Raman spectral evidence of methyl rotation in liquid toluene†‡

Josef Kapitán,*[ab] Lutz Hecht*[a] and Petr Bouř*[b]

Received 12th September 2007, Accepted 16th November 2007
First published as an Advance Article on the web 10th December 2007
DOI: 10.1039/b713965a

In order to rationalize subtle details in the liquid phase toluene Raman backscattering spectra, an analysis was performed based on a quantum-mechanical Hamiltonian operator comprising rotation of the methyl group and the angular dependence of vibrational frequencies and polarizability derivatives. The separation of the methyl torsion from the other vibrational motions appears to be necessary in order to explain relative intensity ratios of several bands and an anomalous broadening of spectral intensity observed at 1440 cm^{-1}. These results suggest that the CH$_3$ group in the liquid phase rotates almost freely, similarly as in the gaseous phase, and that the molecule consequently exhibits effectively C_{2v} point group symmetry. A classical description and an adiabatic separation of the methyl rotation from other molecular motion previously used in peptide models is not applicable to toluene because of a strong coupling with other vibrational motions. Density functional computations, particularly the BPW91 functional, provide reasonable estimates of harmonic frequencies and spectral intensities, as well as qualitatively correct fourth-order anharmonic corrections to the vibrational potential.

Introduction

Recent advances of molecular manipulation techniques[1,2] demand reliable computational models for the prediction of molecular behavior. However, a correct quantum-mechanical description of the microscopic world is often hampered by lack of a sufficiently developed theory[3] and inaccurate computational tools.[4] Particularly, slow molecular motions such as rotations and movements of large molecular parts are difficult to model, as they are associated with only tiny energy changes and are therefore not suitable either for a classical or for full quantum description. In this study, we explore the methyl rotation in liquid toluene, where a simplified quantum-mechanical description provides a suitable basis for the simulation of the Raman spectrum in analogy to the modeling of gas phase spectra. The Hamiltonian involves the rotation of the methyl group as well as force field anharmonicities. Because of its industrial importance[5,6] and chemical properties, toluene has been extensively studied by using vibrational spectroscopy[7] and computational chemistry.[8–10] The methyl group was recognized to be an important factor accelerating the intramolecular vibrational redistribution.[11,12] Quantum computations were successfully used in the past to interpret torsionally induced absorption[13] and supersonic jet spectra.[14]

The suitability of Raman spectroscopy for monitoring the molecular flexibility, particularly for peptides, has been pointed out in the past.[15–18] The rotation of the methyl group in alanine, for example, does even influence the signs of several Raman optical activity bands.[17] However, rigorous quantum modeling in these systems represents a complex problem due to strong solvent interference. Nevertheless, for toluene, only small intermolecular interactions[19] are present and may therefore be safely neglected so that a coherent analytical quantum model of its vibrational behavior may consequently be developed. It actually turns out that the methyl torsion cannot be separated from other higher-frequency vibrational modes for a more detailed spectral interpretation.

Experiment and computation

The backscattered Raman spectrum was measured on the GUROAS3 spectrometer described elsewhere.[20] The instrument 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). Experimental parameters were as follows: room temperature (~293 K), 532 nm excitation wavelength, spectral resolution 6.5 cm^{-1} and total acquisition time 30 s. Samples were held in specially manufactured 4 × 4 × 12 rectangular quartz (Spectrosil) micro fluorescence cell (Optiglass) with an inner path length of 4 mm. The laser power at the sample was 18 mW. The sample was purchased from Fisher Scientific (HPLC grade) and was used without further purification.

The effect of the CH$_3$ group rotation on the spectra was modeled employing a simplified Hamiltonian containing the harmonic part, free-rotor energy and rotation–vibration interaction.[13,14,21–23]

The rotational perturbation was modeled by a six-fold potential according to analysis of gas phase spectra.[7] The dependence of the transition polarizability[24] on the methyl rotation was calculated within density functional theory and

---

[a] *Department of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ. E-mail: kapitan@chem.gla.ac.uk, lutz@chem.gla.ac.uk*
[b] *Petr Bouř, Institute of Organic Chemistry and Biochemistry, Academy of Sciences, Flemingovo nám. 2, 16610 Prague 6, Czech Republic. E-mail: bour@uochb.cas.cz*

† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Further experimental and computatonal details. See DOI: 10.1039/b713965a

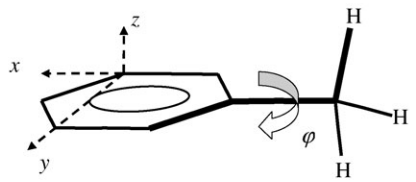

Fig. 1 Schematic diagram of the toluene molecule depicting the rotational ϕ angle and the local coordinate system (dashed axes) used for the polarizability tensor components.

fitted with periodic functions. Further computational details are given in the ESI.‡

Results and discussion

Geometry

The methyl group in toluene (Fig. 1) rotates almost freely. Its rotational barrier determined from the gaseous spectra is most probably $\sim$0.014 kcal mol^{-1},[7] although values up to 0.036 kcal mol^{-1} were reported.[9] It is quite difficult to reproduce such a small energy difference by available computational methods (ref. 8 and 9, Table 1s in the ESI‡). Although such computations are interesting from a theoretical point of view, the knowledge of the theoretical barrier is nevertheless not necessary for the understanding of the liquid phase spectra at room temperature, where the methyl group behaves as a free rotator. Also for the spectral simulations described below the results do not change significantly when the barrier is varied within a reasonable range that is smaller than the Boltzmann thermal energy quantum kT. On the other hand, all the computational levels predict as the most stable conformation where one hydrogen atom of the CH_3 group is positioned in a plane perpendicular to the aromatic ring ($\phi = 90°$). The molecule consequently adopts C_s symmetry. The transition conformation ($\phi = 0°$) exhibits the C_s symmetry, too, as one methyl hydrogen lies in the aromatic plane now identical with the symmetry plane.

Harmonic spectrum

The measured Raman spectrum of neat toluene within the 200–1650 cm^{-1} region can be at least to a large extent rationalized within the harmonic approximation. Many toluene band intensities can already be explained by those of hypothetical 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 that of benzene substituted by a fictitious hydrogen atom of mass 15. Such a substitution reduces the full benzene D_{6h} symmetry to C_{2v}. Many D_{6h} symmetry-forbidden transitions then become allowed. Particularly within the 200–1100 cm^{-1} region the band positions and relative band intensities of the substituted benzene appear to reproduce the theoretical and experimental spectra of toluene (lower two traces in Fig. 2). Greater differences can be observed above 1100 cm^{-1} due to the mechanical coupling of the methyl and phenyl residual motions.

While the CPCM[25] dielectric correction did not provide significant improvement of the vacuum frequencies (SI), spectra obtained by various quantum methods (Fig. 3, Table 2s in the ESI‡) differ significantly. The MP2 harmonic frequencies mostly overestimate the experimentally determined band positions and the theoretical relative intensity pattern deviates significantly from the observation. Particularly for the out-of-plane phenyl hydrogen bending modes calculated to occur at 429, 494 and 858 cm^{-1} the MP2 method does not appear to be appropriate. Only a small decrease of the average error (from

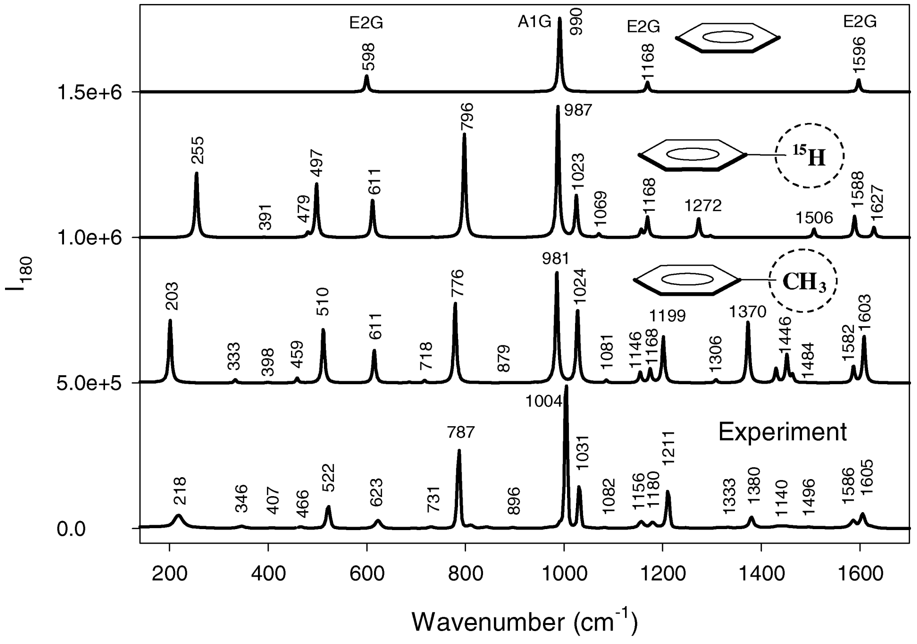

Fig. 2 From top to bottom: simulated (BPW91/6-31++G**) Raman backscattering spectra of benzene, benzene with a hydrogen of relative atomic mass 15, toluene, and the experimental Raman spectrum of toluene. The symmetry of the main benzene bands is indicated. The experimental intensity (y-) scale is used; the calculated spectra are scaled arbitrarily by the same factor.

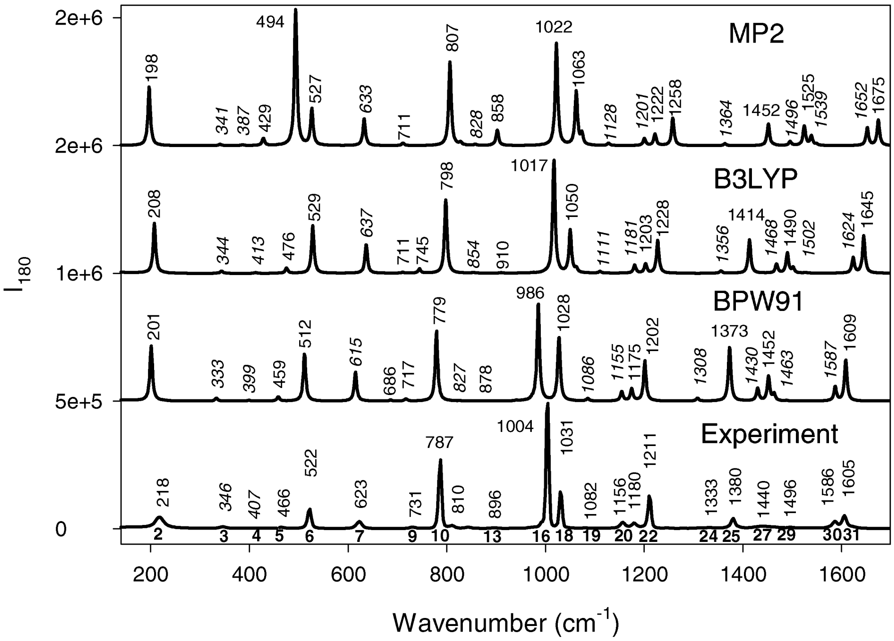

Fig. 3 Raman spectra of toluene simulated at the MP2, B3LYP and BPW91 levels, all computed with the BPW91/6-31++G** basis set, and comparison to the experiment (bottom). Wavenumbers of A″ modes are indicated in italics (to distinguish them from A′ which are not italicized), the bold numbers at the bottom denote fundamental modes (Table 2 in the ESI).‡

88 to 67 cm^{-1}, see Table 2s of the ESI‡) can be achieved when the anharmonic corrections are included. Detailed toluene normal mode assignments can be found elsewhere.[10]

Using the BPW91 method the anharmonic corrections do not appear to improve the harmonic frequencies on average, but occasional better matches do occur. Although current computational tools are not adequate to cope with a full account of anharmonic phenomena,[26] the best BPW91 method already provides a reasonable description of the combination bands visible in the IR spectra (Table 3s in the ESI‡). In the lower-frequency region, the harmonic approximation at this level appears to provide an adequate basis for the modeling. GGA functionals, such as BPW91, are sometimes considered to be inferior to hybrid approaches for computations of the anharmonic corrections.[27] The alleged advantages of the B3LYP hybrid functional, as well as the MP2 method, however, are not apparent for toluene. As is evident from Table 5s,‡ at least at the perturbation (PT2) level all methods

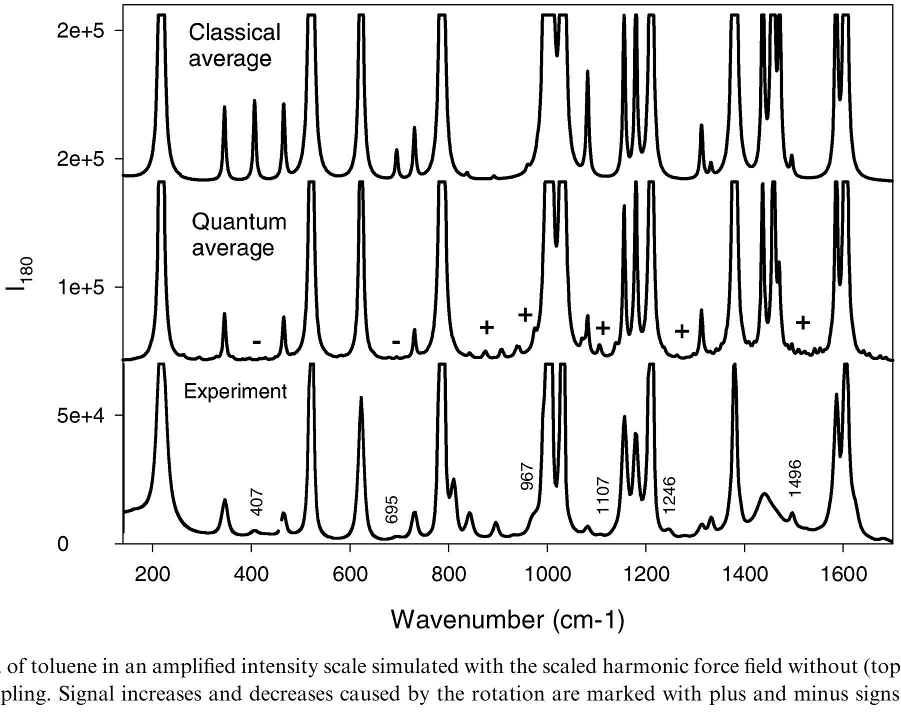

Fig. 4 Raman spectra of toluene in an amplified intensity scale simulated with the scaled harmonic force field without (top) and with (middle) the rotation–vibration coupling. Signal increases and decreases caused by the rotation are marked with plus and minus signs.

Table 1 Calculated differences (in cm^{-1}, for modes 25–30) between the fundamental frequencies in the equilibrium and transition toluene conformers

Mode	MP2/ 6-31++G**Harm	BPW91/ 6-31++G**Harm	BPW91/ aug-cc-pvtzHarm	BPW91/ 6-31++G**VCI	BPW91/ 6-31++G**PT1	BPW91/ 6-31++G**PT2
25	−0.4	−1.2	−1.0	−16.7	−5.6	−3.5
26	−0.5	−1.2	−1.1	−9.0	−12.7	−4.8
27	8.1	2.3	2.9	−2.2	5.6	43.0
28	−3.4	−2.3	−1.7	2.4	2.1	−19.0
29	−0.2	0.0	0.2	2.2	−0.2	2.6
30	0.1	−0.1	0.2	4.0	−1.3	1.5

yield an error within 60–70 cm^{-1} for the anharmonic wavenumbers.

Methyl rotation and band intensities

Although having used a scaled BPW91 harmonic force field (according to the assignment given in Table 2s‡), not all spectral patterns can be explained by harmonic models. Most prominent is the relatively broad band observed between 1400–1500 cm^{-1} involving modes 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 simulated spectrum using the full quantum rotation–vibration model. Several improvements are apparent, such as a near disappearance of the two weak bands measured at 407 and 695 cm^{-1} (indicated by the minus signs in Fig. 4). This reduction in band intensity originates in an effective symmetry increase ($C_s \rightarrow C_{2v}$) caused by the rotation; in the higher symmetry system these transitions become Raman-forbidden. This reminds one of the heavy-hydrogen model and the $D_{6h} \rightarrow C_{2v}$ symmetry change discussed above (Fig. 2). However, although the experimental intensities of these bands are very weak, they do not disappear completely. A reasonable explanation of this phenomenon may be a larger methyl-rotational barrier in the liquid phase than that 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-wavenumber region above ~800 cm^{-1}, however, the rotational motion of the CH_3 group leads to an intensity increase of several bands (indicated by the plus 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 that of the lower-wavenumber shoulder of the band measured at 976 cm^{-1}, this broadening might also be caused by an anharmonic effect which is currently impossible to model accurately.

Band broadenings

The combined harmonic vibration–rotation model only partially explains the broadening of the Raman signal in the 1400–1480 cm^{-1} region. A full explanation has to take into account the dependence of the harmonic frequencies on the methyl rotation as well as additional anharmonic interactions. Indeed, already the differences in the harmonic wavenumbers of the equilibrium ($\phi = 90°$) and transition ($\phi = 0°$) 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. Such frequency dispersion suggests a significant broadening of this band due to the methyl rotation. The anharmonic perturbations (columns 5–7) increase the difference almost by one order of magnitude. The perturbational computation including rotation–vibration coupling (last column in Table 1) predicts an extreme shift of 43 cm^{-1} for the mode 27.

The dependence of the transitional frequencies on the angle ϕ entering the Hamiltonian as the a_{i6} coefficient in eqn (2) in the ESI‡ can clearly explain the unusual broadening of the Raman signal observed at ~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 is compared to the experiment. Although the harmonic differences of the frequencies are significant (several cm^{-1}, the third column of Table 1), they do not provide sufficient broadening even when they are fully incorporated in the (methyl) rotation–vibration Hamiltonian (1) (trace A in Fig. 5). On the other hand, the frequency dispersion obtained by the most complete anharmonic model (last column in Table 1) provide spectra (trace B in Fig. 5) very similar to those observed experimentally, not only displaying sufficient broadening but also qualitatively correct relative intensities of the three bands peaking at ~1436, 1466 and 1490 cm^{-1}.

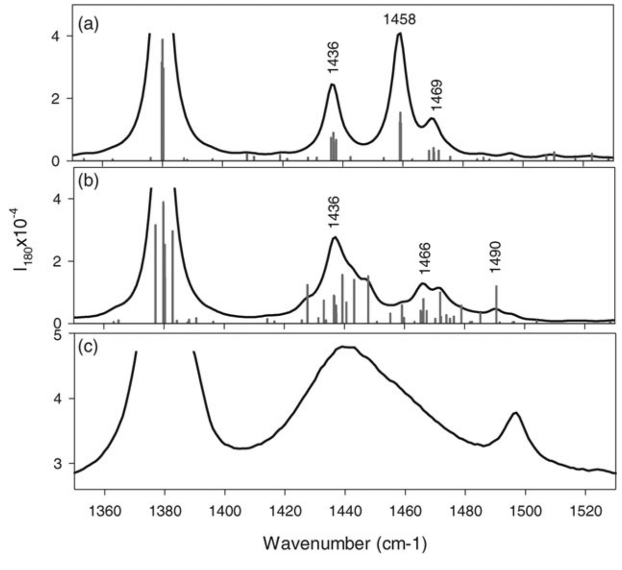

Fig. 5 Raman spectra of toluene within the 1350–1530 cm^{-1} spectral region simulated with the harmonic (trace A, column 3 in Table 1) and anharmonic (trace B, column 7 in Table 1) dependence of the fundamental transition frequencies on the methyl rotation, in comparison with the measured spectrum (C).

Remarks and future prospects

Other than the simplified wavefunction model, alternative Fourier transform methods and Born–Oppenheimer molecular dynamics techniques may also be adapted to perform the spectral simulations.[28] These techniques have attracted much attention in connection with the latest experimental approaches, such as two-dimensional IR spectroscopy.[29] However, the Fourier theory is often restricted to the harmonic approximation, simulation of the Raman intensities is rarely implemented, and for small systems it is difficult to achieve a converging intensity pattern in a sufficiently short computational time.[30]

Although we are able to rationalize many peculiarities of the toluene spectrum the simulations still suffer from a limited precision. Test cluster computations revealed very weak intermolecular interactions. This weakness can be estimated from measurement of the spectra in various solvents (not shown), which do not exhibit significant differences in comparison with the spectrum of neat toluene. Still, the modeling of the dispersion intermolecular forces might be restricted by the limited accuracy of the dispersion forces obtained by DFT.[31–33] Particularly, only an expensive wavefunction method can reliably reproduce the π–π aromatic stacking interaction.[34] Also single-molecule computations are currently limited to the low-anharmonicity region below $\sim$2000 cm^{-1}, whereas for the higher wavenumber region application of the harmonic or perturbed-harmonic calculus is not reliable.[18,26]

Also other experimental techniques could provide alternative information about the vibrational normal modes. Inelastic neutron scattering (INS), for example, has been used for studies of phonon or low-frequency crystal modes.[35,36] However, INS measurements are typically conducted at 20 K, which might somewhat alter the conformational behavior of toluene.

The VCI and PT1 anharmonic calculations were performed with the S4 program (Cartesian-base potential, vibration anharmonicities only[18,37–39]), whereas the PT2 perturbation was performed with GAUSSIAN (normal mode potential, with the rotation–vibration coupling included).[40,41]

Conclusions

The *ab initio* modeling explains most of the experimental features observed in the liquid toluene spectra in the $\sim$100–1800 cm^{-1} region and consequently provides important information on the coupling of various molecular motions. The classical averaging of spectra of different conformers does not provide sufficient agreement with the experiment so that a quantum-mechanical Hamiltonian including the vibrational and methyl-rotational motions has to be considered. The rotation increases molecular symmetry and typically diminishes the intensity of several Raman bands. At $\sim$1440 cm^{-1} coupling of the rotational and vibrational modes causes an anomalous broadening of the Raman signal that could be explained after taking into account anharmonic corrections. The combination of *ab initio* computational techniques and vibrational Raman spectroscopy therefore proves to be a powerful tool for molecular structural studies.

Acknowledgements

The work was supported by the Czech Science Foundation (grants Nos. 203/06/0420, 202/07/0732) and the Grant Agency of the Academy of Sciences (A4005507020). We also thank EPSRC for research grants.

References

1 J. Berná, D. A. Leigh, M. Lubomska, S. M. Mendoza, E. M. Pérez, P. Rudolf, G. Teobaldi and F. Zerbetto, *Nat. Mater.*, 2005, **4**, 704.
2 L. Grill, K. H. Rieder, F. Moresco, G. Rapenne, S. Stojkovic, X. Bouju and C. Joachim, *Nat. Nanotech.*, 2007, **2**, 95.
3 B. T. Sutcliffe, R. Woolley and G., *Chem. Phys. Lett.*, 2005, **408**, 445.
4 T. van Mourik, P. G. Karamertzanis and S. L. Price, *J. Phys. Chem. A*, 2006, **110**, 8.
5 A. D. Dange and V. B. Masurekar, *J. Biosci.*, 1981, **3**, 129.
6 R. A. Faust, *Toxicity summary for toluene*, Oak Ridge National Laboratory, Oak Ridge, TN, 1994.
7 D. R. Borst and D. W. Pratt, *J. Chem. Phys.*, 2000, **113**, 3659.
8 P. C. Chen and F. M. Chang, *Int. J. Quantum Chem.*, 2000, **77**, 772.
9 A. delRio, A. Boucekkine and J. Meinnel, *J. Comput. Chem.*, 2003, **24**, 2093.
10 H. F. Hameka, *THEOCHEM*, 1996, **362**, 325.
11 C. S. Parmenter and B. M. Stone, *J. Chem. Phys.*, 1986, **84**, 4710.
12 J. T. Vivian, S. A. Lehn and J. H. Frederick, *J. Chem. Phys.*, 1997, 6646.
13 N. Kanamaru, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 1230.
14 P. J. Breen, J. A. Warren, E. R. Bernstein and J. I. Seeman, *J. Chem. Phys.*, 1987, **87**, 1917.
15 J. Kapitán, V. Baumruk, V. Kopecký, Jr, R. Pohl and P. Bouř, *J. Am. Chem. Soc.*, 2006, **128**, 13451.
16 J. Kapitán, V. Baumruk, V. Kopecký, Jr and P. Bouř, *J. Am. Chem. Soc.*, 2006, **128**, 2438.
17 J. Kapitán, V. Baumruk, V. Kopecký, Jr and P. Bouř, *J. Phys. Chem. A*, 2006, **110**, 4689.
18 P. Daněček and P. Bouř, *J. Chem. Phys.*, 2007, **126**, 224513.
19 C. Chipot, R. Jaffe, B. Maigret, D. A. Pearlman and P. A. Kollman, *J. Am. Chem. Soc.*, 1996, **118**, 11217.
20 L. Hecht, L. D. Barron, E. W. Blanch, A. F. Bell and L. A. Day, *J. Raman Spectrosc.*, 1999, **30**, 815.
21 E. B. Wilson, C. C. Lin and D. Lide, *J. Chem. Phys.*, 1955, **23**, 136.
22 X. Tan and D. W. Pratt, *J. Chem. Phys.*, 1994, **100**, 7061.
23 D. Papoušek and M. R. Aliev, *Molecular Vibrational/Rotational Spectra*, Academia, Prague, 1982.
24 L. D. Barron, *Molecular Light Scattering and Optical Activity*, Cambridge University Press, Cambridge, 2nd edn, 2004.
25 M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2002, **24**, 669.
26 P. Daněček and P. Bouř, *J. Comput. Chem.*, 2007, **28**, 1617.
27 P. Carbonniere, T. Lucca, C. Pouchan, N. Rega and V. Barone, *J. Comput. Chem.*, 2005, **26**, 384.
28 J. S. Tse, *Annu. Rev. Phys. Chem.*, 2002, **53**, 249.
29 A. T. Krummel and M. T. Zanni, *J. Phys. Chem. B*, 2006, **110**, 24720.
30 J. Horníček, P. Kaprálová and P. Bouř, *J. Chem. Phys.*, 2007, **127**, 084502.
31 J. Šponer and P. Hobza, *Collect. Czech. Chem. Commun.*, 2003, **68**, 2231.
32 J. Černý and P. Hobza, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1624.
33 T. Schwabe and S. Grimme, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3397.
34 V. Špirko, O. Engkvist, P. Soldán, H. L. Selzle, E. W. Schlang and P. Hobza, *J. Chem. Phys.*, 1999, **111**, 572.
35 P. Bouř, C. N. Tam, J. Sopková and F. R. Trouw, *J. Chem. Phys.*, 1998, **108**, 351.

36 F. Fontaine-Vive, M. R. Johnson, G. J. Kearley, J. A. Cowan, J. A. K. Howard and S. F. Parker, *J. Chem. Phys.*, 2006, **124**, 234503.

37 P. Bouř and L. Bednárová, *J. Phys. Chem.*, 1995, **99**, 5961.

38 P. Bouř, S4, Academy of Sciences: Prague, 1994.

39 P. Bouř and L. Bednárová, *J. Phys. Chem.*, 1994, **99**, 5961.

40 V. Barone, *J. Phys. Chem. A*, 2004, **108**, 4146.

41 V. Barone, *J. Chem. Phys.*, 2005, **122**, 014108.