

A NEW ECP BASIS SET FOR ACCURATE CALCULATIONS OF DYNAMIC RAMAN INTENSITIES

L.N. Vidal^{*}; P.A.M. Vazquez

UNICAMP, Department of Physical-Chemistry, Chemistry Institute, 13.083-970, Campinas, SP, Brazil

Keywords: Dynamic Raman Intensity; Dirac-Hartree-Fock; Electrically Polarized Basis Set; Effective Core Potential.

ABSTRACT

Polarized Gaussian basis sets adapted to effective core potentials (ECPs) for ab initio calculations of frequency dependent Raman intensities are presented. The method of electric polarization of Gaussian basis functions developed by Sadlej is applied to the small-size pseudopotential basis sets SBKJC and Stuttgart's ECPnMWB to generate new basis sets, named as pSBKJC and pStuttgart, which are appropriate for calculation of dynamic polarizability and Raman cross sections. The Raman scattering activities of alkali-earth hydrides (MH_2 , $M=Be$ to Ba) and for chalcogenides (H_2X , $X=O$ to Po) were evaluated at the excitation frequency of 632.8 nm using these new basis sets and the all-electron basis set Sadlej-pVTZ. These calculations were performed at the non-relativistic time-dependent Hartree-Fock (TDHF) level and also with its relativistic counterparts, the Dirac-Hartree-Fock/Spin-Free (DHF/SF) (no spin-orbit coupling) and Dirac-Hartree-Fock (DHF) levels. Due to the use of relativistic ECPs, Hartree-Fock calculations using these new basis sets can also recover most of the relativistic effects appearing in the Raman intensities. The overall agreement between the HF/pSBKJC and HF/Sadlej-pVTZ Raman scattering activities is 8.6% while the comparison of HF/pStuttgart with HF/Sadlej-pVTZ data shows a better agreement of 5.3%.

1. INTRODUCTION

The development of *ab initio* methods for the calculation of dynamical polarizabilities of gas phase molecules using linear response theory enabled the computation of Raman spectra, by finite difference methods, at specific excitation frequencies, making possible theoretical predictions at the same excitations used in the experimental measurements [1]. In order to achieve quantitative agreement of the theoretical spectrum within the experimental precision, it was determined that a basis set of at least aug-cc-pVTZ quality and the inclusion of electronic correlation at the coupled cluster singles and doubles (CCSD) level are required [1-6]. Thus, while the requirements for the computation of high quality Raman intensities are well assessed, the computational costs associated to them limit these calculations to small and medium sized molecules. Several strategies were proposed to circumvent this limitation: adequate exploitation of the mo-

lecular symmetry substantially reduces the number of steps in the finite difference procedure [4-6]; the inclusion of electronic correlation by the use of Density Functional Theory (DFT) may achieve results of quality near to that obtained using Moeller-Plessett second order perturbation theory (MP2) [7]; analytical computation of the nuclear polarizability derivatives schemes were developed by Champagne at the THDF level of theory [8] and, more recently, by Gauss for CCSD wavefunctions [9]. The computational cost of Raman intensities is highly dependent on the basis set size. Sadlej developed a polarized basis set capable of delivering polarizabilities and yielding nuclear gradients with almost the same quality as those produced by the larger aug-cc-pVTZ and with a reduction of approximately 95% in the CPU time and 91% in disk requirements [10]. This result strongly suggests that further gains can be achieved by additional reductions in the basis set size. The studies of molecular polarizabilities and Raman intensities dependence on the basis set have shown a strong dependency on the valence shell electrons and functions and on the additional polarization and diffuse functions and a very weak dependence on the inner shells [6], thus suggesting that these can be replaced by effective core potentials. In order to assess the capabilities of ECPs for the calculation of Raman intensities, in this work the Sadlej polarization method was employed to polarize the valence shell of the SBKJC [11] and Stuttgart [12] effective core potential, the resulting basis functions were used to calculate the Raman spectra of a series of hydrides of alkali-earth metals as well as the hydrides of the chalcogen atoms. This paper is structured as follows: in the next section the methodology for the development of the new polarized pseudopotential basis sets is presented and the computational aspects for the calculation of the Raman intensities are described. In the following section the frequency dependent Raman scattering activities of the compounds MH_2 ($M=Be$ to Ba) and H_2X ($X=O$ to Po), evaluated at the time-dependent Hartree-Fock level using the new basis sets, are compared with the scattering activities obtained from time-dependent Hartree-Fock (TDHF), Dirac-Hartree-Fock/Spin-Free (DHF/SF, scalar-relativistic) and Dirac-Hartree-Fock/Dirac-Coulomb (DHF, full relativistic) calculations using the reference basis set for electric property calculations Sadlej-pVTZ. The concluding remarks are the subject of the final section.

^{*} Invidal@iqm.unicamp.br

2. THEORY AND COMPUTATIONAL DETAILS

The polarization procedure first requires the selection of a basis set that must adequately describes the unperturbed system. For this purpose, two families of pseudopotential basis sets were chosen: (1) the Steven's and coworkers valence double- ζ (VDZ) SBKJC [11,13] basis set and (2) the Stuttgart/Cologne ECP n MWB VDZ basis set [12,14]. Both sets use ECPs that were modeled to account for the scalar-relativistic effects (mass-velocity and Darwin corrections) of the inner electrons. Each basis set is then transformed (using first order perturbation theory) into a new electrically polarized set that reflects the action of an electric field onto the spin-orbitals of the system [10]. The rules derived by Sadlej for the generation of the polarized basis set include the addition of one diffuse function for each shell and four primitive polarization functions for the outermost occupied shell of the given atom. For instance, after the polarization procedure the SBKJC basis set for the oxygen atom changes [2s2p] to [3s3p2d] contracted basis functions. The procedure followed here for the determination of polarized basis sets is detailed in reference [10].

The Raman property covered in this work is the scattering activity S_k , defined as:

$$S_k \equiv \left[45 \left(\frac{\partial \alpha(\tilde{\nu}_0)}{\partial Q_k} \right)^2 + 7 \left(\frac{\partial \gamma(\tilde{\nu}_0)}{\partial Q_k} \right)^2 \right] g_k \quad (1)$$

where $\alpha(\tilde{\nu}_0)$ and $\gamma(\tilde{\nu}_0)$ are the mean polarizability and the polarizability anisotropy, respectively, Q_k is the k -th normal coordinate and g_k the degenerescence of the vibrational mode k . The quantity S_k is closely related to the Raman cross section. For example, the Raman Stokes differential cross section corresponding to the intensity of k -th vibrational normal mode, measured perpendicularly to the incident light at some temperature T is given by:

$$\left(\frac{d\sigma}{d\Omega} \right)_k^\perp = \frac{h}{8\epsilon_0^2 c} \frac{(\tilde{\nu}_0 - \tilde{\nu}_k)^4 \tilde{\nu}_k^{-1}}{(1 - e^{-hc\tilde{\nu}_k/k_B T})} S_k \quad (2)$$

where Ω is the collecting solid angle. The superscript \perp indicates that the polarization of the linearly polarized incident light is perpendicular to the scattering plane and the superscript n informs that scattered light is analyzed without the use of polarizers. $\tilde{\nu}_0$ and $\tilde{\nu}_k$ are the wavelengths of the excitation light and of the k -th vibrational frequency, respectively. The constants ϵ_0 , h , c and k_B have their usual meaning. Thus the Raman scattering activity S_k plus the vibrational wavenumber $\tilde{\nu}_k$ give the molecular contribution to the Raman cross section.

The HF/Sadlej-pVTZ calculations were performed with the electronic structure program DALTON [15] and the DHF/SF/Sadlej-pVTZ and DHF/Sadlej-pVTZ calculations by the relativistic *ab initio* code DIRAC [16]. Geometry optimizations and quadratic force constants were evaluated at

the HF/Sadlej-pVTZ level. Dynamic polarizabilities were calculated using the linear response (LR) modules of the codes DALTON and DIRAC but the HF/pSBKJC and HF/pStuttgart frequency dependent polarizabilities were obtained from time-dependent Hartree-Fock calculations using the GAMESS [17] electronic structure program. The Raman scattering activities were evaluated by our Fortran 77 code PLACZEK [5,6], developed for the calculation of Raman properties at arbitrary levels of theory.

3. RESULTS AND DISCUSSION

The dynamic Raman scattering activities of the symmetric stretching mode (the strongest Raman active one) of the MH_2 ($M=Be, Mg, Ca, Sr$ or Ba) and H_2X ($X=O, S, Se, Te$ or Po) molecules evaluated at the excitation frequency of 632.8 nm are presented in Table 1. The reference data are all-electron calculations of three types: (1) non-relativistic LR-HF/Sadlej-pVTZ, (2) scalar-relativistic LR-DHF/SF/Sadlej-pVTZ using the spin-free (SF) Hamiltonian of Dyal [18] and (3) full relativistic LR-DHF/Sadlej-pVTZ using the Dirac-Coulomb Hamiltonian. The analysis of the data contained in this table agrees with the known result [19] that the relativistic effects in the scattering activities of these molecules become important when the atomic numbers of the central atoms are equal to 38 (strontium atom) or higher, but in this work the nature of the relativistic effects is presented. The dominant effects are those of scalar type (no spin-coupling) since the major differences appear when HF data are compared with DHF/SF values. The exception is the BaH_2 scattering activity where all the three types of reference data are significantly different. The existence of triplet electronic transitions, which are allowed in the relativistic framework (DHF wavefunction), may contribute for this abnormal increase in the scattering activity of BaH_2 since the polarizability evaluated in this work is a real function and approaches infinity as the excitation energy approaches an electronic transition. Unfortunately the calculation of vertical excitation energies is not available in the current public version of the DIRAC relativistic electronic structure code but we conduct a LR-HF/Sadlej-pVTZ calculation that predicts a triplet electronic transition at 380.6 nm which is far from the laser excitation wavelength of 632.8 nm. Thus a triplet transition seems not to be causing the differences between the HF and DHF scattering activities. However, because these differences are observed even in the scalar-relativistic calculations (DHF/SF), this suggests some limitations in the Sadlej-pVTZ basis set for the barium atom for use with relativistic wavefunctions.

The scattering activities obtained from TDHF calculations using the new polarized basis sets pSBKJC and pStuttgart are listed in Table 1. When the intensity data from the new basis set is compared with the reference results using the Sadlej-pVTZ basis set, an excellent agreement is observed. Major differences appear only if the heaviest elements (Ba and Po) are considered. In the case of the H_2Po molecule, the only system from the H_2X chalcogen family where differences between DHF/SF and DHF data are substantial, the

ECP basis set shows results closer to the scalar-relativistic DHF/SF/Sadlej-pVTZ scattering activities. Since the pseudopotentials SBKJC and ECPnMWB do not account for spin-orbit effects but only for the scalar mass-velocity and Darwin corrections the better agreement of the HF/pSBKJC and HF/pStuttgart data with the DHF/SF/Sadlej-pVTZ scattering activities is a theoretically consistent result. For BaH₂, the only case in which the relativistic DHF/SF and DHF scattering activities are less than the HF value, both new basis sets follow the behavior observed for the other MH₂ molecules where the HF/pSBKJC and HF/pStuttgart scattering activities are greater than the HF/Sadlej-pVTZ reference values. The new basis sets also reproduce the tendency verified in the all-electron calculations for the MH₂ family whose scattering activity initially increases from BeH₂ to MgH₂ then finds its maximum value in CaH₂ or SrH₂ molecules (depending on the ECP basis set considered), then decreases in the BaH₂ hydride.

Table 1 - Raman scattering activities of the symmetric stretching mode of alkali-earth hydrides and chalcogenides at the excitation wavelengths of 632.8 nm evaluated at the Hartree-Fock, Dirac-Hartree-Fock/Spin-Free and Dirac-Hartree-Fock levels using the Sadlej-pVTZ and the new basis sets pSBKJC and pStuttgart.

	BeH ₂	MgH ₂	CaH ₂	SrH ₂	BaH ₂
HF/Sadlej-pVTZ	283.2	562.0	687.8	627.9	425.6
DHF/SF/Sadlej-pVTZ	283.0	565.1	696.7	652.4	350.2
DHF/Sadlej-pVTZ	283.0	565.1	696.7	652.4	222.7
HF/pSBKJC	279.5	569.5	702.5	668.3	630.0
HF/pStuttgart	280.2	571.3	668.7	703.2	694.6

	H ₂ O	H ₂ S	H ₂ Se	H ₂ Te	H ₂ Po
HF/Sadlej-pVTZ	92.3	204.3	250.8	314.0	360.4
DHF/SF/Sadlej-pVTZ	92.6	205.7	258.8	339.1	434.4
DHF/Sadlej-pVTZ	92.6	205.8	259.6	343.5	467.8
HF/pSBKJC	90.0	201.5	237.4	313.2	423.2
HF/pStuttgart	91.4	214.6	256.6	295.5	385.8

The 2-valence-electron problem

When the alkali-earth elements are described by 2-valence-electron pseudopotentials in molecular electronic structure calculations the geometric and spectroscopic properties may be erroneously predicted because the inner electrons are not explicitly treated. This problem, known “as the incomplete separation of the valence and subvalence shells” was the subject of an earlier study concerning the distances, angles and harmonic vibrational frequencies of Ca, Sr and Ba hydrides where the 10-valence-electron pseudopotential approach was employed to circumvent the limitations of the 2-valence-electron pseudopotential [20]. Thus, in order to access the importance of the inclusion of (n-1)s and (n-1)p electrons on the Raman scattering activities of CaH₂, SrH₂ and BaH₂ molecules, the 10-valence-electron ECP basis set developed by the Stuttgart/Cologne group [20] was electrically polarized, given origin to a new basis set named pStuttgart+8e, and tested in Raman intensity calculations. The scattering activities of the symmetric stretching mode of

these molecules for the excitation frequencies of 632.8, 515.5 and 488.0 nm are listed in Table 2. The analysis of the data presented in this table shows that the Raman intensities are quite affected by the inclusion of the next-to-valence electrons where excessively large intensities are obtained if only the last valence electrons are considered. However the 10-valence-electron pStuttgart+8 basis set can provide scattering activities with accuracies similar to the basis sets pSBKJC and pStuttgart for the chalcogen atoms and still save lots of computer time since the number of basis functions in pStuttgart+8 is much smaller than in the Sadlej-pVTZ basis set. For example, the contracted pStuttgart+8 basis for the barium atom contains [5s5p3d] functions against the [13s11p6d] ones of the Sadlej-pVTZ basis set.

Table 2 - Raman scattering activities of the symmetric stretching mode of the alkali-earth hydrides at several excitation wavelengths evaluated at the Hartree-Fock, Dirac-Hartree-Fock/Spin-Free and Dirac-Hartree-Fock levels using the Sadlej-pVTZ and the new basis sets pStuttgart and pStuttgart+8e.

<i>S_k</i> (632.8 nm)					
	BeH ₂	MgH ₂	CaH ₂	SrH ₂	BaH ₂
HF/Sadlej-pVTZ	283.2	562.0	687.8	627.9	425.6
DHF/SF/Sadlej-pVTZ	283.0	565.1	696.7	652.4	350.2
DHF/Sadlej-pVTZ	283.0	565.1	696.7	652.4	222.7
HF/pStuttgart	280.2	571.3	668.7	703.2	694.6
HF/pStuttgart+8e			702.4	682.5	502.8

<i>S_k</i> (514.5 nm)					
	BeH ₂	MgH ₂	CaH ₂	SrH ₂	BaH ₂
HF/Sadlej-pVTZ	302.8	634.6	847.2	812.9	548.7
DHF/SF/Sadlej-pVTZ	302.5	637.7	857.5	846.1	449.0
DHF/Sadlej-pVTZ	302.5	637.7	857.5	846.2	282.7
HF/pStuttgart	299.5	645.3	819.1	929.4	1047.3
HF/pStuttgart+8e			868.6	892.1	663.3

<i>S_k</i> (488.0 nm)					
	BeH ₂	MgH ₂	CaH ₂	SrH ₂	BaH ₂
HF/Sadlej-pVTZ	309.6	661.2	911.7	893.7	601.9
DHF/SF/Sadlej-pVTZ	309.3	664.3	922.5	930.8	491.7
DHF/Sadlej-pVTZ	309.3	664.3	922.5	931.0	308.4
HF/pStuttgart	306.3	672.4	878.9	1028.0	1230.5
HF/pStuttgart+8e			936.0	984.8	735.5

4. CONCLUSIONS

In this work the first study using ECP basis sets for the calculation of dynamic Raman intensities is presented. For the systems considered in this work (alkali-earth hydrides and chalcogenides) the new polarized pseudopotential basis sets were able to generate Raman scattering activities in excellent agreement with those derived from all-electron calculations using the Sadlej-pVTZ [10] basis set but are significantly less demanding in computational resources. For the lightest molecules a reduction of 16% in disk requirements and of 23% in CPU time was observed in the dynamic polarizability calculations. The new basis can also account for

most of the relativistic effects appearing in the scattering activities, which were shown here to be, in the majority, of a scalar nature.

ACKNOWLEDGEMENTS

The authors thank the National Center for High Performance Computing in São Paulo CENAPAD-SP for computer time. LNV thanks the National Council for Scientific and Technological Development (CNPq) for a doctoral fellowship. The basis sets can be obtained directly from the authors.

REFERÊNCIAS

1. HELGAKER, T.; RUUD, K.; BAK, K.L.; JORGENSEN, P.; OLSEN, J., *Faraday Disc.* 99 (1994) 165-180.
2. PECUL, M.; RIZZO, A., *J. Chem. Phys.* 116 (2002) 1259-1268.
3. PECUL, M.; CORIANI, S., *Chem. Phys. Lett.* 355 (2002) 327-338.
4. NEUGEBAUER, J.; REIHER, M.; HESS, B. A., *J. Chem. Phys.* 117 (2002) 8623-8633.
5. VIDAL, L.N.; VAZQUEZ, P.A.M., *Quim. Nova* 26 (2003) 507-511.
6. VIDAL, L.N.; VAZQUEZ, P.A.M., *Int. J. Quantum Chem.* 103 (2005) 632-648.
7. CAILLIE, C.V.; AMOS, R.D., *Phys. Chem. Chem. Phys.* 2 (2000) 2123-2129.
8. QUINET, O.; CHAMPAGNE, B., *J. Chem. Phys.* 115 (2001) 6293-6299.
9. O'NEILL, D.; KÁLLAY, M.; GAUSS, J., *Mol. Phys.* 105 (2007) 2447-2453.
10. SADLEJ, A.J., *Collect. Czech. Chem. Commun.* 53 (1988) 1995-2016.
11. STEVENS, W.J.; BASCH, H.; KRAUSS, M., *J. Chem. Phys.* 81 (1984) 6026-6033.
12. BERGNER, A.; DOLG, M.; KÜCHLE, W.; STOLL, H.; PREUSS, H., *Mol. Phys.* 80 (1993) 1431-1441.
13. STEVENS, W.J.; KRAUSS, M.; BASCH, H.; JASIEN, P.G., *Can. J. Chem.* 70 (1992) 612-630.
14. DOLG, M.; PETERSON, K.A.; SCHWERTFEGGER, P.; STOLL, H., *Pseudopotentials of the Stuttgart/Cologne group (Revision: July 02, 2007)*, <http://www.theochem.unistuttgart.de/pseudopotentials/index.en.html>.
15. *Dalton, a molecular electronic structure program, Release 2.0 (2005)*, see <http://www.kjemi.uio.no/software/dalton/dalton.html>.
16. JENSEN, H.J.A. *et al.*, *DIRAC, a relativistic ab initio electronic structure program, Release DIRAC04.0 (2004)*, (See <http://dirac.chem.sdu.dk>).
17. SCHMIDT, M.W.; BALDRIDGE, K.K.; BOATZ, J.A.; ELBERT, S.T.; GORDON, M.S.; JENSEN, J.H.; KOSEKI, S.; MATSUNAGA, N.; NGUYEN, K.A.; SU, S.; WINDUS, T.L.; DUPUIS, M.; MONTGOMERY, J.A., *J. Comput. Chem.* 14 (1993) 1347-1363.
18. DYALL, K.G., *J. Chem. Phys.* 100 (1994) 2118-2127.
19. VIDAL, L.N.; VAZQUEZ, P.A.M., *Chem. Phys.* 321 (2006) 209-214.
20. KAUPP, M.; SCHLEYER, P.V.R.; STOLL, H.; PREUSS, H., *J. Chem. Phys.* 94 (1991) 1360-1366.