

The prediction of Raman spectra by density functional theory. Preliminary findings

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Abstract

We report the first calculations of Raman vibrational intensities by density functional theory, implemented within the Q-Chem program. Local (S-VWN) and gradient-corrected (B-LYP) DFT results are compared with experimental and Hartree–Fock results for the N₂, HF and C₂H₆ molecules. Preliminary indications are that local DFT compares less favorably to experiment than either Hartree–Fock or gradient-corrected DFT. The Hartree–Fock and B-LYP results are generally similar except for the HF molecule, where B-LYP is somewhat better. For all methods, best results were obtained by augmenting the basis set with diffuse polarization functions.

1. Introduction

The ability to predict vibrational spectra by ab initio quantum chemical methods has long been established as a tool of great practical utility [1]. For spectroscopic studies of larger, biologically important systems, the correct interpretation of conformationally related intensity variations become of critical importance [2–4]. Consider, for example, the hypochromism observed in the Raman spectra of nucleotides when DNA duplex is formed [3,5], or newly emerging Raman optical activity methods based on small differences in the scattering activity for left and right circularly polarized light [6,7].

Generally, good agreement between experimental

and calculated Raman spectra of small molecules has been obtained by using the Hartree–Fock and double harmonic approximations [7–9]. For larger molecular systems such as amino acids and nucleobases, calibration of the calculated Raman intensities is hampered by the lack of gas-phase or matrix isolation Raman spectra of these systems. An attempt to predict Raman spectrum of a polycrystalline guanine by a combination of scaled quantum mechanical force fields with the HF/6-31G* Cartesian polarizability derivatives resulted in poor agreement with the measured spectra [10]. Moreover, the calculated Raman spectra were found to be highly sensitive to the force field variations. This finding indicates that beyond the point where it is possible to interpret the spectra in terms of simple characteristic vibrations, the force field accuracy requirements for obtaining correct Raman spectra increase with the number of normal modes. For this reason, more accurate calculations of

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Raman spectra at post-HF levels of theory are much needed. Clearly though, as the system gets larger we soon encounter the dilemma which all too often must be faced in *ab initio* calculations: the costs of conventional post-HF methods scale too steeply with system size, making the expense of a more accurate calculation prohibitive.

In recent years, there has been a surge of interest in density functional theory (DFT), which appears to be a promising alternative approach to standard *ab initio* methods for the calculation of many molecular properties [11]. In several systematic validation studies [12–16] DFT has exhibited good performance, and often has given results of quality comparable to or better than MP2 perturbation theory. One must be cautious not to apply DFT indiscriminately, but the future of DFT methods in computational quantum chemistry appears bright.

These encouraging results have provided incentive for the development of enhanced functionalities within DFT programs. However, progress in this area has generally lagged behind that in the *ab initio* realm. While analytic calculation of vibrational frequencies [17], infrared intensities [18] and Raman intensities [8,9] by the Hartree–Fock method has been routine for several years, it was not until very recently that the first analytic Kohn–Sham DFT frequency and infrared intensity calculations were reported [19,20].

The success of DFT methods for the prediction of vibrational frequencies is well established [13,15]; it has been found that the calculated harmonic frequencies generally match well with observed fundamentals. A body of results for molecular response properties is beginning to be obtained as well. Encouraging results have been obtained for static polarizabilities and hyperpolarizabilities [16,21], as well as for infrared intensities [22,23]; these indications make the prospect of calculating Raman intensities by DFT appear attractive, though heretofore there do not seem to have been any such results published in the literature.

2. Method

The details of our Kohn–Sham DFT Raman implementation will be given with the full account of

the present work; here, we merely summarize our computational approach before proceeding to the results. To calculate density functional Raman intensities within the double harmonic approximation, the main new program functionality required is the calculation of the Cartesian polarizability derivatives, which we have implemented in the Q-Chem quantum chemistry system [24].

The derivatives with respect to nuclear motion of the molecular polarizability tensor may be expressed as third derivatives of the total molecular energy E ,

$$\frac{\partial \alpha_{ij}}{\partial x} = - \frac{\partial^3 E}{\partial i \partial j \partial x}, \quad (1)$$

where x is a nuclear coordinate and i and j represent components of an external electric field. These quantities may be evaluated analytically using second-order coupled-perturbed Kohn–Sham (CPKS) theory [20]. For initial performance assessment, though, we have taken a simpler approach which does not require CPKS. The right-hand side of Eq. (1) is written as

$$\frac{\partial^3 E}{\partial i \partial j \partial x} = \frac{\partial^2 g_x}{\partial i \partial j}, \quad (2)$$

where g_x is the component of the nuclear gradient corresponding to x , and the polarizability derivatives are obtained by finite-field numerical second differentiation of analytically calculated energy gradients. This is the same approach first taken by Komornicki and McIver [25] to calculate Raman intensities by Hartree–Fock theory, and is a reasonable balance between computational efficiency and programming effort. Once the polarizability derivatives are available, the Raman intensities may then be constructed using normal modes obtained from an appropriate force field or theoretically calculated Hessian.

The standard double harmonic and non-resonant approximations were used for calculation of Raman scattering activities and depolarization ratios [7,26,27]. The Raman scattering differential cross sections, which correspond to the measured absolute Raman intensities, were evaluated from the scattering activities by multiplication by a factor accounting for temperature, excitation wavelength, and vi-

brational frequency [7,26,27]. The formulas for these were implemented in our program SQMVIB [28], which calculates the normal modes and frequencies from the mass-weighted Cartesian force constant matrix. The Cartesian force constants and polarizability derivatives were read from the output of the Q-Chem [24] and GAUSSIAN 92 [29] programs.

Few experimental studies suitable for assessment of the performance of computational methods in Raman intensity calculations have been reported, most of them dealing with diatomic molecules. Among them, the absolute intensity of the Q-branch of the vibrational band of N_2 is the most important observable because it is usually used as a standard relative to which Raman intensities for other molecules are measured. The HF molecule is a known problematic case for Hartree–Fock theory, and the Raman intensity of the stretching vibration of this molecule is incorrectly predicted [7], making HF a good initial test case. As a benchmark of DFT Raman intensities of more complex molecules, wherein both the quality of the normal modes and polarizability derivatives play a role, the experimental data for gaseous ethane and its deuterated derivatives [30] were chosen. For each isotopomer, only the well-distinguished isolated bands unaffected by Fermi resonance were examined. Because there were no such bands in the Raman spectrum of C_2H_6 , intensities integrated over two frequency regions of this molecule were also included in the results.

To assess the relative quality of local and gradient-corrected DFT methods, two representative functionals were used: the local uniform electron gas approximation S-VWN [31,32] and the gradient-corrected B-LYP functional [33,34]. Two standard Gaussian orbital basis sets, 6-31G(d, p) and 6-311 + G(2d, 2p), were used. The molecular geometries were fully optimized and the Hessian calculated by these two methods as well as Hartree–Fock with the two basis sets. Recent work [16,21] has indicated, however, that it is necessary to use so-called ‘field-induced polarization’ (FIP) functions, which have very diffuse exponents, in order to obtain good DFT results for molecular polarizabilities and hyperpolarizabilities. To gain a preliminary indication of the importance of these for DFT Raman intensities, we also calculated polarizability derivatives using Dunning’s cc-pVTZ basis [35] augmented by the FIP

functions listed by Guan et al. [16] in their study of DFT polarizabilities. The contraction of this basis is $[5s3p1d]/(3s3p1d)$ for H and $[11s5p3d1f]/(5s3p3d1f)$ for the heavy atoms.

3. Results and discussion

Calculated Raman intensities and depolarization ratios of the N_2 and HF molecules are compared with experimental data in Table 1 and 2. For diatomics, scattering activities provide a more direct measure of the quality of the calculated polarizability derivatives. Hartree–Fock calculations with large basis sets slightly overestimate (10%) the scattering activity of N_2 . For the HF molecule, however, the values are around 50% too low. Both DFT methods behave more systematically, giving underestimated scattering activities for N_2 (10%) as well as for HF (40%). Thus, when relative intensities are considered, DFT performs somewhat better than Hartree–Fock theory. This may be of practical importance in larger molecules involving N–N and F–H bonds. Depolarization ratios are correctly reproduced in all calculations which include diffuse functions.

Table 1
Experimental and calculated Raman scattering differential cross sections (R), scattering activities (S) and depolarization ratios (ρ) of N_2

Method	Pol/Geom ^a	R ^b	S ^c	ρ
exp. ^d		43.2 ± 0.8	20.1 ± 0.4	0.03 ± 0.01 ^e
HF	1/2	19.1	11.4	0.09
	2/2	30.6	18.3	0.04
	3/2	37.0	22.1	0.03
S-VWN	1/2	17.5	8.5	0.09
	2/2	28.7	13.9	0.05
	3/2	35.9	17.4	0.03
B-LYP	1/2	18.2	8.4	0.09
	2/2	31.1	14.5	0.05
	3/2	38.0	17.6	0.03

^a The basis sets are denoted as 1: 6-31G(d, p), 2: 6-311 + G(2d, 2p), 3: cc-pVTZ + FIP. The notation x/y means basis set x was used for calculation of polarizability derivatives and basis set y was used for calculation of the geometry and normal modes.

^b $10^{-36} \text{ m}^2/\text{sr}$, excitation wavelength $\lambda_0 = 514.5 \text{ nm}$.

^c $\text{\AA}^4/\text{amu}$.

^d Experimental data for Q-branch (2331 cm^{-1}) of the vibrational band of gaseous N_2 at 300 K [27].

^e From Ref. [36].

Table 2

Experimental and calculated Raman scattering differential cross sections (R), scattering activities (S) and depolarization ratios (ρ) of HF

Method	Pol/Geom	R^a	S^b	ρ
exp. ^c		42 ± 2	50 ± 2	0.03 ± 0.01
HF	1/2	10.5	16.2	0.12
	2/2	12.1	18.7	0.07
	3/2	14.4	22.2	0.05
S-VWN	1/1	14.9	18.1	0.12
	2/2	19.0	22.9	0.06
	3/2	23.1	27.8	0.04
B-LYP	1/1	16.3	19.0	0.13
	2/2	20.92	4.6	0.06
	3/2	24.1	28.3	0.05

^a $10^{-36} \text{ m}^2/\text{sr}$, excitation wavelength $\lambda_0 = 514.5 \text{ nm}$.

^b $\text{\AA}^4/\text{amu}$.

^c Experimental data for Q-branch (3962 cm^{-1}) of the vibrational band of gaseous monomeric HF at 300 K [37].

Raman intensities and depolarization ratios of the vibrational bands in the spectra of gaseous ethane are presented in Table 3. Let us first consider the intensities of C–H and C–D stretching modes observed at 2953 and 2181 cm^{-1} , respectively. Because of their localized character these modes exhibit a high similarity to vibrations in diatomic molecules. As for N_2 and HF, polarizability derivatives calculated with 6-31G(d, p) give intensities that are too small, regardless of the computational method. When diffuse functions are included, both Hartree–Fock and DFT intensities agree with the observed intensities to within experimental uncertainty. Hartree–Fock intensities are smaller than their DFT counterparts, but these differences originate mainly in the frequency dependence, in that Hartree–Fock tends to overestimate vibrational frequencies systematically. The C–C stretching vibration is significantly coupled to the ∂CCH and ∂CCD bending vibrations. These lie at 905 and 843 cm^{-1} in CD_3CH_3 and C_2D_6 , respectively. Intensities of these modes, as well as of the pure ∂CCD modes at 715 cm^{-1} (C_2DH_5) and 670 cm^{-1} (CD_3CH_3) are reproduced well by both HF and DFT when diffuse functions are used.

The basis set plays the most important role in prediction of Raman intensities of ∂HCH bending vibrations. This concerns the 1475 cm^{-1} band in CD_3CH_3 and the integral intensity from the 1250–1700 cm^{-1} region in the Raman spectrum of C_2H_6 .

Table 3

Experimental and calculated Raman scattering differential cross sections (R) and depolarization ratios (ρ) of ethane and its deuterated derivatives

Molecule	Experiment ^a freq (cm^{-1})	HF			S-VWN			B-LYP		
		R ρ			R ρ			R ρ		
		1/1	2/2	3/2	1/1	2/2	3/2	1/1	2/2	3/2
C_2H_6	850–1250	117	0.18	113	0.40	105	0.24	102	0.21	0.20
	1250–1700	85	0.72	282	0.74	106	0.74	64	0.74	0.74
C_2DH_5	715	1.8	~0.0	4.30	0.53	2.8	0.34	2.4	0.26	0.39
	2181	128	0.16	97	0.30	114	0.24	115	0.21	0.21
CD_3CH_3	670	1.3	0.75	3.3	0.75	1.3	0.75	1.0	0.75	1.1
	905	79	0.16	78	0.34	78	0.23	74	0.19	0.23
$\text{C}_2\text{D}_5\text{H}$	1475	38	0.75	128	0.75	50	0.75	31	0.75	0.75
	2953	130	0.23	106	0.35	121	0.28	120	0.24	0.24
C_2D_6	843	58	0.18	80	0.36	74	0.23	70	0.18	0.23
	mean deviation from experiment			41	0.15	9.6	0.07	9.3	0.04	0.07

^a Experimental data taken from Ref. [30]. The Raman differential cross sections and depolarization ratios were determined with 10 and 6% uncertainty, respectively. These were measured at 300 K and excitation wavelength $\lambda_0 = 514.5 \text{ \AA}$. For C_2H_6 , Raman intensities and depolarization ratios over the indicated integration frequency range are given. For other isotopomers, wavenumbers, intensities and depolarization ratios refer to individual bands.

^b $10^{-36} \text{ m}^2/\text{sr}$.

For these modes, the 6-31G(d, p) basis set gives a threefold overestimation of the intensities at the HF level, and the DFT methods appear to be even more sensitive when a basis set of inadequate quality is used. By all methods, reasonable agreement with experiment was reached using the FIP-augmented basis for the polarizability derivatives; this was also seen to be important for obtaining correct depolarization ratios.

4. Conclusion

In conclusion, preliminary indications are that Raman spectra predicted by local DFT compare less favorably to experiment than either Hartree–Fock or gradient-corrected DFT. In this study, the Hartree–Fock and B-LYP results are generally similar except for the HF molecule; here B-LYP is somewhat better, though the agreement with experiment is not as good as for the other molecules studied. For all methods, the best results were obtained with a polarized valence triple-zeta quality basis set augmented with additional diffuse polarization functions. A systematic study of DFT Raman spectra is underway, to assess basis set effects in more detail and to determine whether gradient-corrected DFT provides more reliable spectra than Hartree–Fock in general.

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