The Infrared and Raman Spectroscopic Signals of HF, HCl, HBr and HI

Martin Grayson

Department of Chemistry, the University of Shefield, Sheffield S3 7HF.

Received xxx; Preprint published xxx; Accepted xxx ; Published xxx

Internet Electron. J. Mol. Des. **2003**, *1*, 000–000

Abstract

The infrared and Raman spectra of HF, HCl, HBr and HI have been calculated at only the SCF level to specifically investigate the best method of monitoring HI, in particular in a room temperature reaction of industrial importance where an infrared probe might have been possible.

The Raman calculation was at the SCF level but at the laser operating frequency using the new facilities of the DALTON quantum chemistry program.

As you go down the series of HF through HI the infrared signal goes down to zero but the Raman signal increases giving a clear indication of how HI must be monitored.

.

Availability of Software

The DALTON program, http://www.kjemi.uio.no/software/dalton/dalton.html

The CADPAC program, http://www-theor.ch.cam.ac.uk/software/cadpac.html

The DIRAC program, http://dirac.chem.sdu.dk/

Keywords. Raman, spectrum, SCF, polarizability, dipole derivative.

Abbreviations and notations

SCF, Self Consistent Field

IR, infrared

1 INTRODUCTION

This short communication is about computational work on behalf of the experimental *High Temperature Laboratory* at Sheffield. Computations on the hydrogen halides have yielded useful input to the design of experimental monitoring equipment. The quality of possible calculations was initially an unknown quantity with respect to the performance of core potentials, correlation model, relativistic method and also basis set. The largest molecule HI, contains the heavy atom iodine, and it is known there are significant relativistic corrections to its polarizabilities, therefore there could also be large corrections to the dispersion interactions and large corrections to the polarizability derivatives. As these derivatives are contributors to the Raman spectra it was feared the calculations might not reproduce the experimental spectra. However we found the prediction of the frequencies and intensities by fairly basic methods was good enough to give the necessary input to the experimental design process.

There was some discussion of monitoring hydrogen iodide by spectroscopy. An external expert advised, *you can't do that because as you go from HF to HI the signal drops to zero*. Inexpensive DALTON[1] computations of the IR spectra show indeed it does, but they also show the Raman intensity goes the other way, increasing by a factor of 6 from HF to HI.

This was a significant input to the design of the monitoring apparatus. Interestingly enough one could get the relevant information with almost any level of calculation with any of the commonly available *ab initio* programs. (DALTON was chosen because the Raman signal could be calculated at exactly the operational frequency). As far as the experimentalists are concerned here 10% of the effort in terms of accurate calculation is giving 90% of the result, even though accurate calculation of the properties of interest requires a large basis and a good wavefunction and perhaps even the correlation and relativistic calculations which could only be performed with a program such as DIRAC[2]. The calculations are performed at the SCF level in the *Double Harmonic Approximation* where the vibrational frequencies are calculated with a harmonic well combined with a linear truncation of the function for the dipole moment derivative. Errors introduced to the harmonic well by the SCF approximation are discussed in the review of Stanton and Gauss[3].

However it is also possible that no computation at all was needed to arrive at the correct conclusion. Long and Plane[4] have suggested that the magnitude of the bond polarizability derivative, a principal component of the Raman intensity, is a measure of covalent character. The argument is that if the bonding was totally ionic the polarizability / bond-length derivative would be zero as you would have the sum of separate ion polarizabilities at all distances. The interaction polarizability for atoms forming a chemical bond is negative in most molecules *i.e.* polarizability increases as you distort the bond towards breaking. If one accepts this argument and combines it with the hypothesis of King *et al.* [5] and Sambe[6] that the dipole derivative is a measure of the partial charge on an atom we have the dipole derivatives as a measure of ionic character and polarizability derivatives as a measure of covalent character. The effective charge tensor hypothesis of King *et al.* and Sambe has been expanded by Cioslawski[7] to become a useful alternative to the common methods of partitioning molecular electron density into atomic charges.

Therefore the molecule which has the smallest halogen and the largest electronegativity difference, HF, will have the most intense IR spectrum and the least intense Raman spectrum. Similarly HI with the most covalent bond and a large polarizability and polarizability derivative will have the weakest IR and the strongest Raman spectrum. Another factor depressing the IR signal for HI is that the movement of atoms in a vibrational mode is less because of the larger reduced mass causing the vibrational quantum states to lie lower in the diatomic potential curve.

2 RESULTS AND DISCUSSION

Calculations of the infrared and Raman parameters of the molecules HF through HI were performed using the DALTON and CADPAC[8] programs. The MedPol bases of Sadlej[9,10] were available for all the atoms here so these bases were used for the final calculations. Some preliminary calculations using much smaller basis sets were performed and they qualitatively agreed with the ones presented here but are not suitable for reporting because the absolute values of the polarizability which mere split valence bases can produce are smaller than the experimental values by a factor of up to 2. Sadlej's MedPol basis is specifically designed to reproduce good polarizabilities at a modest computational cost.

The values calculated at zero frequency from DALTON and CADPAC were in agreement but the values presented here are the DALTON ones as they were evaluated at the operational frequency being considered for the Raman experiment. The units of Raman intensity used are the non SI

Ångstrom[4] / atomic mass unit which is used by most *ab initio* quantum chemistry programs and literature values are commonly quoted in these units. The Raman calculations are evaluated at a laser frequency of 488.80 nm.

Table 1 presents the SCF frequencies and dipole moments. As usual the uncorrelated SCF frequencies are a little too high and the dipole moments are also slightly too large. This is because SCF overemphasizes the ionic terms in the wavefunction giving both the wrong dissociation products and a dipole moment with too much charge separation. The larger discrepancy for HI may even be due to the missing relativistic effects as well as the large amount of correlation in the 54 electrons of the molecule. The error in the infrared intensities will be of a similar order but it is not relevant to the trends.

Table – 1, Calculated and Experimental Infrared Frequencies, and Dipole Moments for the Molecules HF through HI, (Reference[11] (experimental) and this work)

Molecule	Freq. / cm^{-1} (Calculated)	Freq. / cm^{-1} (Experimental)	Calculated Dipole Moment (μ) / 10^{-30} Cm	Experimental Dipole Moment (μ) / 10^{-30} Cm
HF	4457.02	4138.32	6.32	6.37
$H^{35}Cl$	3073.86	2990.95	4.05	3.60
$H^{81}Br$	2788.27	2648.98	3.24	2.67
$H^{127}I$	2449.16	2308.09	2.18	1.40

The polarizabilities presented in table 2 match the experimental measurements very well and as usual they are a slight underestimate due to both basis set incompleteness and the phenomenon that molecules composed of saturated bonds usually have a positive correlation contribution to the polarizability.

Table – 2, Calculated and Experimental Isotropic Polarizabilities (α) for the Molecules HF through HI, (†) - experimental values from Hasanein[12], (§) - and reference[13] . The calculated values are this work.

Molecule	Calculated α / 10^{-40} $J^{-1}C^2m^2$	Experimental α / 10^{-40} $J^{-1}C^2m^2$
HF	0.81	(†)0.92
$H^{35}Cl$	2.76	(†)2.87
$H^{81}Br$	3.81	(§)4.01

$H^{127}I$	5.83	(§)6.06

Table 3 shows the calculated infrared and Raman intensities for HF through HI and the clear way the IR signal goes to near zero and the Raman signal increases.

Table – 3, Calculated Infrared and Raman Parameters for the Molecules HF through HI

Molecule	Freq. / cm^{-1}	Intensity / $kmol^{-1}$	Polarization Intensity / ($Å^4$ /amu)	Depolarization Intensity / ($Å^4$ /amu)
HF	4457.02	168.778	29.86	4.23
$H^{35}Cl$	3073.86	56.680	93.09	16.96
$H^{81}Br$	2788.27	15.852	125.66	25.21
$H^{127}I$	2449.16	0.055	171.79	41.13

3 CONCLUSIONS

By definition the High Temperature Laboratory are normally considering situations where the infrared signal is totally swamped out by the background heat and only Raman techniques can be used. However in room temperature situations these computations show clearly how infrared and Raman techniques can be complementary for reasons other than the familiar infrared / Raman exclusion symmetry rules which are always a component of an undergraduate spectroscopy and group theory course. It is clear that HI can be monitored using the Raman technique but probably has an undetectable infrared signal and that the infrared signal can go to near zero due to bonding and potential energy surface considerations as well as symmetry.

Though these calculations have considerable error in them, which is now technically feasible to remove, even for HI, using the relativistic correlated methods in the DIRAC program, the results are presented now as a timely example of how quantum calculations and basic physical chemistry can be used to make predictions of spectra. Definitive calculations using relativity would require some development and checking of basis sets, a small diatomic molecule spectral intensity program to be written and would also need the effects of anharmonicity to be considered.

Acknowledgment

The author acknowledges the encouragement of Dr. Robin Devonshire of the *High Temperature Laboratory* to perform these calculations.

4 REFERENCES

[1] References are presented as a numbered list. Use font Times New Roman size 10. **Do not delete this template**. Substitute the references presented here as examples with your own references. To create a new numbered reference press ENTER at the end of an existing reference. You can delete a reference, or insert a new one. Follow the examples presented below for journal papers with one, two, or more authors, books, edited books, chapters in a book.

[2] H. Kubinyi, Variable Selection in QSAR Studies. I. An Evolutionary Algorithm, *Quant. Struct.-Act. Relat*. **1994**, *13*, 285-294.

[3] M. V. Diudea, Cluj Matrix Invariants, *J. Chem. Inf. Comput. Sci*. **1997**, *37*, 300-305.

[4] J. G. Topliss and R. P. Edwards, Chance Factors in Studies of Quantitative Structure-Activity Relationships, *J. Med. Chem*. **1979**, *22*, 1238-1244.

[5] R. P. Sheridan and S. K. Kearsley, Using a Genetic Algorithm to Suggest Combinatorial Libraries, *J. Chem. Inf. Comput. Sci*. **1995**, *35*, 310-320

[6] J. Sadowski and H. Kubinyi, A Scoring Scheme for Discriminating between Drugs and Nondrugs, *J. Med. Chem*. **1998**, *41*, 3325-3329.

[7] W. Zheng, S. J. Cho, and A. Tropsha, Rational Design of a Targeted Combinatorial Chemical Library with Opiatelike Activity, *Int. J. Quantum Chem*. **1998**, *69*, 65-75.

[8] S. H. Yalkowsky, J. F. Krzyzaniak and P. B. Myrdal, Relationships between Melting Point and Boiling Point of Organic Compounds, *Ind. Eng. Chem. Res*. **1994**, *33*, 1872-1877.

[9] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, AM1: A New General Purpose Quantum Mechanical Molecular Model, *J. Am. Chem. Soc*. **1985**, *107*, 3902-3909.

[10] M. A. Gallop, R. W. Barrett, W. J. Dower, S. P. A. Fodor, and E. M. Gordon, Application of Combinatorial Technologies to Drug Discovery. 1. Background and Peptide Combinatorial Libraries, *J. Med. Chem.* **1994**, *37*, 1233-1251.

[11] L. B. Kier and L. H. Hall, *Molecular Connectivity in Structure-Activity Analysis*, Research Studies Press, Letchworth, 1986, pp. 20-25.

[12] A. T. Balaban (Ed.), *From Chemical Topology to Three-Dimensional Geometry*, Plenum, New York, 1997.

[13] M. V. Diudea (Ed.), *QSPR/QSAR Studies by Molecular Descriptors*, Nova Science, Huntington, N.Y., 2001.

[14] H. Kubinyi, Comparative molecular field analysis (CoMFA); in: *The Encyclopedia of Computational Chemistry*, Eds. P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner, John Wiley & Sons, Chichester, 1998, pp. 448-460.

[15] S. C. Basak, Information Theoretic Indices of Neighborhood Complexity and Their Applications; in: *Topological Indices and Related Descriptors in QSAR and QSPR*, Eds. J. Devillers and A. T. Balaban, Gordon and Breach Science Publishers, Amsterdam, 1999, pp 563-593.

[1] Dalton, a molecular electronic structure program, Release 1.2, written by T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, K. Ruud, H. Ågren, A. A. Auer, K. L. Bak, V. Bakken, O. Christiansen, S. Coriani, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, C. Hättig, K. Hald, A. Halkier, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch , K. V. Mikkelsen, P. Norman, M. J. Packer, T. B. Pedersen, T. A. Ruden, A. Sanchez, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. O. Sylvester-Hvid, P. R. Taylor, O. Vahtras, **2001.**

[2] T. Enevoldsen, L. Visscher, T. Saue, H. J. A. Jensen, J. Oddershede, Relativistic four-component calculations of indirect nuclear spin-spin couplings in MH_4 (M=C, Si, Ge, Sn, Pb) and $Pb(CH_3)_3H$, **2000**, *112*, 3493-3498.

[3] J. F. Stanton and J. Gauss, Analytic second derivatives in high-order many-body perturbation and coupled-cluster theories: computational considerations and applications, *Int. Rev. Phys. Chem,* **2000,** *19,* 61-95.

[4] T. V. Long and R. A. Plane, Calculation of Absolute Raman Intensities of A_1 Modes of Molecules and Ions, *J. chem. Phys*., **1965**, *43*, 457-462.

[5] W. T. King, G. B. Mast and P. P. Blanchette, Infrared Intensity Sum Rule and Effective Charges, *J. chem. Phys*., **1972**, *56*, 4440-4446.

[6] H. Sambe, Effective charge tensors of atoms in a molecule and electric dipole shielding of nuclei, *J. chem. Phys*., **1973**, *58*, 4779-4782.
[7] J. Cioslowski, Electronic Wavefunction Analysis, in *the Encyclopedia of Computational Chemistry*, Eds. P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner, John Wiley & Sons, Chichester, 1998, pp. 892-905.
[8] R. D. Amos, Dipole Moment Derivatives of H_2O and H_2S, *Chem. Phys. Lett*. **1984,** *108*, 185-190.
[9] A. J. Sadlej, Medium-size Polarized Basis-sets for High-level Correlated Calculations of Molecular Electric Properties, Collect. Czech Chem. C..; **1988,** 53 1995-2016.
[10] A.J. Sadlej, Medium-size Polarized Basis-sets for High-level Correlated Calculations of Molecular Electric Properties .5. 4^{th} Row Atoms – Sn through I, *Theor. Chim. Acta*., **1992,** 81, 339-354.
[11] *American Institute of Physics Handbook*. 3rd edition New York: McGraw-Hill 1972.
[12] A. A. Hasanein, Ab Initio Computation of Polarizabilities and Hyperpolarizabilities of Atoms and Molecules, Advances in Chemical Physics}, **1993,**{\bf 85}, Part 2, 415.
[13] C. J. F.Böttcher, O. C. van Belle, P. Bordewijk and A. Rip, Theory of electric polarization, Elsevier 1973.

Biographies

Martin Grayson is Senior Programmer in the Chemistry Department at the University of Sheffield. He has published 31 papers, mostly in computational quantum mechanics.