

This article was downloaded by:

On: 21 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713724383>

The application of overtone spectroscopy to investigation of CH bond lengths and molecular conformations

Bryan R. Henry^a; Kathleen M. Gough^{ab}; Michael G. Sowa^a

^a Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada ^b Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada

To cite this Article Henry, Bryan R. , Gough, Kathleen M. and Sowa, Michael G.(1986) 'The application of overtone spectroscopy to investigation of CH bond lengths and molecular conformations', *International Reviews in Physical Chemistry*, 5: 2, 133 – 138

To link to this Article: DOI: 10.1080/01442358609353374

URL: <http://dx.doi.org/10.1080/01442358609353374>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The application of overtone spectroscopy to investigation of CH bond lengths and molecular conformations

by BRYAN R. HENRY, KATHLEEN M. GOUGH† and MICHAEL G. SOWA

Department of Chemistry, University of Manitoba, Winnipeg, Manitoba,
R3T 2N2, Canada

Overtone spectroscopy, through the local-mode model, can be used to determine CH bond lengths in substituted aromatic molecules. These highly accurate bond lengths correlate remarkably well with geometry-optimized *ab initio* MO calculations at the 4-21G level. The spectra can also be used to obtain dynamic information on such processes as methyl internal rotation in toluene.

1. Introduction

The CH-stretching overtone spectra of a wide variety of molecules have been explained successfully with the local-mode model (for recent reviews see Henry 1981, Child and Halonen 1984). The model considers the higher-energy overtones of CH-stretching vibrations ($\Delta\nu_{\text{CH}} \geq 3$) as involving transitions to excited states, whose components have all their vibrational energy effectively localized in one member of a set of equivalent CH oscillators. Because of this localization, these spectra are extremely characteristic of the properties of the individual CH modes. For example, the spectra have been used to study non-bonded steric interactions (Henry *et al.* 1981). They have also been used extensively in studies of intramolecular vibrational energy redistribution (see, for example, Stannard and Gelbart 1981, Reddy *et al.* 1982, Tarr and Henry 1984, Dübäl and Quack 1984 a, Perry and Zewail 1984, Sibert *et al.* 1984).

In this article, we focus on two particular kinds of information that can be extracted from these spectra. Firstly, we use as an example the gas-phase overtone spectra of the fluorobenzenes and show how these spectra can provide very sensitive information about the non-equivalent aryl CH bond lengths. Changes in these bond lengths correlate remarkably well with changes predicted by relatively simple *ab initio* molecular orbital theories. In fact, this correlation can be used to distinguish between the relative capabilities of different levels of such theories. Secondly, we show how these spectra can be used to obtain information about molecular conformations. In particular we describe investigations of methyl rotation in molecules like toluene, the xylenes and the fluorotoluenes.

2. CH bond lengths

McKean and collaborators (for a review see McKean 1978) have examined intensively the fundamental IR spectra of molecules where all but one of the hydrogens have been replaced by deuterium. They have measured changes in this isolated CH-stretching fundamental frequency for different chemical species, and have found an accurate correlation between changes in this frequency and changes in CH bond length. In particular, a shift of 10 cm^{-1} corresponds to a bond-length change of 0.001 \AA .

† Present address: Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada.

In a sense, one could think of these isolated CH oscillators as chemically produced local modes. Hayward and Henry (1976) have shown that there is a very good correlation between this isolated fundamental frequency and overtone frequencies associated with CH bonds in the undeuterated molecules. More recently, Mizugai and Katayama (1980) in liquid-phase studies, and Wong and Moore (1982) and Gough and Henry (1984 a, b) in gas-phase studies, have noted a correlation between CH overtone frequencies and CH bond lengths that holds over a wide variety of molecules. These overtone frequencies are a particularly sensitive probe of CH bond-length changes. At $\Delta\nu_{\text{CH}} = 6$ a bond-length change of 0.001 Å corresponds to a frequency shift of 69 cm^{-1} (Wong and Moore 1982). Such shifts are easily measurable in gas-phase overtone spectra.

In the analysis of bond-length changes in substituted aromatic molecules, the relationship

$$r_{\text{CH}}^{\text{LM}}(\text{Å}) = 1.084 - (\Delta\bar{\nu}/11\Delta\nu_{\text{CH}})0.001 \quad (1)$$

can conveniently be used (Gough and Henry 1984 a) to determine CH bond lengths from the CH bond length in benzene, and the overtone frequency shift relative to benzene ($\Delta\bar{\nu}$) for a given overtone $\Delta\nu_{\text{CH}}$. Although it is convenient to refer the bond lengths to benzene as a standard, it is important to realize that the overtone frequencies give us changes in bond lengths. Thus it is the bond-length changes that are determined accurately, and these are what will be compared to the predictions of *ab initio* molecular orbital theory (*vide infra*).

The spectrum of 1,3-difluorobenzene can serve as an illustrative example. The gas phase overtone spectrum at $\Delta\nu_{\text{CH}} = 3, 4$ and 5 consists of three unresolved peaks (Gough and Henry 1984 a). Each overtone can be decomposed into three component Lorentzians with approximate area ratios of 1 : 2 : 1. The three peaks can be identified with the three nonequivalent hydrogens, where the centre peak of greatest intensity corresponds to H(4) and H(6). The combined effects of σ electron withdrawal and π electron donation by the fluorine substituents causes the aryl CH bonds to shorten (*vide infra*). These effects will be most pronounced for H(2) and least for H(5). Thus H(2) will have the shortest bond and is associated with the highest frequency peak, and H(5) is associated with the lowest frequency peak.

If we use the correlation of equation (1) and the measured frequency shifts for the three peaks relative to a CH oscillator in benzene, we can calculate the expected CH aryl bond-length changes. The results are tabulated as $r_{\text{CH}}^{\text{LM}}$ in the table, relative to the value 1.084 Å for benzene. The table also contains values of $r_{\text{CH}}^{\text{LM}}$ from overtone frequency shifts in the seven other fluorinated benzenes that were studied by Gough and Henry (1984 a). These values are compared to scaled geometry-optimized *ab initio* molecular orbital values at the STO-3G and 4-21G levels, which were calculated either in our laboratory (Gough and Henry 1984 a, Gough 1984) or by Boggs *et al.* (1982).

The STO-3G CH bond lengths are close to the bond lengths from the frequency shifts, but it is clear that they do not model the small changes in bond length nearly as well as bond lengths from 4-21G calculations. These latter values correlate extremely well with the 'experimental' frequency shift values. In fact, in all cases, the correlation is accurate to within 0.001 Å.

In order to obtain a physical picture of CH bond-length decrease on fluorine substitution, Gough and Henry (1984 a) have examined the changes in electron distribution as determined from a Mulliken population analysis. The analysis shows that fluorine withdraws σ electrons, particularly from the *ipso* carbon and the *ortho*

Experimental and *ab initio* CH bond lengths in some fluorinated benzenes (Å).†

Molecule	Assignment	$r_{\text{CH}}^{\text{LM}}$	$r_{\text{CH}}^{\text{STO-3G}}$	$r_{\text{CH}}^{\text{4-21G}}$
Fluorobenzene	H(2)	1.081	1.082	1.081‡
	H(3)	1.083	1.082 ₅	1.083‡
	H(4)	1.083	1.082	1.083‡
1,2-difluorobenzene	H(3)	1.081	1.082	1.082§
	H(4)	1.082	1.082	1.083§
1,3-difluorobenzene	H(2)	1.079	1.081	1.079‡
	H(4)	1.080	1.081	1.081‡
	H(5)	1.082	1.083 ₅	1.083‡
1,4-difluorobenzene		1.081	1.082	1.081§
1,3,5-trifluorobenzene		1.078	1.080	1.078‡
1,2,3,4-tetrafluorobenzene		1.080	1.082	
1,2,3,5-tetrafluorobenzene		1.078	1.081	
1,2,4,5-tetrafluorobenzene		1.079	1.082	

† All values from Gough and Henry (1984 a) unless otherwise noted.

‡ Boggs *et al.* (1982).

§ Gough (1984).

hydrogens. Fluorine donates π electrons to the *ortho* and *para* carbons. Thus, at the *ortho* position, where the CH bond-length decrease is greatest, the hydrogen becomes more positive and the carbon more negative. Therefore the 'ionic' contribution to CH bonding increases and this is physically what causes the CH bond to shorten.

The gas-phase overtone spectra of toluene and the xylenes at $\Delta\nu_{\text{CH}} = 3$ and 4 show two well separated series of peaks (Gough and Henry 1984 b); one set of peaks corresponds to the aryl CH bonds and the other to the methyl CH bonds. In these molecules, methyl substitution causes the aryl CH bond lengths to increase relative to benzene. Thus, in toluene, there are two peaks in the aryl regions, one at lower frequency and the other at the same frequency as the corresponding peak in benzene. The frequency separation between the higher and lower-frequency aryl peaks (intensity ratio approximately 3:2) corresponds to a bond length difference of 0.002 Å. Calculations at the 4-21G level by Pulay *et al.* (1981) predict that the *ortho* CH bonds are longer than the *meta* and *para* CH bonds by 0.001 to 0.002 Å. Therefore, both on the basis of predicted bond length changes and relative areas, the higher-frequency aryl peak in toluene corresponds to the *meta* and *para* CH bonds and the lower frequency peak to the *ortho* CH bonds.

The overall message of this section is clear. One can obtain a beautifully consistent picture of frequency shifts for overtone peaks associated with non-equivalent CH bonds and predicted bond-length changes. In fact the overtone spectra provide the best currently available experimental technique to determine these CH bond lengths at the level of accuracy provided by *ab initio* molecular orbital theories.

3. Molecular conformations

The methyl regions of the gas-phase overtone spectra of toluene, the three xylenes, and the three fluorotoluenes ($\sim 8375\text{--}8575\text{ cm}^{-1}$) all display structure. Examples of these spectra are presented in the figure for $\Delta\nu_{\text{CH}} = 3$ of *o*-, *m*-, and *p*-fluorotoluene. Similar spectra are observed at $\Delta\nu_{\text{CH}} = 4$. The methyl regions of the spectra of the xylenes (Gough and Henry 1984 b) are virtually identical to the spectra of the

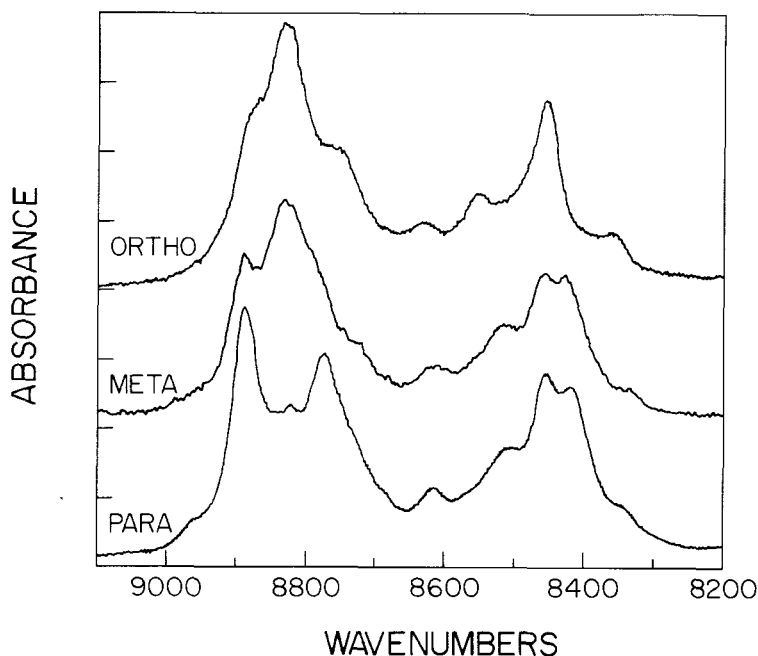


Figure 1. The overtone spectra of gas phase *o*-, *m*-, and *p*-fluorotoluene at 89°C in the region of $\Delta\nu_{\text{CH}} = 3$.

corresponding fluorotoluenes. The latter spectra are slightly shifted to higher frequency due to the bond strengthening effect of the fluoro substituent. The methyl regions of the toluene spectra are very similar to those for the *meta* and *para* molecules (Gough and Henry 1984 b). We can understand this structure in terms of contributions from conformationally non-equivalent hydrogens.

The first application of the local-mode model and overtone spectroscopy to the investigation of molecular conformations occurred with our studies of the liquid-phase spectra of hexamethylbenzene (Henry and Greenlay 1980) and the cyclic alkanes (Henry *et al.* 1980). In these studies, spectral structure was explained on the basis of contributions from conformationally non-equivalent hydrogens. Recently, several groups have extended these observations to the gas phase, where the resolution of the conformationally non-equivalent hydrogens is greatly improved (see, for example, Wong *et al.* 1982, Wong and Moore 1982, Fang *et al.* 1984, Gough and Henry 1984 b). The value of these experiments is that they can obtain information about conformational features that is totally inaccessible to slower techniques like N.M.R.

In *o*-fluorotoluene and *o*-xylene, two peaks are observed in the methyl region with an area ratio of approximately 2:1. In both *o*-fluorotoluene (Susskind 1970) and *o*-xylene (Rudolph *et al.* 1973, Haupt and Müller-Warmuth 1968), the most stable conformer is a planar one where the methyl groups have one CH bond in the ring plane and two at 60°. Note that the less intense peak is at higher frequency. Thus we expect the in-plane CH bond to be shorter than the two at 60°, and from the spectral splitting this difference should be 0.003 Å. These results are in accord with *ab initio* calculations that predict differences of 0.002 Å for *o*-xylene at the STO-3G level (Gough *et al.* 1985) and 0.003 Å for *o*-fluorotoluene at the 4-21 G level (Sowa *et al.* 1986).

As we have noted, the methyl regions of the overtone spectra of toluene, *m*- and *p*-xylene, and *m*- and *p*-fluorotoluene are essentially identical, with three major peaks. For toluene and *m*- and *p*-xylene, the frequencies of the two outside peaks are almost the same as the frequencies of the two peaks in *o*-xylene.

How do we explain these peaks given that the methyl group in toluene (Kreiner *et al.* 1973) and presumably in the *meta* and *para* molecules, is nearly a free rotor? One explanation is again in terms of the spectral resolution of conformationally non-equivalent CH bonds. The correspondence of the frequencies of the two outside peaks in toluene and *m*- and *p*-xylene to the two peaks in *o*-xylene suggests that these outside peaks are also associated with a planar methyl conformation. Thus the highest-frequency peak is associated with the in-plane methyl CH and the lowest-frequency peak with the two methyl CH bonds at 60°. The frequency separation corresponds to a bond-length difference of 0.003 Å, in good agreement with 4-21 G *ab initio* calculations for toluene (Pulay *et al.* 1981), which predict a bond-length difference of 0.002 Å. Gough and Henry (1984 b) have explained this dependence of the methyl CH bond lengths on angle in terms of an angular dependence of the non-bonded antibonding interactions between the methyl hydrogens and the ring carbons.

Why is there a central peak in the methyl regions of the spectra of toluene and the *meta* and *para* molecules, and why is such a peak apparently absent in the spectra of the two *ortho* molecules? As we have noted, the barrier to internal rotation of the methyl groups in toluene and the *meta* and *para* molecules is very low. The central peak could arise from transitions originating from rotational levels above this rotational barrier. A similar interpretation has been given for peaks observed in the fundamental region of several related molecules (Cavagnat and Lascombe 1982, McKean and Watt 1976, McKean *et al.* 1977).

Further support for this interpretation can be found from the details of the curve deconvolution. In *o*-fluorotoluene, the spectrum in the methyl region (~ 8400 – 8600 cm^{-1}) can be most successfully decomposed into three peaks; i.e., there does appear to be a small central peak in the *o*-fluorotoluene spectrum. The relative intensity of the central peak increases from *o*- to *m*- to *p*-fluorotoluene as 0.2 to 0.9 to 1.1 respectively (Sowa *et al.* 1986). A similar increase in the relative intensity of the central peak is observed from *m*- to *p*-xylene. These relative intensities are consistent with our interpretation of the central peak as due to transitions from states lying above the rotational barrier, and a decrease in that barrier from *ortho* to *meta* to *para*-substituted molecules.

Another possible explanation of the structure in the methyl regions of the spectra of these molecules could involve local-mode-normal-mode combination peaks with $v-1$ quanta of CH-stretching and two quanta of HCH bending. Such combination peaks have been observed in the overtone spectra of several molecules (see, for example, Fang and Swofford 1980, Henry and Mohammadi 1981, Mortensen *et al.* 1981, Dübal and Quack 1984 b). However, these combinations tune in and tune out of resonance with the purely CH-stretching peaks for different overtones because of different anharmonicities for the interacting modes. As a result, the energy splitting between the combination and the purely CH-stretching peaks, and the relative peak intensities, change markedly as a function of ν_{CH} . We have not observed either of these effects in the spectra of toluene or of the *meta* and *para* molecules (Gough and Henry 1984 b, Sowa *et al.* 1986). A second reason why we do not favour combination interactions as an explanation of the methyl overtone spectral structures is the recent study by one of us (Gough 1985, unpublished data) of the overtone spectrum of 2-butyne. In this molecule

the methyl groups are subject only to cylindrical symmetry. The gas-phase overtones at $\Delta\nu_{\text{CH}} = 3, 4$ and 5 are dominated by relatively narrow peaks with only what appear to be traces of rotational structure at $\Delta\nu_{\text{CH}} = 3$ and 4. There is no evidence for prominent participation of combination peaks, nor are there manifestations of the type of spectral structure that occurs in toluene, the xylenes, and the fluorotoluenes.

Acknowledgments

We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support and for a graduate fellowship (MGS). We are also grateful to the University of Manitoba for a graduate fellowship (KMG). BRH appreciates the kind of hospitality of the Chemistry Department at the University of British Columbia where this article was prepared.

References

- BOGGS, J. E., PANG, F., and PULAY, P. J., 1982, *J. comput. Chem.*, **3**, 344.
 CAVAGNAT, D., and LASCOMBE, J., 1982, *J. molec. Spectrosc.*, **92**, 141.
 CHILD, M. S., and HALONEN, L., 1984, *Adv. Chem. Phys.*, **57**, 1.
 DÜBAL, H. R., and QUACK, M., 1984 a, *Molec. Phys.*, **53**, 257.
 DÜBAL, H. R., and QUACK, M., 1984 b, *J. chem. Phys.*, **81**, 3779.
 FANG, H. L., MEISTER, D. M., and SWOFFORD, R. L., 1984, *J. phys. Chem.*, **88**, 410.
 FANG, H. L., and SWOFFORD, R. L., 1980, *J. chem. Phys.*, **72**, 6382.
 GOUGH, K. M., 1984, Ph.D. Thesis, The University of Manitoba, Winnipeg, Canada.
 GOUGH, K. M., and HENRY, B. R., 1984 a, *J. Am. chem. Soc.*, **106**, 2781.
 GOUGH, K. M., and HENRY, B. R., 1984 b, *J. phys. Chem.*, **88**, 1298.
 GOUGH, K. M., HENRY, B. R., and WILDMAN, T. A., 1985, *J. Molec. Struct. (Theochem.)*, **124**, 71.
 HAUPT, J., and MÜLLER-WARMUTH, W., 1968, *Z. Naturf. (a)*, **23**, 208.
 HAYWARD, R. J., and HENRY, B. R., 1976, *Chem. Phys.*, **12**, 387.
 HENRY, B. R., 1981, *Vibrational Spectra and Structure*, edited by J. Durig, Volume 10 (Elsevier), p. 269.
 HENRY, B. R., and GREENLAY, W. R. A., 1980, *J. chem. Phys.*, **72**, 5516.
 HENRY, B. R., HUNG, I. F., MACPHAIL, R. A., and STRAUSS, H. L., 1980, *J. Am. chem. Soc.*, **102**, 515.
 HENRY, B. R., and MOHAMMADI, M. A., 1981, *Chem. Phys.*, **55**, 385.
 HENRY, B. R., MOHAMMADI, M. A., and THOMPSON, J. A., 1981, *J. chem. Phys.*, **75**, 3165.
 KREINER, W. A., RUDOLPH, H. D., and TAN, B., 1973, *J. molec. Spectrosc.*, **48**, 86.
 MCKEAN, D. C., 1978, *Chem. Soc. Rev.*, **7**, 399.
 MCKEAN, D. C., BECHER, H. J., and BRAMSIEPE, F., 1977, *Spectrochim. Acta A*, **33**, 951.
 MCKEAN, D. C., and WATT, R. A., 1976, *J. molec. Spectrosc.*, **61**, 184.
 MIZUGAI, Y., and KATAYAMA, M., 1980, *Chem. Phys. Lett.*, **73**, 240.
 MORTENSEN, O. S., HENRY, B. R., and MOHAMMADI, M. A., 1981, *J. chem. Phys.*, **75**, 4800.
 PERRY, J. W., and ZEWAIL, A. H., 1984, *J. chem. Phys.*, **80**, 5333.
 PULAY, P., FOGARASI, G., and BOGGS, J. E., 1981, *J. chem. Phys.*, **74**, 3999.
 REDDY, K. V., HELLER, D. F., and BERRY, M. J., 1982, *J. chem. Phys.*, **76**, 2814.
 RUDOLPH, H. D., WALZER, K., and KRUTZIK, I., 1973, *J. molec. Spectrosc.*, **47**, 314.
 SIBERT III, E. L., REINHARDT, W. P., and HYNES, J. T., 1984, *J. chem. Phys.*, **81**, 1115.
 SOWA, M. G., GOUGH, K. M., and HENRY, B. R., 1986 (to be published).
 STANNARD, P. R., and GELBART, W. M., 1981, *J. phys. Chem.*, **85**, 3592.
 SUSSKIND, J., 1970, *J. chem. Phys.*, **53**, 2492.
 TARR, A. W., and HENRY, B. R., 1984, *Chem. Phys. Lett.*, **112**, 295.
 WONG, J. S., MACPHAIL, R. A., MOORE, C. B., and STRAUSS, H. L., 1982, *J. phys. Chem.*, **86**, 1478.
 WONG, J. S., and MOORE, C. B., 1982, *J. chem. Phys.*, **77**, 603.