

Quantum dynamics of intramolecular CCOH torsional motions in 1-Naphthol followed through the OH stretching chromophore

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Abstract: Intramolecular vibrational dynamics of CCOH torsions and OH stretching vibrations in 1-naphthol were followed by Fourier transform infrared (FTIR) spectroscopy and quantum-theoretical computations. The possibility of unintentional trans \rightarrow cis transformation induced by broad- and narrow-band incident IR radiation during the standard IR experiment was considered in detail. Spontaneous transitions from cis to trans rotamer by both classical rotation over the potential barrier as well as by quantum tunneling were analyzed by combining experimental data and theoretical calculations. Torsional correlation times for the cis \rightarrow trans transitions were calculated by purely classical and quantum mechanical approaches. Both adiabatic and diabatic torsional potentials were considered in this context. At the same time, Anharmonic vibrational frequencies of the OH stretching chromophore were calculated within a one-dimensional approximation for both cis and trans conformers of 1-naphthol. This was done by carrying out a series of pointwise energy calculations at series of intramolecular geometries corresponding to excitation of the OH stretching local mode, subsequently fitting the data to a fifth-order polynomial function, transforming the bond stretching coordinates to Simons-Parr-Finlan coordinates and finally numerically solving the vibrational Schrödinger equation by variational technique. Excellent agreement between theoretical calculations (carried out at MP2/6-311++G(3df,3pd) and B3LYP/6-311++G(3df,3pd) levels) and experimental data were obtained for the differences in OH stretching frequencies in trans and cis conformers ($\Delta\nu(\text{trans}\rightarrow\text{cis})_{\text{ex.}} = +13\text{cm}^{-1}$, $\Delta\nu(\text{trans}\rightarrow\text{cis})_{\text{B3LYP.}} = +12.6\text{cm}^{-1}$). Frequency blue shift-induced upon trans \rightarrow cis conformational change occurs as a consequence of intramolecular vibrational confinement. The OH stretching chromophore is a very sensitive probe for both intra- and intermolecular dynamics of the title system. It is therefore a rather significant indicator of the molecular environment in condensed phase systems.

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Key words: 1-naphthol, OH stretching chromophore, intramolecular torsions, FT-IR spectroscopy, quantum dynamics.

1. INTRODUCTION

Cooperation between the stacking (π - π) interaction and hydrogen bonding is of essential importance in formation of biological systems and organic crystals. As a typical example, the secondary structure of DNA (double stranded system) is stabilized by both π - π and hydrogen bonding between nearest-neighbor bases on opposite strands (Saeki et al.2007; Xiao et al.2021; Kouyama et al.2006). Therefore, gaining information about the cooperation between the two types of noncovalent intermolecular interactions at fundamental level is of key importance for life sciences (Muzomwe et al.2013; Niehaus, 2007). Simple aromatic systems as phenol and naphthol's are typical model systems for studies of such cooperation as they can take part in both hydrogen bonding (through the hydroxyl group) and in stacking interactions (through the aromatic rings) (Pejov et al.2005;2015). For those reasons, both phenols

and naphthol's have been extensively studied, both theoretically and experimentally. Laser spectroscopic techniques applied on size-selected clusters have been inevitable in understanding of the interaction phenomena. However, due to the complexity of the obtained spectral picture, close cooperation between theory and experiment is crucial to understand what has been ‘‘seen’’ by spectroscopic techniques, at molecular level (Petreska et al.2008;2011; Premont Schwarz et al.2013). Most of the routine quantum chemical studies of clusters involving the mentioned model systems have relied on exploration of potential energy surfaces (PESs) in the sense of searches for stationary points there on and subsequent automated computations of mass-weighted second-derivative matrix (Hessian), i.e. finally the harmonic vibrational frequencies within the normal mode concept (Premont Schwarz et al.2015). Hydrogen bonding interaction occurs between segments containing H atom attached to a

“heavy atom”; therefore, vibrational motion of hydrogen is a typical primer of large amplitude motion characterized with substantial Anharmonic character (Premont Schwarz et al.2011). For a fundamentally correct description of the experimentally observed phenomena, therefore, one has to go beyond the standard harmonic approximation and rely on the cut through the complete PES, corresponding to excitation of the O-H vibrational motion (Psciuk et al.2015). Additional complication in the studied systems is the conformational flexibility of the CCOH fragment, i.e. the possibility of existence of various conformers and their mutual interconversion. The possibility to understand and control the dynamics of these intramolecular hindered rotors opens the possibility of controlling the conformationally-gated reactive and nonreactive molecular properties (Tokhadze et al.2003).

2. COMPUTATIONAL DETAILS

2.1. Anharmonic vibrational frequency calculations

In our approach, instead of using an arbitrary scaling procedure to correct for the known systematic errors, we accounted explicitly for the anharmonicity of the O-H stretching motion, using a computationally feasible approach. To obtain the vibrational potential energy function ($V=f(r_{\text{OH}})$) for a O-H oscillator, a series of 20 pointwise, DFT (B3LYP/6-311++G(3df, 3pd)) or MP2 (MP2/6-311++G(3df, 3pd)) energy calculations were performed for each O-H oscillator, varying the O-H distances from 0.900 to 1.375 Å with a step of 0.025 Å. The nuclear displacements corresponding to the O-H stretching vibration were generated keeping the center-of-mass of the vibrating O-H fragment fixed, to mimic as closely as possible the real normal mode. The obtained energies were least-squares fitted to a fifth-order polynomial in Δr_{OH} ($\Delta r = r - r_e$):

$$V = V_0 + k_2 \Delta r^2 + k_3 \Delta r^3 + k_4 \Delta r^4 + k_5 \Delta r^5$$

The resulting potential energy functions were subsequently cut after fourth order and transformed into Simons-Parr-Finlan (SPF) type coordinates:

$$\rho = 1 - r_{\text{OH,e}}/r_{\text{OH}}$$

(where $r_{\text{OH,e}}$ is the equilibrium, i.e. the lowest-energy, value).

The one-dimensional vibrational Schrödinger equation was solved variationally within the harmonic oscillator basis. The fundamental *anharmonic* O-H stretching frequency was computed from the energy difference between the ground ($|0\rangle$) and first excited ($|1\rangle$) vibrational states.

2.2. Quantum mechanical analysis of cis-trans interconversion process

The dependence of the potential energy on the orientation of the -OH group was obtained by fitting to the points determined from the solutions of the Kohn-Sham or CPHF equations for different CCOH dihedral angles in the range between 0 and 180 degrees (computed with a step of 10°). Two types of torsional potential energy calculations were carried out for the free rotor-stator molecule in the present study. In the first approach, all intramolecular parameters were kept fixed while only the relevant torsional angle was varied - a “rigid PES scan”. This type of intersection through the complete PES, corresponding to the CCOH torsional angle at constant values of other parameters, can be used for a sort of adiabatic analysis

of the torsional transitions. In the second approach, the “relaxed PES scan”, all the other intramolecular parameters were allowed to relax at each constant φ (CCOH) value. The CCOH torsional Hamiltonian:

$$\hat{H}_{\text{torsion}} = -\frac{\hbar^2}{2I_\varphi} \frac{\partial^2}{\partial \varphi^2} + V(\varphi)$$

was written with a most general form of a periodic hindering potential expressed as a Fourier series:

$$V(\varphi) = V_0 + \sum_{n=1}^{\infty} [V_n \cos(n\varphi) + V_n' \sin(n\varphi)]$$

where φ denotes the relevant torsional coordinate. The one-dimensional torsional Schrödinger equation was solved variationally, using free rotor basis functions. All calculations in the present study were carried out by Gaussian09 series of programs.

3. RESULTS AND DISCUSSION

Geometries of the two conformers of free 1-naphthol corresponding to the minima on MP2/6-311++G(3df,3pd) potential energy surface (PES) are shown in Figure 2.

The system

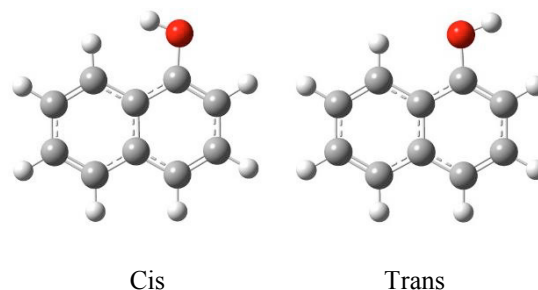


Figure 1. Optimized geometries of cis- and trans conformers of 1-naphthol and the pathway to their interconversion at MP2/6-311++G(3df,3pd) level of theory.

The corresponding computed structural parameters at both DFT (B3LYP/6-311++G(3df, 3pd)) and MP2/6-311++G(3df,3pd) levels of theory are compared to the available experimental data in Tables 1 and 2. Tables 1 and 2, also, contains the theoretical and experimental values of the changes in structural parameters of this molecular system upon trans \rightarrow cis interconversion.

Vibrations

All experiments are carried out at finite temperatures ($\gg 0$ K)

thermal energy could induce interconversion between rotameric forms



or



the source of incident radiation in the IR experiment could itself induce interconversion between rotameric forms



It is therefore important to be able to distinguish the essential spectroscopic features of the two conformers, which are crucial for their detection and, potentially, quantification.

Table 1. Calculated harmonic OH stretching frequencies for the cis and trans conformers and the corresponding “frequency shift” upon trans-cis interconversion

| | MP2 | B3LYP |
|----------------------------------|---------|---------|
| ν (cis) / cm^{-1} | 3880.99 | 3846.90 |
| ν (trans) / cm^{-1} | 3860.23 | 3831.46 |
| $\Delta\nu$ / cm^{-1} | 20.76 | 15.44 |

Table 2. Relaxed CCOH torsional potential computed at MP2/6-311++G(3df,3pd) level of theory, together with the identification of minima

| | MP2 | B3LYP |
|----------------------------------|---------|---------|
| ν (cis) / cm^{-1} | 3731.89 | 3703.14 |
| ν (trans) / cm^{-1} | 3714.13 | 3690.51 |
| $\Delta\nu$ / cm^{-1} | 17.76 | 12.63 |

The computed Anharmonic OH stretching frequencies at both levels of theory are in better agreement with the experimental data in comparison to the harmonic ones. B3LYP Anharmonic values for the frequency shifts are in excellent agreement with the experiment. Higher OH stretching frequencies in the cis conformer are due to the intramolecular vibrational confinement due to the H...H contact (“wall effect”). Two conformers are spectroscopically distinguishable.

3.1. Torsional dynamics

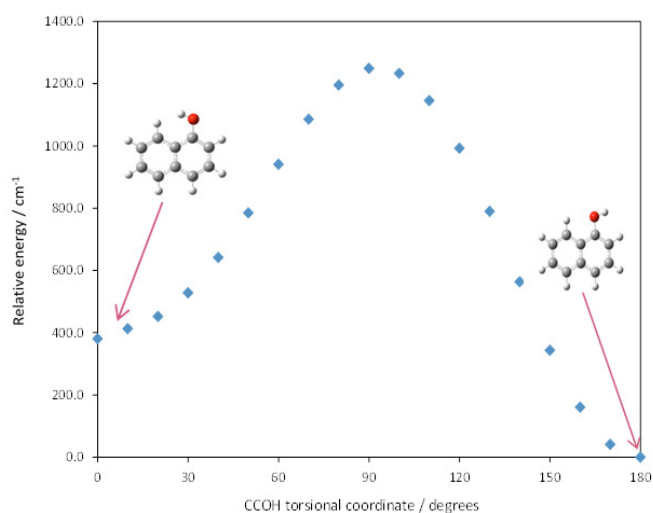
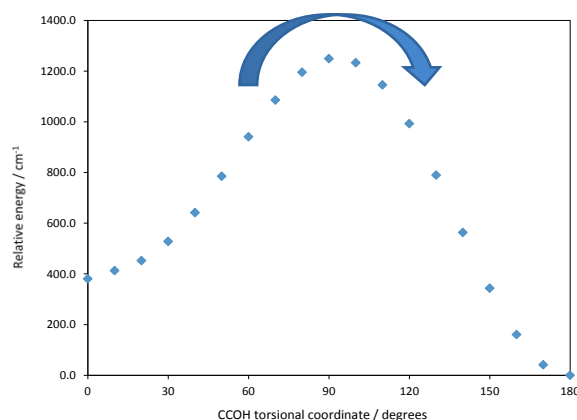
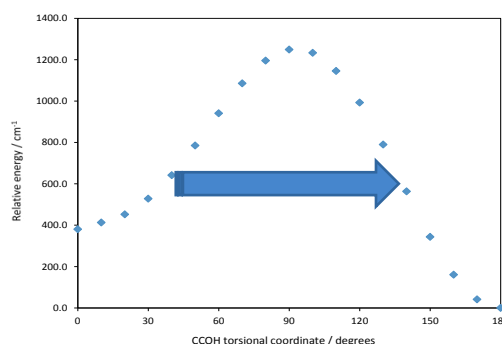


Figure 2. Relaxed CCOH torsional potential computed at MP2/6-311++G(3df,3pd) level of theory, together with the identification of minima



a)



b)

Figure 3. Transition between minima on the torsional potential (i.e. cis-trans conformational interconversion) can occur by: a) Classical over-the-barrier transition (e.g. thermally induced) and b) Quantum tunneling (through-the-barrier transition)

At low temperatures, the trans form of 1-naphthol is more stable conformer. However, the trans \rightarrow cis transformation can be induced by both narrowband and broadband IR radiation. A fundamental question that arises from the previous statement is the following:

Can the less stable conformer of 1-naphthol be unintentionally formed by the incident IR radiation in a standard MIR or NIR experiment??? In other words, can we unintentionally generate the less stable conformer in the course of our efforts towards structural identification of the present conformers?

On the other hand, once the less stable conformer is formed, it can relax back to the more stable one by two main processes:

- (i) classical over-the-barrier rotation
- (ii) Quantum tunneling through the barrier

To compute exactly the transition probability by the quantum tunneling processes, the eigenvalues and eigenfunctions of the torsional Hamiltonian need to be calculated in the first stage. The results from our study obtained at MP2/6-311++G(3df,3pd) and B3LYP/6-311++G(3df,3pd) levels of theory are shown in the figures below. Each level belongs to its own “well”, as can be seen from the spread of the torsional

wavefunctions. Note, however, that states corresponding to energies larger than the torsional barrier correspond to pretty much delocalized wavefunctions. In the case of states close to the barrier, the partial wavefunction delocalization due to interwall tunneling becomes evident.

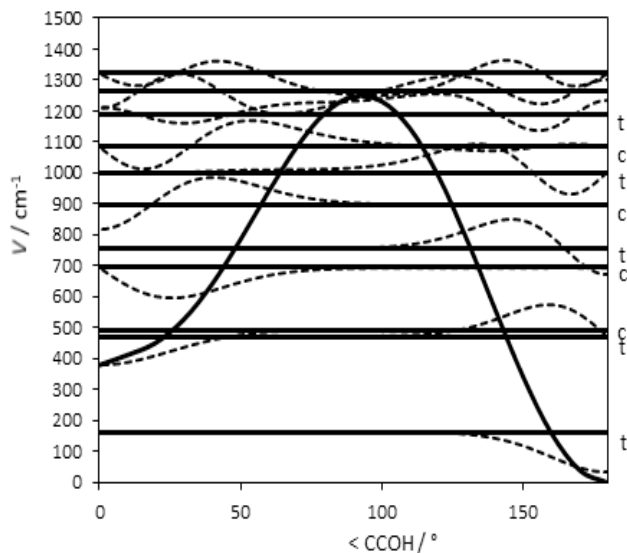


Figure 4. Energy levels and torsional wavefunctions computed for the relaxed CCOH MP2/6-311++G(3df,3pd) torsional potential (t-trans well level; c-cis well level)

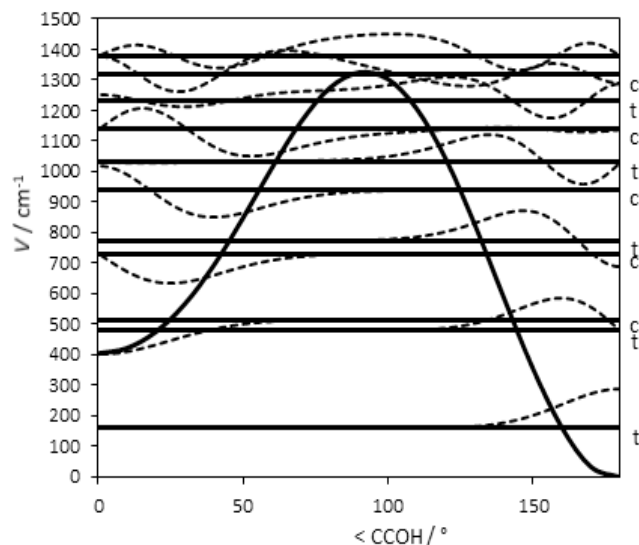
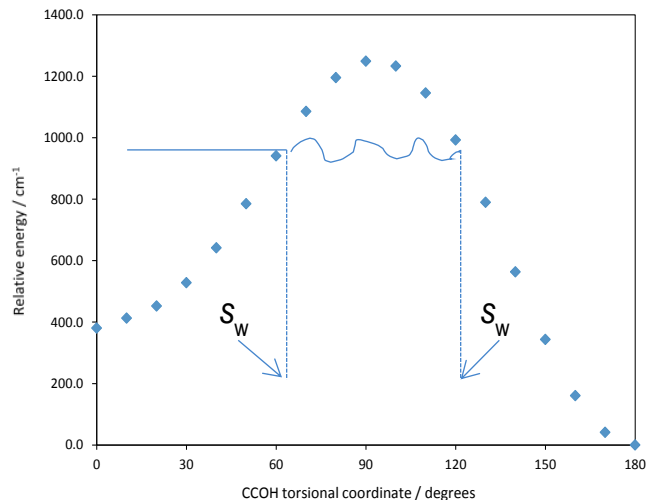


Figure 5. Energy levels and torsional wavefunctions computed for the relaxed CCOH B3LYP/6-311++G(3df,3pd) torsional potential (t-trans well level; c-cis well level)

3.2. Tunneling dynamics

The permeability of the torsional barrier to tunneling processes was estimated employing the quasi-classical (WKB) approximation. Permeability G from energy level E is given by:

$$G_E = \left\{ 1 + \exp \left[\frac{2\sqrt{2\mu}}{\hbar} \int_{s_{w1}}^{s_{w2}} \sqrt{V(s) - E} ds \right] \right\}^{-1}$$



where $sw1$ and $sw2$ denote the classical turning points in the wells separated by the barrier.

The overall thermally activated rate constant for the tunneling process is a Boltzmann-weighted sum over the rates from each torsional level, i.e.:

$$k(T) = \frac{\sum_i k_i \exp\left(-\frac{E_i}{kT}\right)}{\sum_i \exp\left(-\frac{E_i}{kT}\right)}$$

The computed rate constants imply that both conformers can be identified on timescales characteristic for the infrared spectroscopic measurements. However, WKB – based results in the context of the studied phenomenon should be taken cautiously. This is so since the observed tunneling is a dissipative phenomenon. Thus, an exact quantum mechanical evaluation of the tunneling probability should take into account the environmental influence in a much more exact manner. Our further efforts are directed towards achievement of this aim.

4. CONCLUSIONS

On the basis of the relaxed potential energy profiles of the torsional motion along the cis \rightarrow trans transformation coordinate computed at MP2/6-311++G(3df,3pd) and B3LYP/6-311++G(3df,3pd) level of theory, we have concluded that the cis conformer is the less stable one. The same conclusions could be derived also from statistical thermodynamics of the stationary points located at the cis and trans minima on the potential energy surfaces (both of which correspond to real minima). We have also computed the Anharmonic OH stretching frequencies for the cis and trans conformers of 1-naphthol and the corresponding differences.

This was done by series of pointwise calculations of energies at series of geometries corresponding to positions of O and H atoms within the phenolic OH group upon excitation of the O-H stretching vibrations. We did both geometry generation and Anharmonic frequency calculations with our own nonstandard computer codes. The recent experimental value obtained in solid cryogenic matrices is approximately $+13\text{ cm}^{-1}$. Our DFT value is therefore in excellent agreement with the experimental data. Such notable shift in principle implies that the two forms of 1-naphthol could be distinguished by IR spectroscopic methods even in the liquid phase, applying contemporary curve resolution methods on our experimental IR data.

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