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

Martin Grayson

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

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

Martin Grayson*

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

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Abstract

Motivation. The infrared and Raman spectra of HF, HCl, HBr and HI have been calculated at SCF, DFT and MP2 levels 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.

Method. The calculations were performing using the frequency independent polarizabilities of the common methods and a DALTON Raman calculation at the SCF level but using polarizability derivatives at the laser operating frequency.

Results. For the correlated calculations there is good agreement between experiment and theory. SCF is wrong by the expected systematic error on frequency but the calculations as a whole agree with the limited experimental information on the Raman spectra.

Conclusions. If we consider the series of diatomic hydrides HF through HI the infrared signal goes down to zero but the Raman signal increases giving a clear indication of how the concentration of HI might be monitored.

Keywords. Raman spectrum; SCF, self consistent field; polarizability; dipole derivative.

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

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* Correspondence author; E-mail: M.Grayson@sheffield.ac.uk.

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.

After the calculations were completed it was discovered that the very issue of the relativistic corrections to the polarizability derivatives had been addressed in a thorough way by Pecul and Rizzo in 2003 [1]. These corrections are found to be *significant* but not *material* for the heavier molecules HBr and HI.

There was some discussion in the laboratory of the feasibility of monitoring hydrogen iodide in an active device by spectroscopy. An external expert advised, *you can't do that because as you go from HF to HI the measurable signal drops to zero*. On examining the PNNL (Pacific Northwest National Laboratory) data [2] it was readily apparent that this is the case as the infrared intensity falls in a ratio 1:0.33:0.05:0.002 *i.e.* the signal is 500 times weaker for HI than for HF.

Inexpensive DALTON [3] computations of the IR spectra also show the fall off in intensity, giving an even larger fall of intensity by a factor of 3061. However these calculations also show the Raman intensity does not fall through this series, 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 [4]). 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 correlation and relativistic calculations, as shown to be needed for HBr and HI by Pecul and Rizzo [1], the combination of which could be performed with a program such as DIRAC [5]. These 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 [6] There is an extensive table of scaling factors in Cramer [7] assembled from the references therein where it can be seen that SCF calculations systematically overestimate the frequency by 10%.

However it is also possible that no computation at all was needed to arrive at the correct conclusion. Long and Plane [8] have suggested that the magnitude of the bond polarizability derivative, da/dr , 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.* [9] and Sambe [10] 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 Cioslowski [11] 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, CADPAC [12] and GAUSSIAN [13] programs. The MedPol bases of Sadlej [14,15] were available for all the atoms here so these bases were used for the final SCF / Raman calculations in Tables 1, 3 and 4. 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.

Table 1. Calculated and experimental infrared frequencies, and dipole moments for the molecules HF through HI, (reference [16] (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 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 according to the procedure in reference [4]. The units of Raman intensity used are the non SI Ångstrom⁴/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 2. Calculated infrared frequencies using SCF, DFT and the MP2 methods

Molecule	Freq. / cm ⁻¹ (Experimental)	Freq. / cm ⁻¹ (Calculated, SCF)	Freq. / cm ⁻¹ (Calculated, B3LYP)	Freq. / cm ⁻¹ (Calculated, MP2)
HF	4138.32	4457.02	4085.12	4192.45
H ³⁵ Cl	2990.95	3073.86	2947.85	3119.01
H ⁸¹ Br	2648.98	2788.27	2664.37	n.a.
H ¹²⁷ I	2308.09	2449.16	2307.09	n.a.

Table 2 shows a sequence of calculations to illustrate the performance of density functional theory with the commonly used B3LYP functional. GAUSSIAN-03 and the 6-31G** basis [17,18] were used for all these calculations except for HI where a 3-21G** [19] basis had to be used because of availability. (Similar problems prevented the use of the Sadlej MedPol basis for these calculations.) A fuller description of DFT and the B3LYP functional is beyond the scope of this article. Readers should consult a good textbook such as Cramer [7] or Jensen [19] and follow original references to the pioneering work of Kohn, Hohenberg and Sham and the many developers of modern functionals therein.

The B3LYP model is the most popular modern DFT functional and is made of an optimised mixture of terms consisting of local density functionals and a proportion of a full Hartree–Fock calculation. It is therefore slightly more costly than a mere HF SCF but it provides a high level of electron correlation in the many molecular situations to which it is applicable. As expected B3LYP produces a frequency much nearer the experimental frequency than pure Hartree–Fock calculations.

Table 3. Calculated and experimental isotropic polarizabilities (α) for the molecules HF through HI, (†) – experimental values from Hasanein [20], (§) – and reference[21]. The calculated values are this work.

Molecule	Calculated $\alpha / 10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^2$	Experimental $\alpha / 10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^2$
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

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 4 shows the calculated infrared and Raman intensities for HF through HI using the DALTON frequency dependent polarizability method and the clear way the IR signal goes to near zero and the Raman signal increases.

Table 4. Calculated infrared and raman parameters for the molecules HF through HI at a laser frequency of 488.80 nm

Molecule	Freq. / cm^{-1}	Intensity / kilometres mol^{-1}	Polarization Intensity / ($\text{\AA}^4 / \text{amu}$)	Depolarization Intensity / ($\text{\AA}^4 / \text{amu}$)
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

The polarization intensity, (the Raman intensity in the direction parallel to the incident light), and the depolarization intensity, (the Raman intensity in the direction exactly perpendicular to the incident light), are presented as they are experimental observables. δ the depolarization ratio is the perpendicular polarization intensity I^{\perp} divided by the polarization intensity I^{\parallel} [22].

$$\delta = I^{\perp} / I^{\parallel}$$

where δ is 0 for spherical particles but for an A_1 vibrational mode, (the only mode for a diatomic is A_1), δ must be less than 3/4. The only mode for a diatomic is a *polarized band*. For HF through HI the depolarization ratios are 0.14, 0.18, 0.20 and 0.24.

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.

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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.