Comparison study of the prediction of Raman intensities using electronic structure methods

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Raman intensities have been computed for a series of test molecules (N_2, H_2S, H_2O, H_2CO, CH_4, C_2H_2, C_2H_4, C_2H_6, SiO_2, NH_3, CH_2F_2, and CH_2Cl_2) using Hartree–Fock, second-order Møller–Plesset perturbation theory (MP2), and density functional theory, including local, gradient-corrected, and hybrid methods (S-VWN, B-LYP and B3-LYP, and MPW1-PW91) to evaluate their relative performance. Comparisons were made with three different basis sets: 6-31G(d), Sadlej, and aug-cc-pVTZ. The quality of basis set used was found to be the most important factor in achieving quantitative results. The medium sized Sadlej basis provided excellent quantitative Raman intensities, comparable to those obtained with the much larger aug-cc-pVTZ basis set. Harmonic vibrational frequencies computed with the Sadlej basis set were in good agreement with experimental fundamentals. For the quantitative prediction of vibrational Raman spectra, the Sadlej basis set is an excellent compromise between computational cost and quality of results. © *1999 American Institute of Physics.* [S0021-9606(99)30543-2]

I. INTRODUCTION

Recent advances in Raman instrumentation, such as Raman microscopy and 2D imaging, promise to increase the already widespread use of Raman spectroscopy as a key probe in modern surface chemistry and materials research.[1–4] It is a standard tool for structural characterization, following system evolution and probing the dynamics of chemical systems. Despite the important role it plays in present-day analytical applications, very few reports of the first-principle theoretical prediction of Raman spectra have appeared in the scientific literature. The application of the technique to complex systems is greatly assisted by quantum chemical calculations, yielding theoretical normal mode frequencies and ground state Raman band intensities. Theoretical Raman spectra may also be used to elucidate structure in difficult regimes, such as solvated systems. Consider, for example, the determination of lithium–perchlorate electrolyte ion pair geometries by *ab initio* methods and experimental corroboration by Raman spectroscopy.[5] It is important that quantum chemical methods give quantitatively acceptable intensities as well as vibrational frequencies.

The prediction of vibrational properties for polyatomics using electronic structure methods is becoming increasingly common in the chemical literature. This can be largely attributed to the increasing availability of robust energy derivative programs, in which first and second energy derivatives are computed analytically.[6] The prediction of vibrational frequencies and infrared intensities has been the topic of numerous reports. In the computation of these properties, density functional theory (DFT) outperformed traditional *ab initio* methods. In articles by Scott and Radom,[7] and Wong,[8] harmonic vibrational frequencies calculated by DFT methods were found to be in better agreement with observed fundamentals.[9] Recent studies of theoretical infrared intensities compared DFT with Hartree–Fock and second-order Møller–Plesset perturbation theory (MP2).[10–12] Previous studies showed that with increasing electron correlation the theoretical intensities converge toward experimental values.[13] Work in our laboratory has shown that hybrid DFT gives infrared intensities in better agreement with experiment than Hartree–Fock and MP2.[14]

Raman intensities depend on the square of the polarizability derivative which requires the calculation of the third derivative of the system energy with respect to coordinates and electric field ($\partial\alpha/\partial Q_k = \partial^3 E/\partial Q_k \partial F_i \partial F_k$). Compared to infrared intensities (which depend on the square of the dipole moment derivatives), there have been very few studies of the first-principle prediction of Raman intensities in the literature. Published reports are primarily for individual molecules, and usually at the SCF (self-consistent field) level[15–18] and in some cases by DFT methods.[11,19,20] There seem to be no systematic surveys comparing different theoretical methods with different basis sets for a representative collection of molecules. In part this may be due to the relative scarcity of reliable experimental data and because suitable computer programs have only recently become more readily available. In the present work, Raman intensities are computed by Hartree–Fock, MP2, local, gradient-corrected, and hybrid DFT methods with a number of different basis sets, to provide an overview of relative performance. These methods are used to compute Raman intensities for a set of test molecules including one, two, and three heavy atom systems (N_2, H_2S, H_2O, H_2CO, CH_4, C_2H_2, C_2H_4, C_2H_6, SiO_2, NH_3, CH_2F_2, and CH_2Cl_2).

II. METHODS

The calculations in this study were performed using the GAUSSIAN 98 suite of programs.[21] Following full geometry

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optimizations at each level of theory, harmonic frequencies and dipole moment derivatives were computed analytically for Hartree–Fock, MP2 (2nd order Møller–Plesset perturbation theory, frozen core)[22] and the various DFT methods employed in this study. Polarizability derivatives were computed using numerical differentiation of the analytic dipole derivatives with respect to the applied electric field. Static Raman intensities (zero-frequency, nonresonant) were computed in the double harmonic approximation,[23] ignoring cubic and higher force constants and omitting second and higher polarizability derivatives. The vibrational properties were computed for the test molecules in their ground state, enforcing their respective point group symmetry. The DFT methods employed here consisted of the S-VWN local functional, corresponding to the Slater–Dirac exchange functional (S) (Ref. 24) with the Vosko–Wilk–Nusair fit for the correlation functional (VWN),[25] the B-LYP gradient-corrected functional, corresponding to Becke's gradient corrected exchange functional (B) (Ref. 26) with the Lee–Yang–Parr fit for the correlation functional (LYP) (Ref. 27) and two hybrid functionals: B3-LYP and MPW1-PW91, corresponding to Becke's three parameter exchange functional (B3) (Ref. 28) with the Lee–Yang–Parr fit for the correlation functional (LYP), and Barone's and Adamo's Becke-style one parameter exchange functional (MPW1) (Ref. 29) with Perdew and Wang's gradient-corrected correlation functional (PW91).[30] Calculations were carried out with the following basis sets: 6-31G(d) to evaluate the performance of the basis set most frequently used for vibrational calculations (split valence double zeta augmented with one set of polarization functions on heavy atoms),[31,32] Sadlej's polarized triple zeta basis set, optimized for electric properties $[5s,3p,2d/7s,5p,2d/3s,2p]$,[33–35] and Dunning's augmented correlation-consistent triple zeta basis set, aug-cc-pVTZ $[5s,4p,3d,2f/6s,5p,3d,2f/4s,3p,2d]$.[36–38] Basis set dependence for the S-VWN and B3-LYP density functionals was investigated by systematically adding diffuse[39] and polarization functions[40] to the 6-31G split valence double zeta basis set. Complete tables of numerical data are available on the world wide web.[41]

III. RESULTS AND DISCUSSION

A. Large basis set (aug-cc-pVTZ) performance

When computing molecular properties using electronic structure methods, the quality of results obtained is usually limited by shortcomings in two dimensions: incomplete treatment of electron correlation and basis set truncation.[42] When comparing results obtained from different theoretical models, use of the largest feasible basis set allows better assessment of the methods themselves, diminishing basis set truncation effects. Previous studies have found that, for the quantitative prediction of electric field response properties, large polarized basis sets are required.[43,44] This is attributed to the need to describe the tail region of the wave function satisfactorily, whose electron density is less rigidly held and therefore contributes most to the molecular polarizability.[45–47] To evaluate the performance of the methods approaching the large basis set limit, calculations were carried out for the set of test molecules using the triple zeta correlation-consistent polarized basis set of Dunning augmented with a set of diffuse functions, aug-cc-pVTZ. These results are compared with experimental intensities where available.[48]

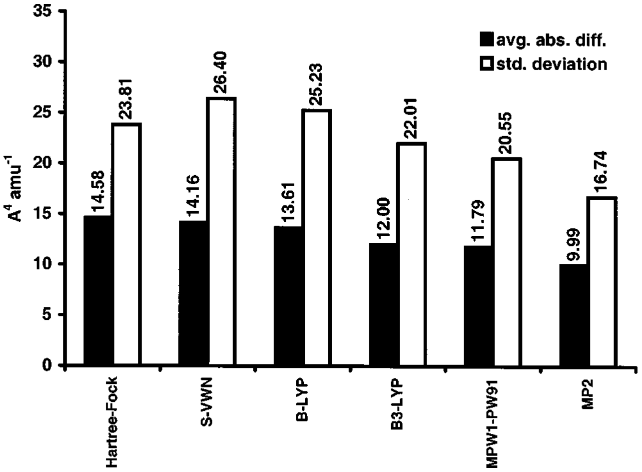

FIG. 1. Average absolute difference and standard deviation from experimental Raman intensities with the aug-cc-pVTZ basis set.

Figure 1 shows the average absolute difference from experimental intensities using the aug-cc-pVTZ basis set and the standard deviation for each of the methods considered here. The average difference, average absolute difference, and standard deviation are also presented in Table I for comparison with other basis set levels which follow in the present work. A surprising observation is that all methods examined here have average absolute differences that are remarkably similar when compared to experiment. Hartree–Fock falls furthest from experiment, as expected, with an average absolute difference and standard deviation of ca. 15 and 24 A^4 amu^{-1}, respectively. What is surprising is that the effect of including electron correlation is considerably smaller for computed Raman intensities than for infrared intensities.[14] Local and gradient-corrected DFT perform almost identically when compared to experiment, with average absolute difference and standard deviation of ca. 14 and 26 A^4 amu^{-1}. The two hybrid methods predict intensities in closer agreement with experiment than Hartree–Fock, S-VWN, or B-LYP, although the improvement is small. The MP2 results are in best agreement with experimental data, having the lowest absolute difference and standard deviation; however, its average absolute difference from experiment is only ca. 5 and 2 A^4 amu^{-1} closer than those of Hartree–Fock and hybrid DFT, respectively. The vibrational mode for which all methods considered here predicted the largest deviation from observed value is the e_g CH stretching vibration of ethane. All methods in the study overestimated the intensity of this mode. Another vibration of note is the a_g CH stretch of ethene. For this band of ethene, all correlated methods considered here predicted an intensity in worse agreement with experiment than Hartree–Fock.

Absolute Raman intensities are more difficult to measure experimentally than absolute infrared intensities.[49] The experimental uncertainty in the bands used for the above com-

TABLE I. Average difference, average absolute difference, and standard deviation from experimental Raman intensities in A^4 amu^{-1}.

		Hartree–Fock	S-VWN	B-LYP	B3-LYP	MPW1-PW91	MP2	Rel. CPU time[a]
6-31G(*d*)	avg. diff.	1.01	−1.74	−1.56	−2.59	−3.00	−8.35	1.0
	avg. abs. diff.	30.31	30.96	31.22	30.17	29.70	30.15	
	std. deviation	50.05	49.11	49.71	49.27	48.74	50.40	
Sadlej pVTZ	avg. diff.	8.50	15.07	16.15	11.32	10.07	7.38	5.1
	avg. abs. diff.	15.07	16.92	17.74	13.77	13.63	11.47	
	std. deviation	24.44	28.82	28.51	23.43	22.30	19.67	
aug-cc-pVTZ	avg. diff.	5.84	11.43	11.16	7.12	5.04	2.34	46.9
	avg. abs. diff.	14.58	14.16	13.61	12.00	11.79	9.99	
	std. deviation	23.81	26.40	25.23	22.01	20.55	16.74	
	rel. CPU time[b]	1.0	1.5	1.7	1.8	2.1	32.9	

[a] Relative CPU time for a harmonic frequency calculation computing Raman intensities for H_2CO using B3-LYP.

[b] Relative CPU time for a harmonic frequency calculation computing Raman intensities for H_2CO.

parison were all greater than or equal to 10%, and for many the uncertainty was even higher. The uncertainty in the experimental data for the set of molecules considered may contribute to the apparent insensitivity to the inclusion of electron correlation with the large Dunning basis set. Differences between experiment and theory due to the neglect of frequency dependencies of the polarizability derivatives and vibrational anharmonicities in the calculations, may also mask the effect of electron correlation. An alternative means of assessing the electron correlation effect is to compare the DFT and MP2 Raman intensities directly to those obtained from an uncorrelated method, i.e., Hartree–Fock. Table II presents the average difference, average absolute difference, and standard deviation from Hartree–Fock for the correlated methods considered here for the complete set of test molecules. The differences reaffirm that the inclusion of electron correlation using density functional theory or MP2 has a relatively small effect on computed Raman intensities with any of the three considered basis sets. An earlier study of theoretical Raman intensities for H_2O showed similar behavior in comparing configuration interaction calculations with Hartree–Fock.[50] The local DFT methods are furthest from Hartree–Fock and hybrid DFT closest, which could be rationalized based on inclusion of exact exchange. Note that MP2, the most often used conventional correlated *ab initio* method, gives Raman intensities only ca. 9 A^4 amu^{-1} in difference with Hartree–Fock. This is important since MP2 Raman intensities come at a much greater cost than Hartree–Fock intensities (more than 32 times the relative CPU cost for a molecule as small as formaldehyde using the aug-cc-pVTZ basis set, see Table I).

B. Performance of the 6-31G(*d*) basis set

For the prediction of molecular geometries and vibrational properties, the Pople split valence double zeta basis set with one set of polarization functions on heavy atoms, 6-31G(*d*), has become the most often used basis set. Previous experience has shown that it is an economical choice yielding harmonic vibrational frequencies which can be easily scaled for comparison with observed fundamentals[7,8] and infrared intensities which are qualitatively acceptable,[14,44] particularly when DFT methods are used.

Figure 2 shows the average absolute difference and standard deviation from experiment with the 6-31G(*d*) basis set for each of the methods considered here. Raman intensities computed with this basis show even less variation with the level of theory than with the large Dunning basis considered above. All the methods perform equally well in predicting Raman intensities with average absolute difference and stan-

TABLE II. Average difference, average absolute difference, and standard deviation from Hartree–Fock Raman intensities in A^4 amu^{-1}.

		S-VWN	B-LYP	B3-LYP	MPW1-PW91	MP2
6-31G(*d*)	avg. diff.	−1.51	−1.47	−2.44	−2.72	−5.98
	avg. abs. diff.	8.22	7.63	6.03	5.76	9.43
	std. deviation	12.77	11.85	9.68	9.15	14.53
Sadlej pVTZ	avg. diff.	5.90	6.57	2.79	1.49	0.74
	avg. abs. diff.	11.90	10.82	7.13	6.51	9.56
	std. deviation	21.28	18.83	12.48	11.41	17.35
aug-cc-pVTZ	avg. diff.	5.41	5.31	1.83	0.30	−1.09
	avg. abs. diff.	11.08	9.60	6.18	5.91	8.76
	std. deviation	20.01	17.32	11.50	10.41	15.84

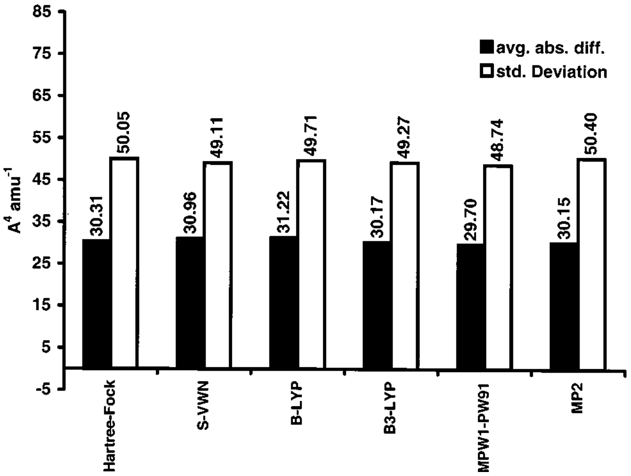

FIG. 2. Average absolute difference and standard deviation from experimental Raman intensities with the 6-31G(d) basis set.

dard deviation from experiment of ca. 30 and 50 A^4 amu^{-1}, respectively (roughly twice as large as found with the bigger aug-cc-pVTZ basis set). This suggests that the basis set effect on the absolute Raman intensities could be rather large. However, the difference between the DFT and Hartree–Fock results for the 6-31G(d) is somewhat smaller than with the Dunning basis, as shown in Table II, indicating that the effect of electron correlation is less pronounced than with larger basis sets.

C. Performance of Sadlej's medium size specialized basis set

A general trend for predicting molecular properties is that as the size of basis set is increased, the quality of results improves because of greater flexibility in the molecular wave function. For some properties, good results can be obtained with modest sized basis sets, provided the basis functions are developed appropriately. Sadlej has developed a medium sized basis set fit to reproduce molecular polarizabilities.[33–35] It might be expected that this basis set would also perform well in the prediction of Raman intensities, since they depend on the polarizability derivatives with respect to atomic displacement.

Figure 3 shows Raman intensities computed with Sadlej's basis set compared to those obtained with the much larger aug-cc-pVTZ basis set. Excellent agreement is found between Raman intensities predicted with the two basis sets. The Sadlej basis was found to have an average absolute difference and standard deviation of ca. 3 and 5 A^4 amu^{-1} from aug-cc-pVTZ, respectively. In comparison with experimental Raman intensities, the performance of the Sadlej basis set is similar to the aug-cc-pVTZ basis, with average absolute difference and standard deviation from experimental values only a little larger than for aug-cc-pVTZ. Since these calculations are ca. ten times faster (see Table I), the Sadlej basis set provides very substantial savings in computational effort with almost no degradation in the quality of Raman intensities obtained.

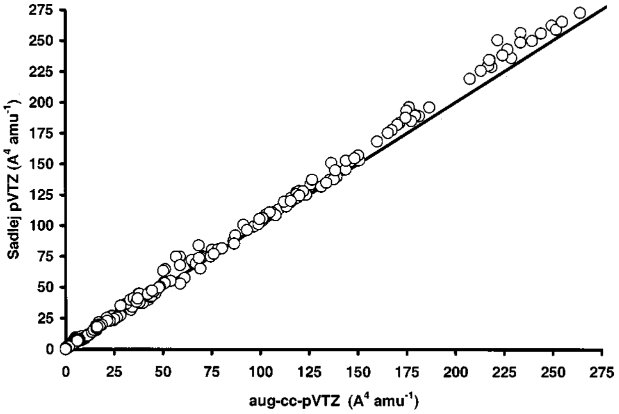

FIG. 3. Comparison of Raman intensities with Sadlej's polarized triple zeta basis set and with Dunning's aug-cc-pVTZ basis set.

D. Basis set dependence for local and hybrid DFT

The quality of basis set needed to predict converged chemical properties is of great interest to researchers seeking to maximize the quality of results and minimize the computational effort. Since polarized split valence basis sets of double zeta quality [e.g., 6-31G(d)] represent the middle ground in terms of cost and quality in the prediction of molecular properties, it represents a logical starting point to test the basis set dependence by systematically adding additional diffuse and polarization functions.

The average absolute difference and standard deviation of S-VWN Raman intensities compared to S-VWN/Sadlej intensities are shown in Fig. 4. As additional basis functions are added to the 6-31G basis, the Raman intensities converge towards the Sadlej and aug-cc-pVTZ values. The rate of convergence is slower than that observed for infrared intensities.[14] Addition of heavy atom polarization functions to the 6-31+G basis set lowers the average absolute difference ca. 2 A^4 amu^{-1} each time. The sensitivity to hydrogen polarization functions is a little less, lowering the average absolute difference ca. 1 A^4 amu^{-1}. The addition of a set of diffuse functions on hydrogens has a larger effect, lowering the average absolute difference by ca. 3 A^4 amu^{-1}.[51] Even

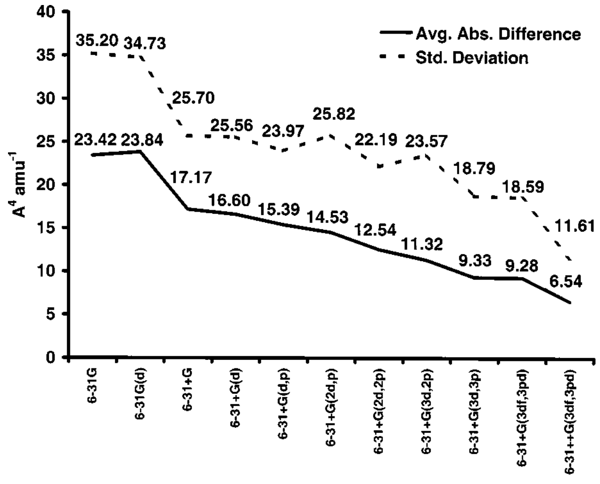

FIG. 4. The Raman intensity basis set dependence for local DFT (S-VWN) with respect to results obtained with the Sadlej electric property basis set.

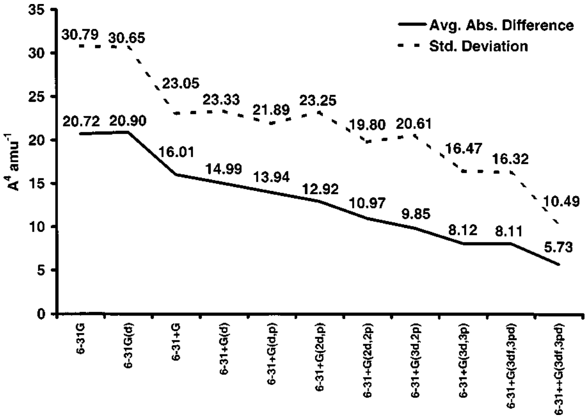

FIG. 5. The Raman intensity basis set dependence for hybrid DFT (B3-LYP) with respect to results obtained with the Sadlej electric property basis set.

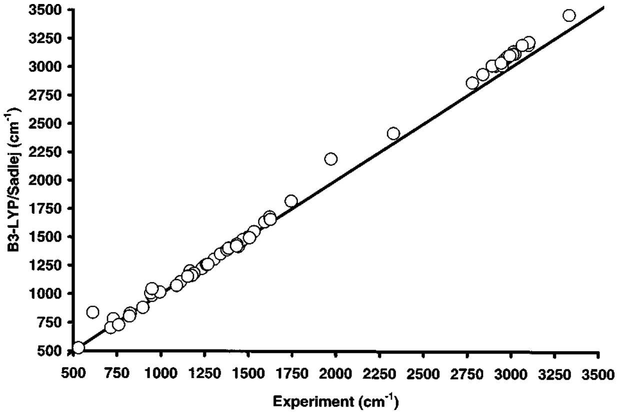

FIG. 6. Comparison of B3-LYP Sadlej harmonic frequencies with experimental fundamental frequencies.

with all the extra polarization and diffuse functions, the S-VWN/6-31++G(3df,3pd) Raman intensities have an average absolute difference and a standard deviation of ca. 7 and 12 A^4 amu^{-1}, respectively, from the Sadlej basis results.

Figure 5 shows the basis set dependence of computed Raman intensities for a hybrid density functional method (B3-LYP). The convergence pattern for B3-LYP is very similar to S-VWN. The addition of heavy atom polarization functions to the 6-31+G basis set lowers the average absolute difference by ca. 1 A^4 amu^{-1} each time. A set of diffuse functions on hydrogens lowers the average absolute difference by ca. 2 A^4 amu^{-1}. With the B3-LYP method, comparison of the intensities with the 6-31++G(3df,3pd) basis and the Sadlej basis yields an average absolute difference of ca. 6 A^4 amu^{-1} and a standard deviation of ca. 10 A^4 amu^{-1}. Since the Sadlej basis is about the same size as the 6-31+G(2d,2p) basis set, but performs as well as the aug-cc-pVTZ basis (Fig. 3) and better than the 6-31++G(3df,3pd) basis (Figs. 4 and 5), it is clearly the best choice of the basis sets considered in the present work for the prediction of Raman intensities.

E. Frequency prediction using hybrid DFT and the Sadlej basis

It is well-known that theoretical harmonic vibrational frequencies are typically larger than the observed fundamentals due to basis set effects, electron correlation, and neglect of anharmonicity. To improve the agreement between computed harmonic frequencies and observed fundamentals, the computed frequencies are usually scaled for comparison. Various scaling strategies exist to help bring computed frequencies into greater agreement with observed wavenumbers.[52–55] Usually the simplest scaling strategy is adopted, that of homogeneous scaling. Previous work by Scott and Radom[7], and Wong[8] have shown that DFT consistently predicts vibrational frequencies in better agreement with observed fundamentals than conventional *ab initio* methods, with hybrid DFT having low mean absolute errors and scaling factors close to unity. Work in our lab has shown that hybrid DFT methods are outstanding performers in predicting infrared intensities.[14] Vibrational frequency prediction using the Sadlej basis set has not yet been addressed in the chemical literature. It is of interest then, to investigate the quality of vibrational frequencies predicted using the Sadlej basis set and hybrid DFT (B3-LYP).

Figure 6 shows the harmonic frequencies computed at the B3-LYP/Sadlej level compared to experimental fundamental frequencies. The agreement is very good and the average difference, average absolute difference, and standard deviation are 57, 64, and 71 cm^{-1}, respectively. The small difference between the average absolute difference and average difference suggests homogeneous scaling will be effective in bringing the computed harmonics into even greater coincidence with experimental wavenumbers. Regression analysis for this small data set suggests a preliminary empirical scaling factor of ca. 0.9663. After scaling, the average absolute difference is 36 cm^{-1}. Work is in progress to establish scaling factors for the Sadlej basis set using the larger set of molecules employed by Scott and Radom.[7]

IV. CONCLUSIONS

The results presented here suggest that at levels of theory applicable to larger molecules, electron correlation is less significant than basis set effects in the calculation of Raman intensities. Density functional theory provides numerical intensities comparable to MP2 at significantly less cost. Taking into consideration the results of this study as well as those assessing DFT vibrational frequencies[7,8] and infrared intensities,[14] DFT offers the most cost effective choice for the prediction of molecular vibrational properties. Raman intensities are quite sensitive to basis set effects and require much larger basis sets than infrared intensities to obtain quantitative results. The Sadlej electric property basis set, although medium sized, predicts Raman intensities similar in accuracy to those obtained with the much larger aug-cc-pVTZ basis set. Vibrational frequencies obtained using the Sadlej basis set with the B3-LYP functional were found to be in good agreement with experimental fundamentals. Therefore, for the theoretical prediction of Raman spectra, the Sadlej basis set is extremely cost-effective and yields excellent quantitative results.

ACKNOWLEDGMENTS

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[1] M. Delhaye, M. C. Dhamelincourt, and E. Dasilva, Rev. Inst. Fr. Petrol. **48**, 183 (1993).

[2] J. E. Katon, Vib. Spectrosc. **7**, 201 (1994).

[3] K. P. J. Williams, I. C. Wilcock, I. P. Hayword, and A. Whitley, Spectroscopy **11**, 45 (1996).

[4] M. J. Rodriguez, Spectroscopy **13**, 14 (1998).

[5] B. Klassen, R. Aroca, and G. A. Nazri, J. Phys. Chem. **100**, 9334 (1996).

[6] P. Pulay, in *Ab Initio Methods in Quantum Chemistry*, edited by K. P. Lawley (Wiley, New York, 1987), p. 241.

[7] A. P. Scott and L. Radom, J. Phys. Chem. **100**, 16502 (1996).

[8] M. W. Wong, Chem. Phys. Lett. **256**, 391 (1996).

[9] For example, reported scaling factors for DFT methods with the 6-31G(d) basis set are 0.9833 for S-VWN and 0.9945 for B-LYP. By contrast, the scale factors for conventional methods are 0.8953, 0.9427, and 0.9537 for Hartree-Fock, MP2, and QCISD, respectively (from Refs. 7,8).

[10] F. De Proft, J. M. L. Martin, and P. Geerlings, Chem. Phys. Lett. **250**, 393 (1996).

[11] D. Porezag and M. R. Pederson, Phys. Rev. B **54**, 7830 (1996).

[12] D. Papousek, Z. Papouskova, and D. P. Chong, J. Phys. Chem. **99**, 15387 (1995).

[13] J. R. Thomas, B. J. DeLeeuw, G. Vacek, T. D. Crawford, Y. Yamagucki, and H. F. Schaefer, J. Chem. Phys. **99**, 403 (1993).

[14] M. D. Halls and H. B. Schlegel, J. Chem. Phys. **109**, 10587 (1998).

[15] A. Komornicki and J. W. MvIver, J. Chem. Phys. **70**, 2014 (1979).

[16] M. J. Frisch, Y. Yamaguchi, J. F. Gaw, H. F. Schaeffer, and J. S. Binkley, J. Chem. Phys. **84**, 531 (1985).

[17] R. D. Amos, Chem. Phys. Lett. **124**, 376 (1986).

[18] G. B. Bacskay, S. Saebo, and P. R. Taylor, Chem. Phys. **90**, 215 (1984).

[19] B. G. Johnson and J. Florian, Chem. Phys. Lett. **247**, 120 (1995).

[20] A. Stirling, J. Chem. Phys. **104**, 1254 (1996).

[21] GAUSSIAN 98, Revision A.6, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.

[22] C. Møller and M. S. Plesset, Phys. Rev. B **46**, 618 (1934).

[23] *Vibrational Intensities in Infrared and Raman Spectroscopy*, edited by W. B. Person and G. Zerbi (Elsevier, New York, 1982).

[24] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.

[25] S. J. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[26] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[27] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[28] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[29] C. Adamo and V. Barone, Chem. Phys. Lett. **274**, 242 (1997).

[30] J. P. Perdew, in *Electronic Structure of Solids*, edited by P. Ziesche and H. Eschrig (Akademie, Berlin, 1991).

[31] P. C. Hariharan and J. A. Pople, Theor. Chim. Acta **28**, 213 (1973).

[32] J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. Defrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, Int. J. Quantum Chem., Quantum Chem. Symp. **15**, 269 (1981).

[33] Sadlej's polarized electric property basis set was obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0 Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352 (http://www.emsl.pnl.gov:2080/forms/basisform.html).

[34] A. J. Sadlej, Collect. Czech. Chem. Commun. **53**, 1995 (1988).

[35] A. J. Sadlej, Theor. Chim. Acta **79**, 123 (1992).

[36] T. H. Dunning, Jr., J. Chem. Phys. , **90**, 1007 (1989).

[37] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6769 (1992).

[38] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **98**, 1358 (1993).

[39] T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. v. R. Schleyer, J. Comput. Chem. **4**, 294 (1983).

[40] M. J. Frisch, J. A. Pople, and J. S. Binkley, J. Chem. Phys. **80**, 3265 (1984).

[41] The supplementary material is available on the world wide web at: http://www.chem.wayne.edu/schlegel/supp-mat/

[42] W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).

[43] C. E. Dykstra, *Ab Initio Calculation of the Structure and Properties of Molecules* (Elsevier, Netherlands, 1988).

[44] Y. Yamaguchi, M. Frisch, J. Gaw, H. F. Schaefer, and J. S. Binkley, J. Chem. Phys. **84**, 2262 (1986).

[45] K. Raghavachari and J. A. Pople, Int. J. Quantum Chem. **20**, 167 (1981).

[46] H. J. Werner and W. Meyer, Mol. Phys. **31**, 855 (1976).

[47] G. H. F. Dierksen and A. J. Sadlej, Theor. Chim. Acta **63**, 69 (1983).

[48] For comparison with experiment, the following subset of the set of test molecules was used, due to the availability of appropriate experimental intensities: N_2, H_2O, CH_4, C_2H_2, C_2H_4, C_2H_6, NH_3 and CH_2F_2.

[49] B. Person and G. Zerbi, in *Vibrational Intensities in Infrared and Raman Spectroscopy* (Elsevier, Amsterdam, 1982), state that ''the difficulties of measuring experimental Raman intensities are considerably greater'' than for infrared intensities.

[50] I. G. John, G. B. Backsay, and N. S. Hush, Chem. Phys. **51**, 49 (1980).

[51] For completeness, we also investigated the effect on Raman intensities of adding a second full set of diffuse functions to the aug-cc-pVTZ basis set (d-aug-cc-pVTZ) for H_2CO. The observed intensity change was small at the triple zeta level, ca. 0.1 A^4 amu^{-1}.

[52] P. Botschwina, W. Meyer, and A. M. Semkow, Chem. Phys. **15**, 25 (1976).

[53] G. Fogarasi and P. Pulay, J. Mol. Struct. **39**, 275 (1977).

[54] P. Pulay, G. Fogarasi, G. Pongor, J. E. Boggs, and A. Vargha, J. Am. Chem. Soc. **105**, 7037 (1983).

[55] Y. N. Panchenko, Russian Chemical Bulletin **45**, 753 (1996).