global symmetry at the methyl-rotor site as an indicator of information transfer across the benzene ring

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The rotational spectrum of *para*-tolualdehyde ($\text{CH}_3\text{-C}_6\text{H}_4\text{-CHO}$) has been measured using microwave spectrometers in three laboratories, with the goal of quantifying the influence of the aldehyde group at the top of the benzene ring on the internal rotation barrier seen by the methyl group at the bottom of the ring. This barrier consists of a six-fold component, which results from the local C_{2v} symmetry of the benzene ring seen by the methyl top (as in toluene), and an additional three-fold component, which results from information on the non- C_{2v} symmetry at the aldehyde site being transmitted across the ring to the methyl top site.

The nearly free internal rotation of the methyl group splits each of the rotational transitions into two components, one of *A* and one of *E* symmetry. Assignment and fit of 786 *A*-state and *E*-state transitions in the $v_t = 0, 1,$ and 2 torsional levels to an internal rotation Hamiltonian with centrifugal distortion and barrier terms of three-fold ($V_3 = 28.111(1) \text{ cm}^1$) and six-fold ($V_6 = -4.768(7) \text{ cm}^{-1}$) symmetry with respect to the internal rotation angle, resulted in residuals equal to experimental uncertainty. Isotopic data from all eight mono-substituted ^{13}C species and the one ^{18}O species were obtained in natural abundance and used to determine an r_s substitution structure.

Various chemical and physical implications of this structure and the two barriers will be discussed. In particular, our initial intuitive assumption that the information transmission mechanism would involve a conjugation of the n electrons of the aldehyde $\text{C}=\text{O}$ with the n electrons of the benzene ring to force a partial Kekulé structure of the ring, is not supported by the substitution structure or quantum chemistry calculations. Other molecules potentially exhibiting this same type of information transfer across a conjugated aromatic ring system will be mentioned.

Effective rotational hamiltonian for two-rotor systems with symmetric and asymmetric internal rotors (like Ethanol) applied to Ethylphosphine, $\text{CH}_3\text{CH}_2\text{PH}_2$

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Spectra of molecules with a 3-fold internal rotor become much more interesting in the presence of another large-amplitude motion (LAM) that leads to tunneling between equivalent asymmetric forms which may also tunnel to a different conformer. An effective rotational Hamiltonian has been derived for such a system of which ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, is a typical example [1]. The ERHAM code [2] was modified to treat ethanol-type systems, using “ancient” unpublished microwave data from vibrational ground and excited states of ethylphosphine, $\text{CH}_3\text{CH}_2\text{PH}_2$, as test data. For gauche ethylphosphine, the splitting between the a-type Coriolis-coupled ground states is 5.215(6) MHz whereas it is 229.9(2) MHz in the ν_{24} state (PH_2 torsion) and 51.35(7) MHz in the ν_{23} state (CH_3 torsion). The tunneling energy coefficients eps_{01} for the methyl internal rotation are -0.63(2) MHz and 2.93(5) MHz (sign undeterminable), respectively. These results look promising; however, up to now, sets of assigned frequencies had to be omitted from fits to experimental uncertainty of 25 kHz: (a) for the ground state, all c-type transitions $J_{4,J-3} - J_{3,J-3}$ ($41 < J < 48$) for systematic large deviations (reason unknown); (b) for the ν_{24} state, half of the quartets of the $J_{3,J-2} - J_{2,J-2}$ series ($28 < J < 32$) because of interactions with a state of the trans conformer) and some of the $K_a = 1, 2$ low- J transitions (incorrect assignments or unknown reasons).

[1] J.C. Pearson et al., J. Mol. Spectrosc. (2008) 251, 394

[2] P. Groner, J. Mol. Spectrosc. (2012) 278, 52

Proton in a double-well potential: Acetylacetonone and its derivatives by microwave spectroscopy

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The extended nature of the proton wave function, the shape of the ground and final state potentials in which the proton is located has been investigated in gaseous acetylacetonone and three of its derivatives, benzoylacetone, dibenzoylmethane [1] and 3,5-heptanedione by quantum chemical calculations, microwave spectroscopy and core level photoemission study. These molecules show intramolecular hydrogen bonds, in which a proton is located in a double well potential, whose barrier height is different for the four compounds, allowing us to examine the effect of the shape of double well on photoemission and rotational spectra. For all of them, two distinct O 1s core hole peaks are observed, previously assigned to two chemical states of oxygen in the ground state. We provide an alternative assignment by taking full account of the finite temperature of the samples based on quantum chemical calculations and symmetry consideration.

A13.

[1] J. Phys. Chem. Lett. 2018, 9, 521.

Sensing the molecular structures of alkyl methyl ketones by internal rotation in the microwave spectrum

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A1.4.

Predicting and understanding the barriers to internal rotation in ketones is a difficult task, even with the assistance of modern quantum chemical methods. Previous studies on ketones containing an acetyl methyl group as an internal rotor have shown that the barrier height ranges from about 170 cm^{-1} to 440 cm^{-1} apparently without any trend. In the present work, we systematically recorded a series of alkyl methyl ketones, which are (a) pentan-2-one, (b) hexan-2-one, (c) heptan-2-one and (d) octan-2-one (see Figure 1), using pulsed molecular jet Fourier transform microwave spectrometers operating in the frequency range of 2 – 40 GHz. All spectra exhibit torsional splittings due to internal rotation of the acetyl methyl group and they were fitted to measurement accuracy with the programs XIAM and BELGI.

For each molecule, at least two conformers could be identified in the spectrum. The first conformer type features a straight alkyl chain and an acetyl methyl barrier height of $185 \pm 3 \text{ cm}^{-1}$. In case of the second kind of conformers the alkyl chain is bent with the γ -carbon (the third carbon atom of the alkyl chain counted from the carbonyl group) in a synclinal position. Here, the barrier height is $235 \pm 3 \text{ cm}^{-1}$. In addition, a third conformer with a barrier value of 182 cm^{-1} was found for hexan-2-one. In this conformer, the δ -carbon of the alkyl chain is located in a synclinal position.

These observations allow to link the experimentally deduced barrier heights with the positions of the γ -carbon and thus to establish a first rule to predict the barrier heights of acetyl methyl groups in ketones: If the γ -carbon of an alkyl methyl ketones is located in the C-(C=O)-C plane, the barrier height is about 185 cm^{-1} . If the γ -carbon position is synclinal, a barrier of approximately 235 cm^{-1} is observed.

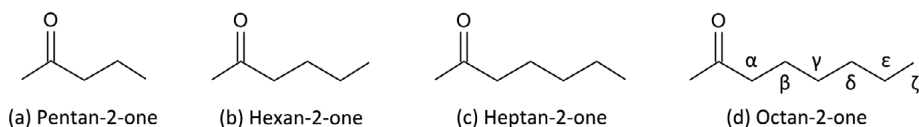


Figure 1: Systematic investigations on alkyl methyl ketones.