



Coupled-cluster calculations of Raman intensities and their application to N_4 and N_5^-

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Abstract

Raman intensities are evaluated by numerically differentiating the analytically calculated coupled-cluster singles and doubles (CCSD) polarizabilities with respect to small geometric perturbations. The CCSD Raman intensities are calibrated by comparison to several molecules with experimentally known Raman Intensities. The CCSD Raman intensities agree well with experiment. Predictions for tetrahedral N_4 , and the pentazole anion N_5^- are reported. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Infrared (IR) and Raman spectroscopy are standard tools in the arsenal of spectroscopists and practicing chemists and complementary in the information they provide. To quote Kettle [1] “the one technique is, in a sense, incomplete without the other”. Sharp bands in the Raman are frequently broad in the IR and vice versa. Nevertheless, Raman spectroscopy has several practical advantages. No sample preparation is required, leaving the sample intact for other investigations. The depolarization ratios provide information about the symmetry of the vibrations, and the intense and narrow combination bands in Raman spectra facilitate easier measurements of isotopic shifts.

As is well known, accurate calculation of IR frequencies and intensities requires the inclusion of

electron correlation effects by using methods which go beyond the Hartree–Fock (HF-SCF) method [2]. Remarkable progress has been made in developing high-level accurate correlated methods to calculate IR parameters [3]. Although there are some successful modeling efforts limited to depolarization ratios [4], the first-principle theoretical developments for accurate Raman intensity calculations have not attracted the same attention as IR spectra. Raman intensity calculations are limited to Hartree–Fock (HF-SCF) [5–7] Kohn–Sham (KS-SCF) [8], configuration interaction (CI) methods [9,10] and MBPT(2) (available in GAUSSIAN-98 and ACES II). This is mainly because the Raman intensities require polarizability derivatives which as the derivative of a second-order property, are much harder to compute than the dipole (first-order property) derivatives required by IR intensities. However, there are some numerical simplifications, too, as all the diagonal elements of the polarizability have the same sign while the dipole moment, like the β -hyperpolariza-

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bility, can be sensitive to the subtle differences in charge density [11].

Coupled-cluster (CC) methods for polarizability calculations have only recently become available [12–14], and CC-based Raman intensities have not been reported so far. It is evident from prior post-HF calculations that the correlation corrections will be essential for the Raman intensities to be predictive. We hope such calculations will also stimulate experimental studies, since one of the major obstacles today is frequently not having enough reliable experimental results to calibrate the accuracy of calculated results.

This Letter describes the calculation of Raman intensities and depolarization ratios by using CC wave functions. A brief description of the theory is presented in Section 2, followed by several applications in order to evaluate the performance of the proposed method. In our continuing effort to establish the existence of polynitrogen molecules like tetrahedral N_4 [15–17] and new derivatives of the pentazole anion, N_5^- [18], we report high-level CC energies, vibrational frequencies, and IR and Raman intensities for these unknown species.

2. Theory

The Raman intensities are defined by the following two quantities. The intensity activity coefficient (I),

$$I = (45\alpha')^2 + 7(\gamma')^2, \quad (1)$$

and the depolarization ratio (ρ),

$$\rho = \frac{3(\gamma')^2}{45(\alpha')^2 + 4(\gamma')^2} \quad (2)$$

where α' and γ' are the derivatives of the trace and anisotropy of the polarizability tensor. For the polarizability $\alpha_{ij} = (\partial^2 E / (\partial \varepsilon_i \partial \varepsilon_j))_{\varepsilon_{i,j}=0}$, the derivative

$$\frac{\partial \alpha_{ij}}{\partial R_k} = \frac{\partial}{\partial R_k} \left(\frac{\partial E}{\partial \varepsilon_i \partial \varepsilon_j} \right). \quad (3)$$

In Eq. (3), ε_i and ε_j are electric field perturbations in i , ($i = x, y, z$) and j , ($j = x, y, z$) directions, R_k is a nuclear coordinate in k , ($k = x, y, z$) directions, and E is the total energy of the system.

As we can see from Eq. (3), the Raman intensities are related to a third derivative of energy. Purely analytical calculation of third derivatives for post-HF methods is not practical as yet, and at least one derivative must be evaluated numerically. Certainly, the final results have no effect on which order the derivatives are taken, but the overall efficiency can be affected. Since the analytical gradients can be calculated efficiently for a wide range of post-HF methods, it is more efficient to first take the geometric derivative analytically, and then twice differentiate the resulting gradient with respect to electric field perturbations than first taking two electric field derivatives analytically, and then differentiate the resulting polarizability numerically with respect to geometric perturbations. However, the latter, though less efficient, is easier to implement within the ACES II program system.

In our group, the CC treatment of polarizabilities has evolved as an extension of the CC treatment of excited states, equation-of-motion CC (EOM-CC). The sum-over-states (SOS) [2,19] polarizabilities based on EOM-CCSD states were first reported by Stanton and Bartlett [19] using SOS approximation for the property. As pointed out in that paper, this ‘CI-like approximation’ for a second-order property does not necessarily correspond to the second derivative of the CCSD energy [19], even with fixed orbitals, because of its failure to satisfy the higher-order analogs of the Hellmann–Feynman theorem [20,21]. Alternatively, the CCSD second derivative can be obtained analytically with a quadratic formula. A detailed discussion is presented elsewhere [21]. A comparative numerical analysis is presented by Rozyzcko et al. [14]. Here, to avoid any ambiguity any we use EOM-CCSD quadratic scheme since it is exactly the analytical second derivative of the CCSD energy for polarizabilities.

3. Computational methods

All the calculations reported in this study were performed by using the ACES II program system [22]. The IR and Raman frequencies and intensities were evaluated at the SCF, CCSD level using Sadlej’s polarization (POL) basis sets [23]. Spherical har-

monic Gaussian functions have been used in all the calculations.

4. Results

4.1. H_2O , NH_3 , and CH_4

For calibration purposes, we study H_2O , NH_3 and CH_4 where reliable experimental Raman intensities are available. In Table 1, the SCF and CCSD results obtained with the POL basis along with the CI, KS-DFT and experiment results are presented. The equilibrium geometries are optimum for POL basis sets and the particular method (SCF or CCSD). Several previous SCF results using different basis set are available in the literature [24]. The POL basis sets were chosen from our prior experience of their performance in polarizability and excited state calculations, and we do not plan to address the basis set effects within the context of this Letter. The absolute mean correlation effects for all three molecules are about 12% with respect to SCF results (intensities

which are smaller than $10 \text{ \AA}^4/\text{a.m.u.}$ are ignored to obtain meaningful median percentages). This is consistent with our previous observation of correlation effects on polarizabilities. The depolarization ratios are essentially insensitive to correlation effects, assisting their modeling [4].

The CCSD result for the B_2 mode of H_2O shows the largest deviation from experiment while for the other two modes the CCSD and experimental results are essentially the same. The only available experimental depolarization ratio which is not determined by symmetry is the A_1 symmetric stretch of H_2O , and the calculated depolarization ratio (regardless of the method) is almost identical to experiment. In the case of NH_3 , the average deviation of CCSD results is 15%, and it is a significant improvement over the HF-SCF results (33%). The calculated CCSD Raman intensity shows an improvement over the CI and KS-DFT results for the only one experimentally known intensity of NH_3 . For CH_4 , the average deviations from experiment for HF-SCF and CCSD are 20% and 8%, respectively. This can be compared with corresponding 4% and 12% deviations of CI and KS-DFT, respectively.

Table 1

A comparison of CCSD Raman intensities with CI, KS-DFT and experiment for H_2O , NH_3 and CH_4

Molecule	Symmetry	Vib. frequency (cm^{-1})		IR intensity (km/mol)		Raman intensity ($\text{\AA}^4/\text{a.m.u.}$)				
		SCF	CCSD	SCF	CCSD	SCF	CCSD	CI	KS-DFT ^c	Expt.
H_2O	A_1	1784.8	1669.6	92	69	1 (0.75)	1 (0.71)	1.1 ^a	1.0 (0.71)	0.9 ± 2 (0.74) ^d
	A_1	4124.8	3814.7	17	3	88 (0.06)	111 (0.04)	102	112 (0.04)	108 ± 14 (0.03)
	B_2	4221.6	3933.5	84	51	25 (0.75)	26 (0.75)	31	25 (0.75)	19.2 ± 2.1 (0.75)
NH_3	A_1	1129.5	1100.9	168	119	0.6 (0.43)	2 (0.29)		1.4 (0.23)	
	E	1784.6	1674.0	36	24	2 (0.75)	3 (0.75)		4.5 (0.75)	
	A_1	3693.3	3455.6	1	7	155 (0.02)	182 (0.01)		208 (0.01)	182 ± 2 ^e
	E	3826.3	3590.9	12	2	80 (0.75)	77 (0.75)		104 (0.75)	
CH_4	T_2	1430.5	1319.5	26	22	0.1 (0.75)	0 (0.75)	0.04	0.01 (0.75)	≤ 0.24 (0.75) ^f
	E	1657.1	1560.1	0	0	9 (0.75)	10 (0.75)	6.7	7.4 (0.75)	7.0 ± 0.4 (0.75)
	A_1	3147.7	3005.9	0	0	236 (0.00)	226 (0.00)	212 ^b	252 (0.00)	230 ± 12 (0.00)
	T_2	3271.6	3149.6	99	69	153 (0.75)	133 (0.75)	129	149 (0.75)	128 ± 7 (0.75)

^a See Ref. [9].

^b See Ref. [10].

^c See Ref. [8].

^d See Ref. [32,33].

^e See Ref. [34].

^f See Ref. [35].

In principle, because of the presence of geometric derivatives, the IR/Raman frequency and intensity calculation should be consistently done at the optimum equilibrium geometry for a particular theoretical model (basis set and calculation level). However, the basis sets which are designed to perform well for geometries and energies do not always perform well for other properties such as dipole moments and polarizabilities. As a result, in practice, it is not unusual to use geometries which are not optimal for the theoretical model used in polarizability calculations. In order to estimate the numerical errors introduced by using different basis sets, we have obtained IR/Raman frequencies and intensities for the same set of three molecules with the POL basis set, but now at the experimental equilibrium geometry. The results are reported in Table 2. The average deviation between the two groups of intensities at the SCF and CCSD level in Tables 1 and 2 are about 3–4 units while the frequencies show somewhat larger deviations. The depolarization ratios are nearly unaffected. Also, the use of the experimental geometry as expected, does not necessarily improve the agreement

of calculated intensities with experiment. In essence, we can conclude that as long as the energy gradients are sufficiently small, the Raman and IR intensities are stable near the optimum equilibrium geometry.

4.2. C_2H_6 and C_2H_4

We have also selected two other molecules in our study, i.e., C_2H_6 and C_2H_4 . These molecules have experimental Raman intensities, but their reliability is less certain. For example, both molecules have two sets of experimental data which differ significantly (see Ref. [8]). There are no other ab initio correlated results reported for these molecules. In Table 3 we report both the SCF and CCSD results along with the KS-DFT and most recent experimental results. For both molecules, the CCSD results show a significant improvement over the HF-SCF results. Except for a few cases (comparatively smaller intensities), the CCSD results are always within the error bars of the experiment, and that is not always the case for KS-DFT results.

Table 2
A comparison of CCSD Raman intensities with experiment for H_2O , NH_3 and CH_4

Molecule	Symmetry	Vib. frequency (cm^{-1})		IR intensity (km/mol)		Raman intensity ($\text{\AA}^4/a.m.u.$)		
		SCF	CCSD	SCF	CCSD	SCF	CCSD	Expt.
H_2O	A_1	1804.1	1638.9	93	71	1 (0.75)	1 (0.68)	0.9 ± 2 (0.74) ^b
	A_1	3964.0	3948.7	16	4	92 (0.07)	108 (0.04)	108 ± 14 (0.03)
	B_2	4064.4	4073.3	85	55	27 (0.75)	25 (0.75)	19.2 ± 2.1 (0.75)
NH_3	A_1	1195.0	999.3	159	133	0.5 (0.50)	2 (0.27)	
	E	1797.7	1655.3	25	26	1 (0.75)	1 (0.75)	
	A_1	3602.5	3579.2	2	6	161 (0.02)	175 (0.01)	182 ± 2^c
	E	3727.8	3725.1	9	5	86 (0.75)	72 (0.75)	
CH_4	T_2	1421.5	1279.5	27	27	0 (0.75)	0 (0.75)	≤ 0.24 (0.75) ^d
	E	1654.4	1548.8	0	0	8 (0.74)	8 (0.75)	7.0 ± 0.4 (0.75)
	A_1	3183.2	3153.4	0	0	233 (0.00)	215 (0.00)	230 ± 12 (0.00)
	T_2	3310.4	3308.9	96	42	150 (0.75)	124 (0.75)	128 ± 7 (0.75)

^a At the experimental geometry using POL basis set.

^b See Refs. [32,33].

^c See Ref. [34].

^d See Ref. [35].

Table 3

A comparison of CCSD Raman intensities with KS-DFT and experiment for C₂H₄ and C₂H₆^a

Molecule	Symmetry	Vib. frequency (cm ⁻¹)				Raman intensity (Å ⁴ /a.m.u.)	
		SCF	CCSD	SCF	CCSD	KS-DFT ^b	Expt. ^c
C ₂ H ₄	B _{2g}	1111.9	968.5	10 (0.75)	3 (0.75)	10 (0.75)	16.5 (0.75)
	B _{1g}	1324.3	1222.0	0.3 (0.75)	0.3 (0.75)	1.0 (0.75)	≤ 2.9 (0.75)
	A _g	1456.4	1353.7	57 (0.19)	34 (0.22)	28 (0.01)	17.8 (≤ 0.002)
	A _g	1813.6	1679.0	68 (0.02)	26 (0.01)	30 (0.27)	26.7 ± 3.3 (0.19)
	A _g	3287.6	3129.2	189 (0.13)	224 (0.09)	259 (0.09)	180 ± 28 (0.11)
	B _{1g}	3355.9	3204.4	119 (0.75)	109 (0.75)	130 (0.75)	71 ± 15 (0.65)
C ₂ H ₆	A _{1g}	1067.0	1031.0	15 (0.18)	14 (0.15)	7.3 (0.11)	16.9 ± 1.7 (0.18)
	A _{1g}	1539.1	1417.4	0.3 (0.21)	0.1 (0.21)	0.05 (0.22)	2.2 ± 2.0 (0.72)
	A _{1g}	3162.0	3017.1	355 (0.01)	345 (0.01)	399 (0.002)	360 ± 77 (≤ 0.06)
	E _g	1301.8	1197.8	0.2 (0.75)	0.1 (0.75)	0.1 (0.75)	< 0.5
	E _g	1594.1	1483.4	19 (0.75)	21 (0.75)	17 (0.75)	18.3 ± 4.6 (0.72)
	E _g	3214.1	3085.6	259 (0.75)	235 (0.75)	256 (0.75)	170 ± 43 (0.75)

^a Only the Raman active bands are reported.^b See Ref. [8].^c Compiled from Ref. [36].

4.3. N₄ and N₅⁻

The polynitrogens are an elusive group of ‘meta-stable’ molecules (see Refs. [15–18,25–30] for a discussion), that can be potential candidates for high-energy density materials (HEDM). Much theo-

retical work has been devoted to studying the energetics, vibrational frequencies, and decomposition paths of polynitrogen species, especially for tetrahedral N₄ (see Ref. [17] for list of references). However, the synthesis of polynitrogen compounds has been a challenge, and only a few homoleptic polyni-

Table 4

Vibrational frequencies, IR and Raman intensities of N₄ and N₅⁻

Molecule		MBPT(2)/ DZP ^a	CCSD/ DZP ^a	CCSD/ aug-cc-pVTZ ^b	CCSD(T)/ aug-cc-pVTZ ^b
N ₄ (T _d) ^c	r _e	1.476	1.450	1.443	1.461
	E	893	776	730 (0.0, 9.4, 0.75)	724
	T ₂	698(0.0)	1013(15.9)	934 (11.7, 30.4, 0.75)	936 (9.8)
	A ₁	1236	1412	1298 (0.0, 45.6, 0.00)	1296
N ₅ ⁻ (D _{5h})	r _e			1.318	1.329
	E ₂ ^{''}			782.7 (0.0, 0.0, 0.75) ^d	
	E ₂ [']			1059.5 (0.0, 3.6, 0.75)	
	E ₂			1124.2 (0.0, 2.0, 0.75)	
	A ₁ [']			1222.4 (0.0, 47.8, 0.04)	
	E ₁ [']			1286.1 (27.2, 0.0, 0.75)	

^a See Ref. [16]. These results are first presented in 1990 (see Ref. [15]).^b The present work.^c B3LYP/TZ2P frequencies are 752.2, 966.7 and 1360.5 cm⁻¹, respectively.^d The IR and Raman intensities and Raman depolarization ratios are in parenthesis.

trogens are known in the literature. They includes the long-known N_2 , and N_3^- , the recently synthesized N_5^+ [26], and N_4^+ [27,28]. The characterization of N_5^+ has greatly benefited from having accurate theoretically calculated IR, Raman and NMR spectral parameters [26] and is a good illustration of the use of predictive theory in experimental characterization of newly synthesised molecules. It is likely that N_4 will be observed and new derivatives of N_5^- are synthesized, so we have chosen to provide predictive quality IR/Raman data for these species. In Table 4, we report aug-cc-pVTZ geometries and IR/Raman frequencies and intensities for N_4 and N_5^- (for N_5^- , IR and Raman intensities are obtained with the POL basis at the aug-cc-pVTZ geometry). These results provide the current best estimates to be used in their experimental characterization. The post-HF treatment of N_4 vibrational frequencies started in 1990 [15,29], and then was extended to the CC level [16,30]. The aug-cc-pVTZ basis, which consists of 184 (5s,4p,3d,2f) functions is the most extensive yet used, and the CCSD(T) results for 'harmonic' vibrational frequencies should be nearly predictive. The limits can be estimated from extensive results for CC methods that include connected quadruples, T_4 for N_2 [31], which would suggest that further basis set effects, particularly for the treatment of the core electrons, which fortunately tend to partly cancel with effects due to T_4 , would suggest a ± 5 – 10 cm^{-1} error for the harmonic frequencies. B3LYP DFT calculations provide frequencies that are +28, +31, and +64 cm^{-1} higher (see footnote to Table 4).

5. Conclusions

Raman intensities were calculated using the CCSD method for several molecules with experimentally known intensities. Our goal was to assess the performance of CCSD compared to experiment and other theoretical methods (HF-SCF, CI and KS-DFT). The correlation effects on Raman intensities are about 12%. The overall performance of CCSD compared to experiment is satisfactory. However, it is impossible to offer definitive conclusions based on a study limited to only a few molecules. More reliable exper-

imental measurements must be done. It is our hope that having accurate methods to calculate intensities would inspire more experimental measurements. We have not addressed the basis set issues here, but we expect basis sets which perform well for polarizability calculations would perform well on Raman intensities, if they are also good for geometries. An assessment of different methods is also a challenge with the limited set of reliable experimental results. It is certainly clear that methods which go beyond HF-SCF are necessary to obtain acceptable results, but it is not all that clear the relative performance of different correlation methods CI, KS-DFT and CCSD. Certainly, CCSD seems to behave more consistently.

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