

Spin–torsion dominated hyperfine splittings in the first excited torsional state ($v_t = 1$) of Methanol

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Doublet, triplet and quartet hyperfine splittings have been observed in the E–species component of the first excited torsional state ($v_t = 1$) of CH₃OH. Four series of lines dominate the available data: (i) a $K = 6 \leftarrow 7$, Q branch series of quartets, with $7 \leq J \leq 15$; (ii) a $K = 3 \leftarrow 2$, Q branch series, with $3 \leq J \leq 18$, which starts as quartets, changes to doublets at $J = 7$, and then finally to singlets at $J = 17$; (iii) a $K = -2 \leftarrow -3$, P branch series of doublets, with $8 \leq J \leq 12$; and (iv) a $K = 8 \leftarrow 7$, Q branch series, with $8 \leq J \leq 24$, which starts as triplets and becomes doublets at $J = 15$. There are also a few isolated doublets and quartets, which do not form long spectroscopic branches. We have modeled the hyperfine quartet and doublet splittings with empirically chosen symmetry–allowed spin–torsion and spin–rotation interaction terms appropriate for the two $I = \frac{1}{2}$ spin systems arising from the OH proton and from the CH₃ protons, respectively, and have achieved a least–squares fit of 144 hyperfine components (88 hyperfine intervals to six hyperfine parameters with a standard deviation (0.97 kHz) near experimental measurement accuracy. The physical effects included in the present Hamiltonian differ from those included in the Hamiltonian for our earlier work on hyperfine splittings in $v_t = 0$ E states, because the experimentally observed $v_t = 1$ splittings are found to decrease approximately as $1/J$, whereas the $v_t = 0$ splittings increase approximately as J . The position and relative intensities of the weak central features of the triplets can be explained as three–level Λ –type crossover resonances. Our fitted C_{xx} –OH, C_{yy} OH and C_{zz} OH empirical spin–rotational parameters compare well with ab initio calculations in the literature, and our fitted C_{za} OH and C_{za} CH₃ empirical spin–torsion parameters agree and disagree with ab initio calculations in the literature.

Extension of the normal mode approach to nonrigid polyatomic molecules

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In this talk, we will present an extension of our theoretical approach initially designed for semirigid molecules to more complex systems having at least one large amplitude motions (LAM) commonly known as nonrigid (floppy) molecules. This study will be essentially based on the Hamiltonian introduced in 1970 by Hougen, Bunker and Johns [1], the so-called HBJ model which could be considered as the nonrigid extension of the Watson–Eckart Hamiltonian. A complete and detailed derivation based on the HBJ approach with application to triatomic floppy molecules was made by Jensen [2]. A formulation in terms of internal coordinates has been carried out in [3]. One of the specificities of the present work is the possibility of using most of the tools previously developed in our laboratory for semirigid molecules (reduced Hamiltonian, compressed basis sets, tensor operators, etc.), with only some minor changes. Here, we have chosen a formulation quite different from what is usually done in the literature. To this end, the numerical treatment of the LAM coordinate is replaced by an algebraic formulation where all matrix elements (both for the small and large amplitude vibrations) are computed analytically to make variational calculations faster [4]. Illustrative examples will be given.

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Essentially free internal rotation of the Propynyl Methyl group investigated by microwave spectroscopy

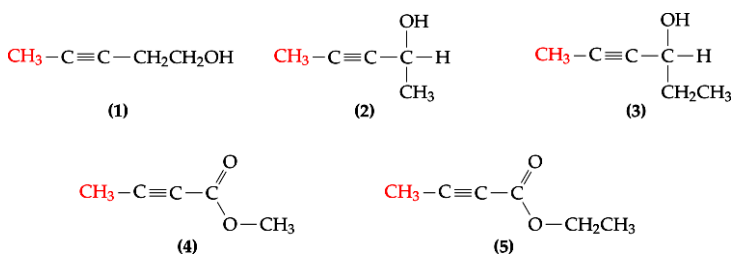
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Fourier transform microwave spectroscopy has become the most important method to investigate large amplitude motions of a molecule, where internal rotation is among the main fields of interest. Due to higher resolution and more accurately determined molecular parameters in comparison to for example fluorescence or electronic spectroscopy, many barriers to internal rotations have been determined by this method. Still only very few molecules with barriers lower than 30 cm⁻¹ have been studied. The rotational spectra of such molecules are hard to assign and model because of large torsional splittings up to several GHz and because high order terms in the Hamiltonian are often required to reproduce the spectra to experimental accuracy. A very low barrier to internal rotation arises by separating the methyl rotor from the rest of the molecule by the acetylenic group with cylindrical symmetry. Only six molecules of the type CH₃-C≡C-R had been studied by microwave spectroscopy before (R = CD₃, SiH₃, CH₂OH, COF, COOH, CH₂Cl [1–6]). The three-fold barrier to internal rotation of the CH₃-C≡C- methyl group (the propynyl methyl group) is lower than 10 cm⁻¹ in all cases.

This work presents the microwave studies and quantum chemical calculations carried out at the MP2/6-311++G(d,p) level of theory on 3-pentyn-1-ol (**1**, R = CH₂CH₂OH, V₃ = 9.4552(94) cm⁻¹ [7]), 3-pentyn-2-ol (**2**, R = CH(OH)-CH₃, V₃ ≈ 9.0 cm⁻¹), 4-hexyn-3-ol (**3**, R = CH(OH)-CH₂CH₃, 3 conformers, V₃ = 7.161012(7) cm⁻¹, 4.2365(26) cm⁻¹ and 7.9016(39) cm⁻¹), methyl-2-butynoate (**4**, R = COOCH₃, V₃ = 0.4690(36) cm⁻¹) and ethyl-2-butynoate (**5**, R = COOCH₂CH₃, 2 conformers, V₃ = 0 cm⁻¹ and 0 cm⁻¹). The experimental spectra were reproduced to measurement accuracy using the programs XIAM and BELGI. The determined barriers to internal rotation are very low as expected, and seem to decrease with increasing length of the carbon chain.



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Microwave spectroscopic and quantum chemical studies of the coupled large amplitude motions in *S*-Phenyl Thioacetate

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S-Phenyl thioacetate belongs to the thio analogs of the class of unsaturated acetates, which were well-investigated using microwave spectroscopy e. g. butadienyl acetate [1], vinyl acetate [2], and isopropenyl acetate [3]. In contrary to the planar butadienyl and vinyl acetate, isopropenyl acetate has a non-planar structure. This leads to a significant difference in the barrier height to internal rotation of the acetyl methyl group ($151.492(34)$ cm^{-1} for vinyl acetate and $135.3498(38)$ cm^{-1} for isopropenyl acetate). *S*-phenyl thioacetate is a challenging project, especially regarding the questions of planarity and barrier height.

Quantum chemical calculations were performed with the B3LYP and MP2 methods in combination with different basis sets. All levels of theory yielded a pair of enantiomers as the most stable structure of *S*-phenyl thioacetate. The acetyl methyl group undergoes internal rotation with a predicted barrier height in the range of 48–72 cm^{-1} , depending on the applied method. A further large amplitude motion, the tunneling of the phenyl group, also occurs. Accordingly, the potential energy curves for the phenyl torsion features double minima and the $v_t = 0$ state is lower in energy than the local maxima. Though the $v_t = 1$ state transitions are too weak to be detected under our measurement conditions, Coriolis interaction still leads to significant shifts of the $v_t = 0$ state lines if compared to the predicted frequencies. This tunneling motion of the phenyl ring coupled with the methyl internal rotation with relatively low barrier height complicated the assignment tremendously. Nevertheless, the microwave spectrum was assigned successfully. However, developing an appropriate Hamiltonian to correctly capture the large amplitude motions of *S*-phenyl thioacetate is indispensable and currently in progress.

Finally, a comparison is drawn to the oxygen-analogue phenyl acetate, phenyl formate [4], as well as the *anti,anti*- and *anti,gauche* conformers of ethyl thioacetate [5].

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Separately fitting the torsional symmetry species of molecules with one or multiple internal rotor(s)

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In the last decade molecular jet based Fourier transform microwave (MJ-FTMW) spectrometers have become more and more popular. The complexity of molecules studied by the MJ-FTMW method also increased dramatically. Molecules with one or two internal rotor(s) and low potential barriers are quite commonly investigated systems today, and also studies on three- or four-rotor molecules exist.

In many cases all torsional symmetry species can be observed in the ground state ($v_t = 0$) but not in the excited states. Therefore, it is usually not possible to discriminate between V_3 and V_6 contributions to the potential function. It is also difficult to fit potential coefficients and the moment(s) of inertia of the internal rotor(s) simultaneously, and the determination of potential coupling terms often fails.

For all these reasons it is useful to fit the different symmetry species separately. This is a well-known method for the A species where a rigid rotor Hamiltonian supplemented by centrifugal distortion terms can be applied. It is also possible to do this with any other symmetry species if angular momentum operators of odd power, e.g. P_z , P_x , P^2P_z , are included in the Hamiltonian. We wrote a computer code, which allows to define any possible operator composed of linear combinations of products of P_z , $P_x = P_x + iP_y$, and $P_- = P_x - iP_y$ directly in the input file. In addition, nuclear quadrupole coupling of one nucleus can be treated in a first order approach.

We will present details of the new computer code and give some applications for molecules with one to four internal rotors with and without nuclear quadrupole coupling, as well as discuss how the odd-power parameters can be interpreted in terms of torsional barriers, and how they can be used to identify an observed symmetry species. Because the new code is rather fast, some sample fits will be run during the presentation.