

Theoretical Investigation of Internal Rotation Barriers and Raman Spectra of 4-(dimethylamino)cinnamaldehyde

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Introduction

Density Functional Theory (DFT) has become the method of choice in the determination of molecular geometry and vibrational structure. Our research focused on the theoretical study of the internal rotation barriers and SERS spectra of 4-(dimethylamino) cinnamaldehyde (DMAC) and the related species, 4-(dimethylamino) cinnamic acid (DMACA)

A number of questions arise in any theoretical study:

- How accurate is the method of choice for the state of interest? Are cost-effective alternatives available?
- Is the choice of basis set crucial?
- Do solvent effects matter?

We address these issues and others related to the calculated harmonic frequencies and the interpretation of the experimentally observed SERS and Raman spectra.

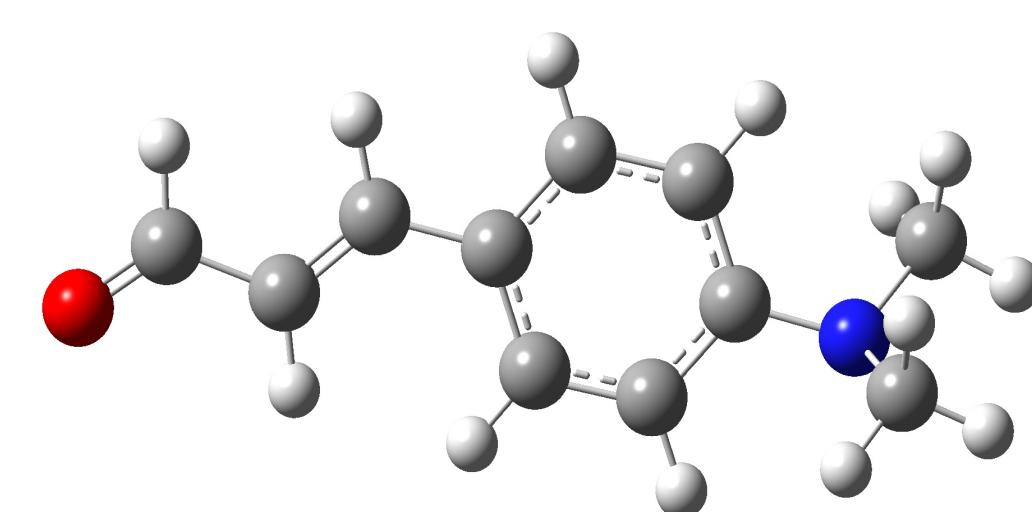


Figure 1.
trans-(4-dimethylamino)
cinnamaldehyde

Theoretical Methods

All DFT calculations were performed using Gaussian '03 [1], with the B3LYP density functional. Basis sets used ranged from 6-31G to 6-311G**(df,pd) basis sets. A basis set study of butadiene also employed more complete basis sets, including up to augmented quadruple zeta functions.

In the basis set study of butadiene, DFT optimizations were carried out with "Very Tight" convergence criteria and "ultrafine" grids for numerical integration. In the DMAC and DMACA studies, convergence criteria and numerical integration parameters were used at their default values.

Results – Basis Set

Feller and Craig[2] have reported a large basis set full-CI study of butadiene in its *trans*, *cis*, and *gauche* conformers. Their calculations reproduced the experimental features[3]. A series of DFT(B3LYP) calculations with up to 6-311G**(df, pd) basis sets on butadiene reproduced the theoretical results of Feller and Craig with errors less than 2.6 kJ/mol. Use of 6-311G* basis sets was sufficient; use of higher quality correlation-consistent basis sets produced no decrease in error; we conclude that most of the error is due to the use of DFT(B3LYP) and that 6-311G* is the most useful basis at this level of calculation. Solvent effects on conformer energies were less than 0.2 kJ/mol.

Results

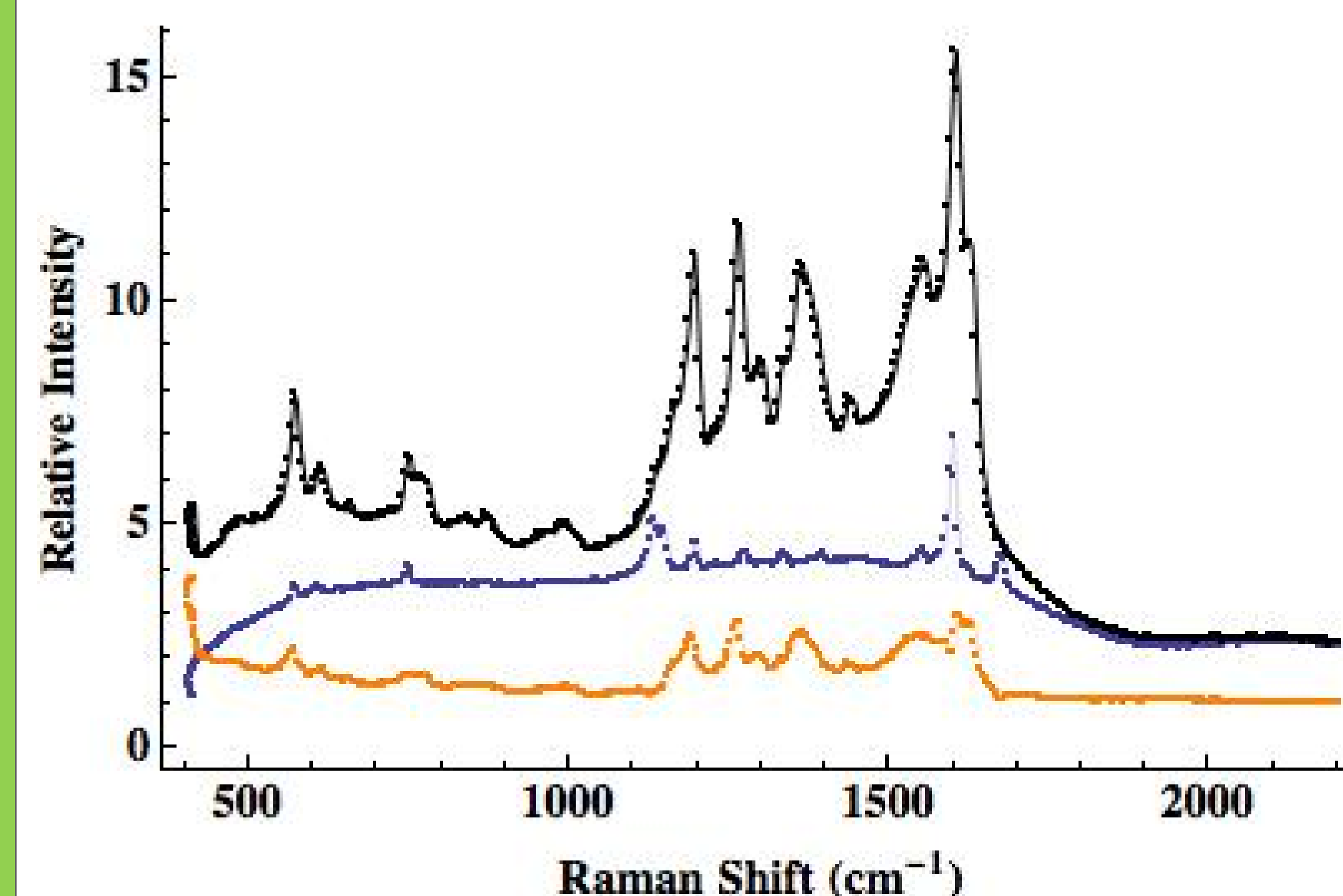


Figure 2 Theoretical SERS spectrum of DMAC compared to that of experimental. Peaks of enhancement are seen in the vicinity of 1200-1600 cm^{-1} .

	Expt [4]	DMAC <i>trans</i>	DMAC <i>cis</i>	DMACA <i>trans</i>
$\tilde{\omega}(\text{cm}^{-1})$	571	563 (211)	547 (113)	1180 (247)
$I(\text{Intensity})$	1191	1139 (2752)	1206 (1790)	1214 (322)
	1263	1300 (1973)	1315 (1485)	1296 (597)
	1362	1360 (1044)	1334 (1501)	1649 (2360)
	1548	1538 (450)	1555 (4572)	
	1608	1571 (610)	1581 (11842)	
	1628	1617 (15799)		

Table 1. Selected Vibrational modes of DMAC and DMACA

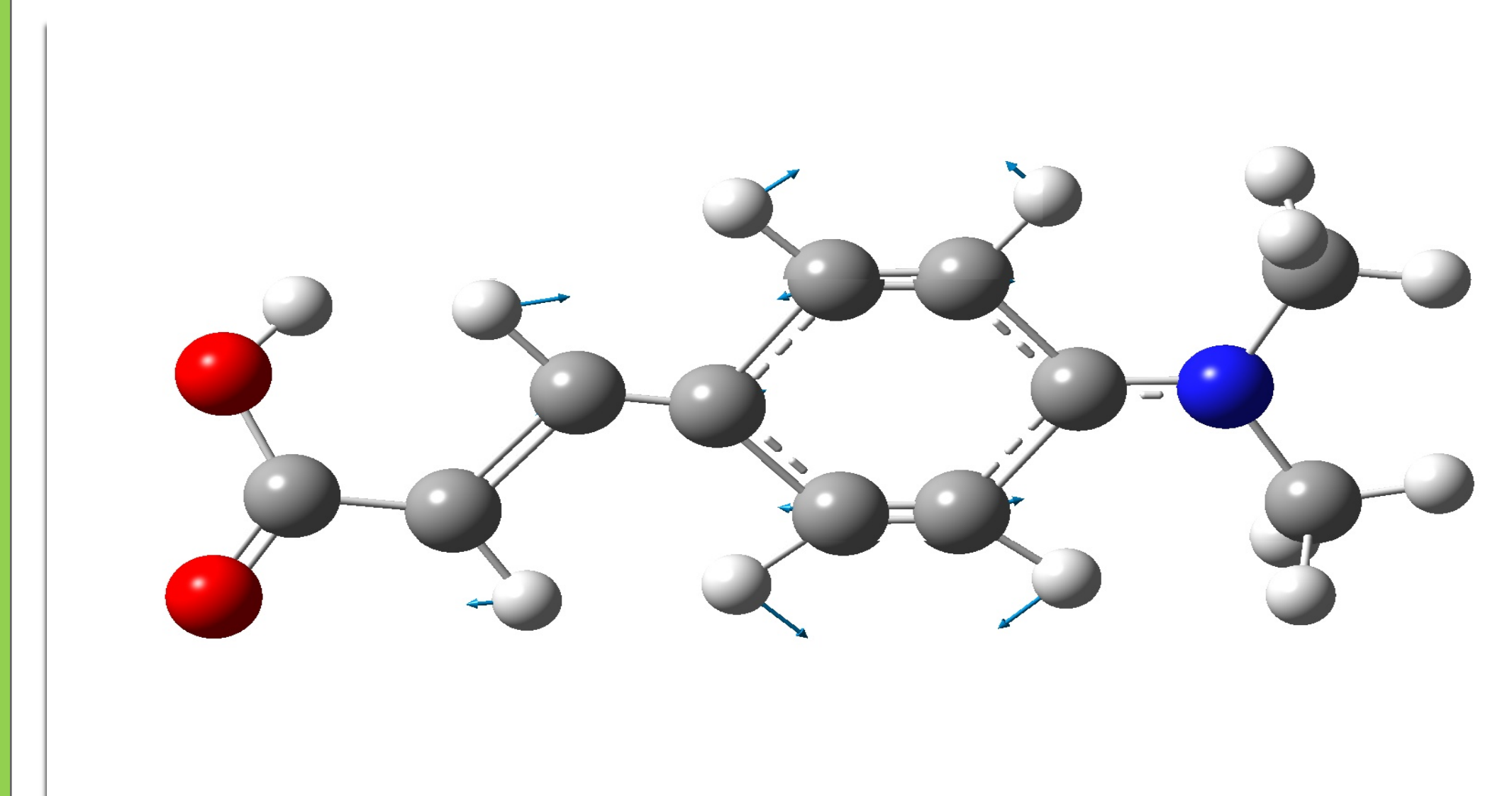


Figure 3. Vibration of DMACA at 1649 cm^{-1} along with displacement vectors. Note the in plane motion

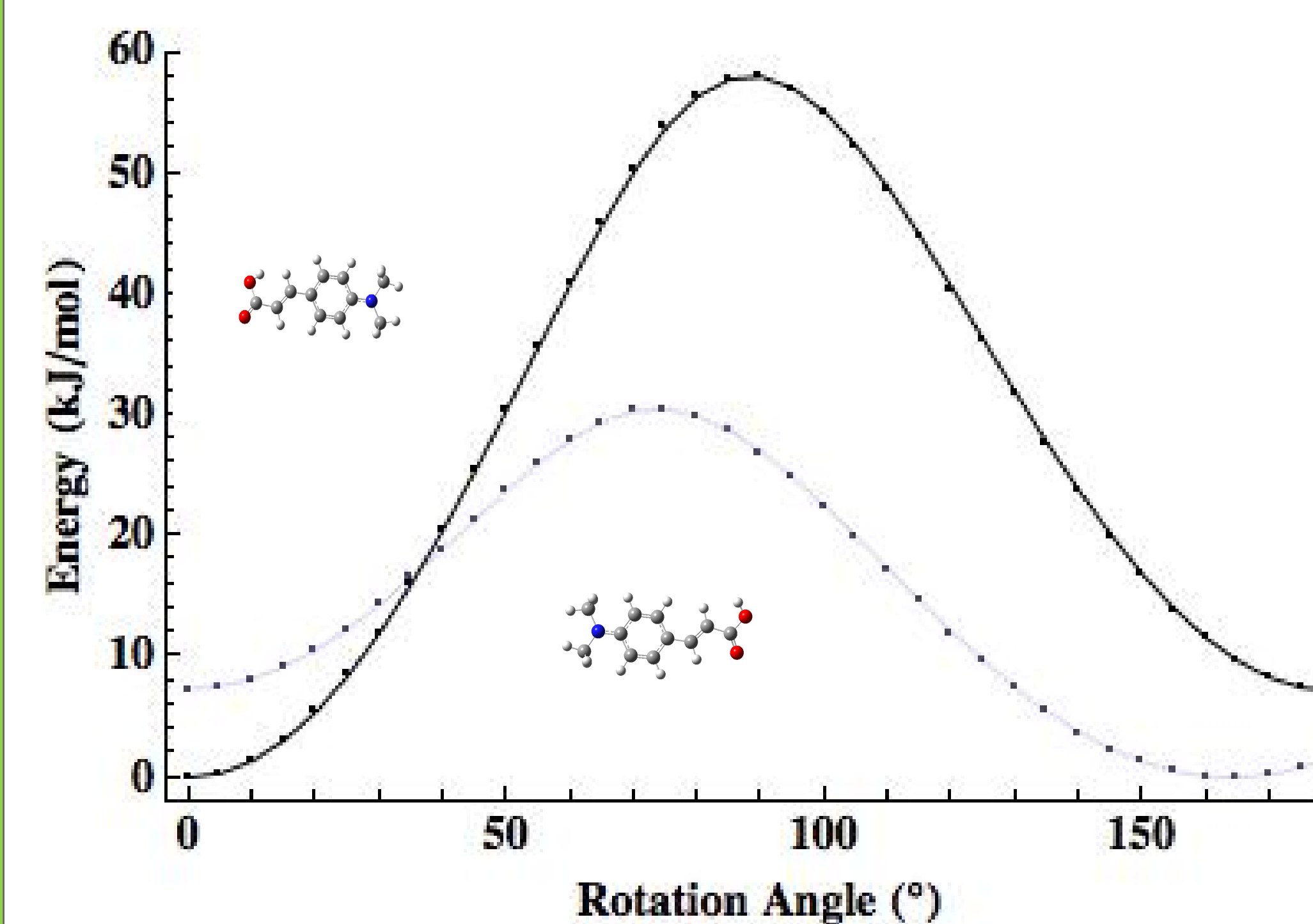


Figure 4. Surface scan of DMAC and DMACA.

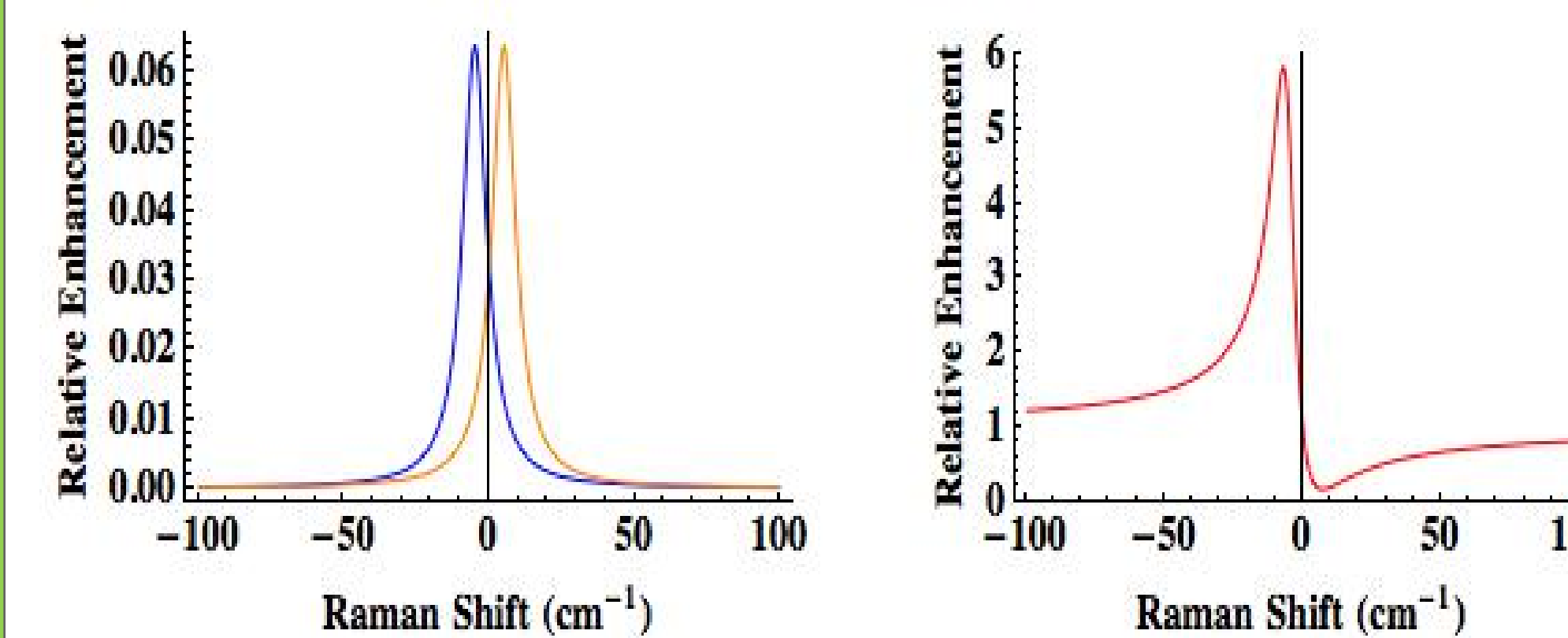


Figure 5. Ratio of two Lorentzians shifted by their full width at half maximum. Note the asymmetric minimum in the ratio

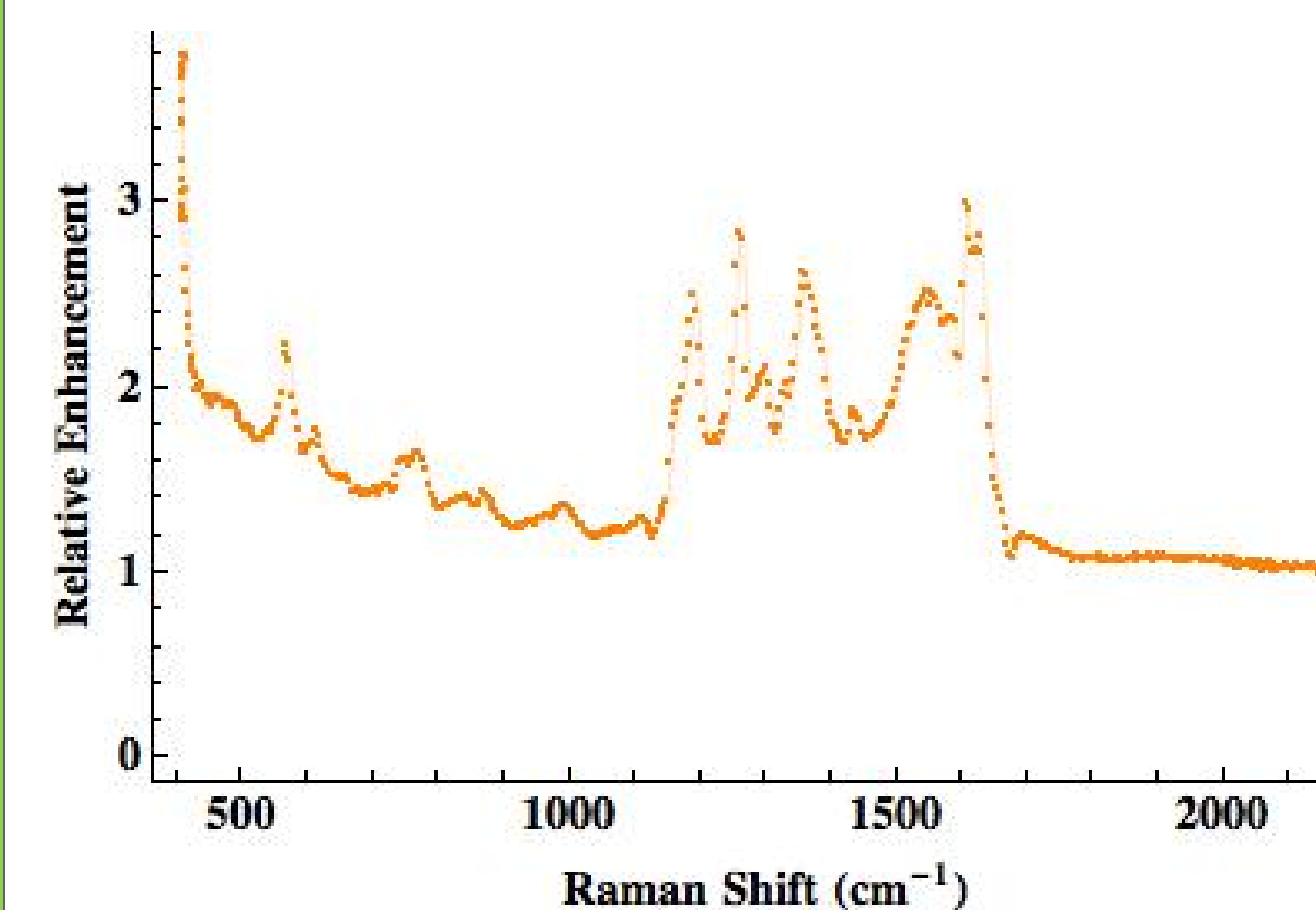


Figure 6. Ratio of SERS to Raman signal of DMAC. Note the dips in the ratio, possibly indicating a change in the chemical environment.

Conclusions

A 6-311G* basis set w/DFT (B3LYP) proved to be cost-effective giving accurate results with less computational time. Calculated solvent (heptane and water) effect on transition barrier of both DMAC and DMACA was less than 1 kJ/mol. Based on results [fig. 4] *trans*-DMAC is more stable than its *cis* conformation. However, *cis* DMACA proved more stable than *trans* DMACA conformation. *Cis-trans* isomers of DMAC and DMACA co-exist but do not interconvert at a significant rate.

Vibrations responsible for enhancement are delocalized in-plane stretches of the carbon skeleton. Significant differences between the Raman of DMAC and DMACA were found. Features in the SERS are associated with changes in the Raman shift.

Literature cited

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Acknowledgments

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For further information

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