Evidence of the Methyl Rotation in Liquid Toluene in the Raman Spectrum

Josef Kapitán* and Petr Bouř*
Abstract

Fine features of the liquid phase toluene Raman backscattering spectra were analyzed on the basis of quantum Hamiltonian comprising the methyl group rotation and the angular dependence of vibrational frequencies and polarizability derivatives. The separation of the rotation from the other vibrational motions appeared necessary in order to explain relative intensity ratios of several bands and an anomalous broadening of the spectral intensity around 1440 cm\(^{-1}\). The results suggest that the CH\(_3\) group in the liquid phase rotates almost freely, similarly as in the gaseous phase, and the molecule effectively exhibits the C\(_{2v}\) symmetry. A classical description and an adiabatic separation of the methyl rotation from other molecular motion previously used in peptide models is not applicable for the toluene because of a strong coupling with other motions. Density functional computations, particularly the BPW91 functional, provided good estimates of harmonic frequencies and spectral intensities, as well as qualitatively correct anharmonic corrections to the vibrational potential.
Introduction

Latest advances of molecular manipulation techniques\textsuperscript{1,2} demand reliable computational models enabling one to predict molecular behavior. However, correct quantum description of the microworld is often hampered by undeveloped theory\textsuperscript{3} and inaccurate computational tools.\textsuperscript{4} Particularly, slow molecular motions are difficult to model, as they are associated with tiny energy changes and often suitable neither for classical nor for full quantum description. In this study, we investigate the methyl rotation in liquid toluene, where a simplified quantum description provides a good basis for simulation of the Raman spectrum similarly as for the gas phase. The Hamiltonian involves the rotation of the methyl group as well as the force field aharmonicities. Because of its industrial importance\textsuperscript{5,6} and chemical properties the toluene has been profoundly studied by the means of the vibrational spectroscopy\textsuperscript{7} and computational chemistry.\textsuperscript{8-10} The methyl group itself was recognized as an important factor accelerating the intramolecular vibrational redistribution.\textsuperscript{11,12} The quantum computational techniques were successfully used in the past to interpret torsionally induced absorption\textsuperscript{13} and supersonic jet spectra.\textsuperscript{14}

The suitability of the Raman spectroscopy for monitoring of molecular flexibility, particularly for peptides, has been pointed out in the past.\textsuperscript{15-18} The methyl group rotation in alanine could even change signs of several Raman optical activity bands.\textsuperscript{17} A rigorous quantum modeling in these systems is complicated due to the strong interaction with the solvent. For the toluene, however, small intermolecular interactions\textsuperscript{19} can be neglected and a coherent analytical quantum model of the vibrational behavior can be developed. But its motion cannot be separated from other higher-frequency vibrational modes for detailed spectral interpretation.

Experiment and Computation

The interpreted backscattered Raman spectrum was recorded at room temperature on the GUROAS3 spectrometer described elsewhere.\textsuperscript{20} Apparatus is based on a fast stigmatic spectrograph HoloSpec HS-f/1.4 (Kaiser Optical Systems) equipped with a holographic transmission grating and back-thinned CCD chip (Wright Instruments, Model P 312).
The effect of the CH$_3$ group rotation on the spectra was modeled with the aid of a simplified Hamiltonian containing the harmonic part, free-rotor energy and rotation-vibration interaction.$^{13,14,21-23}$ The rotational perturbation in Eq. (1) was modeled by a six-fold potential according to gas phase spectra analyses.$^7$ The dependence of the transition polarizability$^{24}$ on the methyl rotation was calculated within the density functional theory and fitted with goniometric functions. Complete experimental conditions and computational details are given in the Supporting Information (SI).

![Fig. 1](image_url)  
**Fig. 1** The $\phi$ angle definition and the local coordinate system (dashed axes) used for the definition of the polarizability components in toluene.

**Results and Discussion**

**Geometry.** The methyl group in toluene (Fig. 1) rotates almost freely and the rotational barrier determined from the gaseous spectra is most probably around $\sim 0.014$ kcal/mol,$^7$ although values up to $0.036$ kcal/mol were reported.$^9$ It is quite difficult to reproduce such a small energy difference by available computational methods. (References$^8,9$, Table 1 in SI). Although interesting from the theoretical point of view, however, the knowledge of the theoretical barrier height is not necessary for understanding of the liquid phase spectra at room temperature, where the methyl group behaves as a free rotator. On the other hand, all the computational levels predict as the most stable conformation geometry where one hydrogen atom of the CH$_3$ group lies in a symmetry plane perpendicular to the aromatic system ($\phi=90^\circ$).
The molecule then exhibits the $C_3$ symmetry. The transition conformation ($\varphi=90^\circ$) exhibits the $C_3$ symmetry, too, as one methyl hydrogen lies in the aromatic plane now identical with the symmetry plane.

Fig. 2 From top to bottom: simulated (BPW91/6-31++G**) Raman backscattering spectra of benzene, benzene with a hydrogen of atomic mass 15, toluene, and the experimental toluene spectrum. Symmetry of the main benzene bands is indicated.

**Harmonic spectrum.** The observable Raman spectrum at the region of 200-1650 cm$^{-1}$ can be to a significant extent explained within the harmonic approximation. Moreover, many intensity features can already be derived from the spectrum of benzene perturbed by a heavy residue. This is shown in Fig. 2 where the spectrum of benzene is simulated at the BPW91/6-31++G** level and compared to the spectrum of benzene substituted by a fictitious hydrogen atom of mass 15. Such a substitution perturbs the benzene $C_{6h}$ symmetry and makes visible many symmetry-forbidden transitions. Particularly within 200-1100 cm$^{-1}$ the peak frequencies and relative intensities of the substituted benzene reproduce the theoretical and experimental spectra of toluene (lower two traces in Fig. 2) quite faithfully. Greater
differences can be observed above 1100 cm\(^{-1}\) due to the mechanical coupling of the methyl and phenyl residual motions.

Whereas the CPCM dielectric correction did not provide significant improvement of the vacuum frequencies (SI), spectra obtained by various quantum methods (Figure 3, Table 2s in SI) differ significantly. The MP2 harmonic frequencies mostly overestimate the experimental values and the corresponding relative intensity pattern significantly deviates from the observation. Particularly for the out of phenyl plane hydrogen bending modes (numbers 5, 6 and 12 calculated at 429, 494 and 858 cm\(^{-1}\)) the MP2 method does not appear appropriate. Only a small decrease of the average error (from 88 to 67 cm\(^{-1}\), see Table 2s) can be achieved when the anharmonic corrections are included. Detailed toluene normal mode assignment can be found elsewhere.\(^{10}\)

The BPW91 method provides the best agreement. The anharmonic corrections do not improve the harmonic frequencies for this functional on average, but occasional improvements do occur. Although current computational apparatus is not adequate for a full account of the anharmonic phenomena,\(^{25}\) the best BPW91 method already provides a reasonably good description of the combination bands visible in the IR spectra (Table 3s in SI). At the lower-frequency region, however, the harmonic approximation at this level appears to be an excellent basis for the toluene spectrum modeling.
Fig. 3 Raman toluene spectra simulated at the MP2, B3LYP and BPW91 levels, all with the BPW91/6-31++G** basis set, and comparison to the experiment. Frequencies of A''-symmetry modes are indicated in italics, the bold number at the bottom denote fundamental modes (Table 2 in SI).

**Methyl rotation and band intensities.** Further on (Figures 4-5), we use the BPW91 harmonic force field scaled according to the assignment given in Table 2s. Not all spectral features, however, can be explained by the harmonic models. Most notable is the broad experimental signal between 1400-1500 cm\(^{-1}\) involving modes number 26-29, and also minor differences in intensities of several weaker bands. The weaker bands are magnified in Fig. 4 where the classical Boltzmann averaging of toluene rotamer spectra is compared to the simulation with the full rotation-vibration model. Several improvements are apparent, such as a near disappearance of the two bands at 407 and 695 cm\(^{-1}\) (see the - signs in Fig. 4). This is caused by an effective symmetry increase (C\(_5\)→C\(_{2v}\)) caused by the rotation; in the higher symmetry system these transitions become Raman-forbidden, similarly as in the heavy-hydrogen model (Figure 2). However, although the experimental intensities of these bands are very weak, they do not
disappear completely. One of reasonable explanation of this phenomenon may be a higher methyl-rotational barrier in the liquid phase than found in the gas phase. Indeed, even with the small gas phase value (4.7 cm$^{-1}$) the bands do not disappear completely in the simulations and their intensity and width can be modulated by an arbitrary barrier increase (not shown). In the higher-frequency region (approximately above 800 cm$^{-1}$), however, the rotation leads to an intensity increase of several bands (see the (+) signs in Fig. 4) and broadening of the signal. This is also in qualitative agreement with the experimental shape, although in particular cases, such as the shoulder at the experimental band at 976 cm$^{-1}$, might also be caused by an anharmonic effect which is presently impossible to model accurately.

**Fig. 4** Raman toluene spectra in an amplified intensity scale simulated with the scaled harmonic force field without (top) and with (middle) the rotation-vibration coupling. Signal increases and decreases caused by the rotation are marked by the + and – signs.

**Band broadenings.** The combined harmonic-rotation model, however, explains the broadening of the experimental region within 1400-1480 cm$^{-1}$ only partially. A full explanation has to take into account
the dependence of the harmonic frequencies on the methyl rotation as well as the anharmonic interactions. Indeed, already the differences in the harmonic frequencies of the equilibrium ($\varphi=90^\circ$) and transition ($\varphi=0^\circ$) conformers in this region (columns 2-4 in Table 1) are rather high, up to 8.1 cm$^{-1}$ for mode number 27 predicted by the MP2 method, and suggest a significant broadening of this band due to the rotation. The anharmonic perturbations (columns 5-7) increase the difference almost by one order in magnitudes. The perturbational computation including the rotation-vibration coupling (last column in the Table) predicts an extreme shift of 43 cm$^{-1}$ for the mode number 27.

The dependence of the transitional frequencies on the angle $\varphi$ entering the Hamiltonian as the $a_{16}$ coefficient in Eq. (2) in SI can clearly explain the unusual broadening of the Raman signal around 1440 cm$^{-1}$. This is demonstrated in Fig. 5 where the broadening simulated for the harmonic and anharmonic fundamental frequency dependence on the rotation angle can be compared to the experiment. Although the harmonic differences of the frequencies are significant (several cm$^{-1}$, third column of Table 1), they do not provide sufficient broadening even when they are fully implied in the (methyl) rotation-vibration Hamiltonian (1) (trace A in Fig. 5). However, the values obtained by the most complete anharmonic model (last column in Table 4) not only provide spectra (trace B in Fig. 5) with band broadenings very close to the those observed experimentally, but also correct the relative intensity rations of the three bands centered around 1436, 1466 and 1490 cm$^{-1}$. 
Table 1 Calculated differences (in cm\(^{-1}\)) between the fundamental frequencies for the equilibrium and transition conformers for modes 25-30

<table>
<thead>
<tr>
<th>Mode</th>
<th>MP2/6-31++G** harm</th>
<th>BPW91/6-31++G** harm</th>
<th>BPW91/aug-cc-pvtz harm</th>
<th>BPW91/6-31++G** VCI</th>
<th>BPW91/6-31++G** PT1</th>
<th>BPW91/6-31++G** PT2</th>
</tr>
</thead>
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<tr>
<td>25</td>
<td>-0.4</td>
<td>-1.2</td>
<td>-1.0</td>
<td>-16.7</td>
<td>-5.6</td>
<td>-3.5</td>
</tr>
<tr>
<td>26</td>
<td>-0.5</td>
<td>-1.2</td>
<td>-1.1</td>
<td>-9.0</td>
<td>-12.7</td>
<td>-4.8</td>
</tr>
<tr>
<td>27</td>
<td>8.1</td>
<td>2.3</td>
<td>2.9</td>
<td>-2.2</td>
<td>5.6</td>
<td>43.0</td>
</tr>
<tr>
<td>28</td>
<td>-3.4</td>
<td>-2.3</td>
<td>-1.7</td>
<td>2.4</td>
<td>2.1</td>
<td>-19.0</td>
</tr>
<tr>
<td>29</td>
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<td>0.0</td>
<td>0.2</td>
<td>2.2</td>
<td>-0.2</td>
<td>2.6</td>
</tr>
<tr>
<td>30</td>
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<td>-0.1</td>
<td>0.2</td>
<td>4.0</td>
<td>-1.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The VCI and PT1 anharmonic calculations were performed with the S4 program (Cartesian-base potential, vibration anharmonicities only\(^{18,26-28}\)), whereas the PT2 perturbation was performed with GAUSSIAN (normal mode potential, with the rotation-vibration coupling included\(^{29,30}\)).
Fig. 5 Raman toluene spectra within 1350-1530 cm$^{-1}$ simulated with the harmonic (trace A, column 3 in Table 4) and anharmonic (B, column 7 in Table 4) dependence of the fundamental transition frequencies on the methyl rotation, as compared to the experiment (C).
Conclusions

The modeling explained most of the experimental features observed in the liquid toluene spectra in the 100-1800 cm\(^{-1}\) region and provided important information about the coupling of various molecular motions. The classical averaging of spectra of different conformers did not provide sufficient agreement with the experiment and the quantum Hamiltonian including the vibrational and methyl-rotational motions had to be considered. The rotation increases molecular symmetry and diminishes intensity of several Raman bands. Around 1440 cm\(^{-1}\) coupling of the rotational and vibrational modes causes an anomalous broadening of the Raman signal that could be explained after the anharmonic corrections were considered. The combination of the ab initio techniques and the vibrational Raman spectroscopy thus appears as a very beneficial tool for molecular structural studies.

Acknowledgement

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References


(27) P. Bouř, S4 program; Academy of Sciences: Prague, 1994.

