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Core–valence correlation effects on IR calculations: the BF_3 and BCl_3 cases

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Abstract The first theoretical results of core–valence correlation effects are presented for the infrared wavenumbers and intensities of the BF_3 and BCl_3 molecules, using (double- and triple- ζ) Dunning core–valence basis sets at the CCSD(T) level. The results are compared with those calculated in the frozen core approximation with standard Dunning basis sets at the same correlation level and with the experimental values. The general conclusion is that the effect of core–valence correlation is, for infrared wavenumbers and intensities, smaller than the effect of adding augmented diffuse functions to the basis set, e.g., cc-pVTZ to aug-cc-pVTZ. Moreover, the trends observed in the data are mainly related to the augmented functions rather than the core–valence functions added to the basis set. The results obtained here confirm previous studies pointing out the large discrepancy between the theoretical and experimental intensities of the stretching mode for BCl_3 .

Keywords BCl_3 · BF_3 · Core–valence correlation · Dunning basis sets · Infrared intensities

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Introduction

For several years, the vibrational spectrum of a molecule has been used to study its electronic behavior. Infrared intensities, in particular, are closely related to the electronic structure of molecules since they correlate directly with the dipole moment derivatives with respect to their vibrational normal coordinates [1]. Since the molecular dipole moment can be described with different approximations (through the use of different charge models like AIM, Mulliken, ChelpG, etc.), several models appear in the literature in attempt to interpret calculated intensities in terms of changes in the electronic structures of molecules [2–4].

When these analyses are carried out computationally, it is desirable to apply state-of-the-art levels of theory to achieve, in theory, the best possible result, i.e., the closest one to the experiment. With this purpose, several papers [5–8] have already discussed results and the difficulties of such calculations, with the general conclusion that reasonably good results for both frequencies and intensities are commonly achieved (frequencies are commonly easier to predict [7, 9] since they can be corrected by scale factors to account for anharmonicity [10]) with standard levels of theory, while quantitatively accurate results can only be obtained through high-level *ab initio* quantum treatments and larger basis sets [8]. Another common difficulty is observed when an attempt to apply such robust techniques to large organic and biological systems is made, rather than to small and symmetric test set systems. In such cases *ab initio* methods are almost always completely prohibitive [11]. As a result density functional theory methods are the best alternatives and some papers treating infrared intensities with this approach are also available in literature [10, 12].

Galabov and co-workers [13] tested several different levels of theory aiming to obtain an efficient combination that would yield accurate results for several molecules. It was concluded

that the CCSD(T) method with triple-zeta Dunning's basis sets provides good overall results for the molecules tested, even though quadruple- and quintuple-zeta basis sets were also tested. Galabov's approach, in a sense, is similar to most of the work present in literature, since it uses *ab initio* methods and large basis sets within the frozen-core approximation. The notion that chemical properties are dominated by valence shell electrons is a well-established axiom in quantum chemistry and indeed holds for the great majority of investigated systems, in spite of some reports that the core-valence correlation can be as important as the valence portion for some molecules such as small hydrides [14].

Wilson, Decius, and Cross, in their landmark textbook [1], pointed out almost 60 years ago that the vibrational motion of the nuclei necessarily leads to a change in the electronic density distribution. This charge distribution (which determines the atomic charges and, consequently, the dipole moment) is composed of both valence and core electrons, so it is reasonable to assume that both types of electrons are involved in the electronic density behavior. Indeed, theoretical results point out that the origin of the core-valence correlation is within the polarization of atomic cores caused by the valence electrons, a phenomenon directly related to changes in the electronic structure that accompanies the vibrational motion [15]. For small molecules with a simpler electronic arrangement (such as CH₄, NH₃, and H₂O) the core is not expected to play an important role in the phenomenon, as the total number of electrons is quite small and the vibrations involve mainly the displacement of hydrogen atoms. Halogenated molecules (such as BF₃, BCl₃, NF₃, CF₄, CCl₄) however are expected for being very reliant on the electronic core description. Since the changes in the electronic structures are directly related to the infrared intensities, the improvement of the core description could improve the results of the calculated intensities to some extent.

These analyses can be carried out by using basis sets that account for core-valence correlation. The chosen basis for this purpose, developed by Dunning and co-workers, are similar to the earlier well-established cc-pVXZ and aug-cc-pVXZ (X=D, T, Q, ...) sets developed in post-Hartree-Fock treatments, but not specifically focused on just the valence shell. The so-called *correlation consistent polarized core-valence* sets (cc-pCVXZ [16]) account for the standard core-core and core-valence correlation effects and its exponents are optimized based on differences between all-electron and valence-electron correlated energies. However, it was later perceived that the inclusion of core electrons in the electronic description of the system is dominated by the core-valence effects. Since the convergence of the core-core correlation energy is faster than the core-valence one, the next step was the development of the *weighted core-valence* basis set (cc-pwCVXZ [17]) which successfully improved the core-valence correlation convergence.

Among the molecules that have infrared gas phase data reported in the literature, nearly all of them have already been studied through theoretical calculations with success (within the frozen core (FC) approximation). However boron trichloride (BCl₃) had its intensities reported only once in literature [18] many years ago and the values presented there do not agree with the theoretical ones [19, 20]. Some authors even considered experimental error to be the cause of the discrepancy between the measurements [20]. For that reason, BCl₃ was chosen for testing core-valence correlation treatments with the aim of obtaining benchmark intensity results, i.e., closer to the experimental values. Since the BF₃ molecule is also halogenated and has a structure similar to BCl₃ it was also included in this work, although its calculated and experimental intensities agree quite well. The comparison between the two molecules can be useful for electronic structure comparisons, since both molecules have similar normal coordinates.

Calculations

The calculations were based on the results presented by Galabov and co-workers [13], where the CCSD(T) method was employed with several Dunning basis sets. The core-valence correlation in the present paper was accounted for by use of the cc-pCVXZ, cc-pwCVXZ, aug-cc-pCVXZ, and aug-cc-pwCVXZ basis sets and compared with the standard cc-pVXZ and aug-cc-pVXZ calculations, where X=D, T (Q and 5 were used whenever possible). Since the best overall results obtained by Galabov were achieved using CCSD(T) method with a triple-zeta basis set, one would expect to achieve values in even better agreement with experiment by adding core-valence correlation. Both geometry optimizations and infrared calculations were performed with the CFOUR program [21] due to its robustness in treating high-level coupled cluster calculations. All the basis sets that were not available in the default GENBAS file were obtained from the EMSL Basis Set Exchange [22, 23] database.

Results and discussion

The experimental and calculated wavenumbers for the three normal coordinates of BF₃ and BCl₃ are presented in Table 1.

The inclusion of the core-valence and weighted core-valence correlations in the basis sets results in lower wavenumbers for the normal vibrations of BF₃, except for Q₄ from the cc-pwCVTZ basis. The variations between basis sets can be subtle (around 10 to 20 cm⁻¹ for Q₂ of BF₃ with the double-zeta basis sets) or rather impressive (70 to 140 cm⁻¹ for Q₂ of BF₃ with the double-zeta basis sets). Moreover, the inclusion of core-valence correlation and augmented

Table 1 Experimental and theoretical wavenumbers for BF_3 and BCl_3 molecules calculated at the CCSD(T) level, in (cm^{-1}) units

Basis set	BF_3				BCl_3			
	Q_1	Q_2	Q_3	Q_4	Q_1	Q_2	Q_3	Q_4
cc-pVDZ	868.3	712.6	1471.5	482.9	480.9	464.0	996.0	258.9
cc-pCVDZ	868.0	713.2	1470.0	483.5	481.7	464.5	997.4	259.3
cc-pwCVDZ	868.1	712.5	1467.4	483.5	487.0	462.8	1,006.7	259.9
aug-cc-pVDZ	841.6	710.9	1404.9	458.1	487.5	448.9	999.0	256.0
aug-cc-pCVDZ	842.6	704.1	1407.5	457.8	494.7	436.6	1012.8	254.5
aug-cc-pwCVDZ	841.4	699.9	1403.6	456.6	471.5	455.6	964.3	253.5
cc-pVTZ	903.9	706.1	1498.9	486.0	476.2	461.6	972.4	257.1
cc-pCVTZ	903.1	702.6	1497.0	486.2	481.5	463.0	981.3	258.4
cc-pwCVTZ	904.1	703.5	1497.3	487.6	500.1	465.5	1020.4	261.2
aug-cc-pVTZ	896.2	658.0	1470.8	469.8	474.5	455.6	965.3	253.5
aug-cc-pCVTZ	886.1	571.1	1446.1	454.9	480.2	456.8	975.9	255.4
aug-cc-pwCVTZ	886.0	570.2	1441.4	454.8	473.0	359.5	951.6	249.6
cc-pVQZ	903.8	705.3	1493.7	487.9	—	—	—	—
aug-cc-pVQZ	906.7	762.7	1503.3	498.6	—	—	—	—
cc-pV5Z	914.1	831.3	1521.4	506.1	—	—	—	—
Experimental [18, 24]	888 [25]	720	1505	482	471 [26]	460	956	243

functions simultaneously generates a synergic effect that decreases the frequency values more sharply. For example, addition of either core valence correlation or augmented functions to the cc-pVTZ basis leads to decreases of -2.6 and -48.1 cm^{-1} for Q_2 of BF_3 whereas including both simultaneously results in a much greater decrease of -135.9 cm^{-1} . Nevertheless, for BCl_3 the trend is not so evident, and the values observed are borderline random for the basis sets tested. Finally, two important conclusions can be obtained from Table 1: a) the extrapolation to a complete basis set probably would not improve considerably the results since it does not seem to be converging for any of the normal modes tested, and b) increasing the size of a basis set does not lead to better agreement with the experimental value as the quadruple- and quintuple-zeta basis set results are indeed farther from the experimental measurements than the double- and triple-zeta ones. The quintuple-zeta results are particularly disappointing regarding the computational cost required. Table 2 presents the experimental and calculated intensities for BF_3 and BCl_3 at the same theoretical levels.

The intensities of the molecules display some trends, but they are not uniform. Analyzing BF_3 with the double-zeta basis sets, it can be seen that, usually but not always, the greatest effect on the three intensities is due to the inclusion of augmented diffuse functions, while the effect of core-valence correlation is very subtle (Q_4 of BF_3 is an exception). Regarding triple-zeta basis sets the same pattern is observed, with the inclusion of augmented functions increasing the intensity values (especially for Q_3), while the effect of core-valence treatment is virtually null. BCl_3 displays an opposite trend, as its infrared intensities for both the double- and triple-

zeta functions are decreased by the inclusion of augmented functions for the Q_2 and Q_3 absorption bands. The remaining band, Q_4 , does not show any particular trend, or it is not observable as the intensities are quite low, rendering all the wave function effects to be insignificant compared to the experimental error. The effect of core-valence correlation is once more nearly absent for double-zeta basis sets, but for

Table 2 Experimental and theoretical intensities for BF_3 and BCl_3 molecules calculated at the CCSD(T) level, in ($\text{km}\cdot\text{mol}^{-1}$) units

Basis set	BF_3			BCl_3		
	Q_2	Q_3	Q_4	Q_2	Q_3	Q_4
cc-pVDZ	101.8	404.0	13.1	7.5	388.7	1.0
cc-pCVDZ	101.4	405.0	13.0	7.2	388.9	1.0
cc-pwCVDZ	100.5	403.9	12.9	6.5	388.6	1.0
aug-cc-pVDZ	97.0	432.6	13.0	6.6	354.4	1.2
aug-cc-pCVDZ	96.6	432.7	13.1	5.2	347.6	1.2
aug-cc-pwCVDZ	96.4	433.4	13.0	5.1	349.5	0.9
cc-pVTZ	101.6	415.8	13.1	5.7	355.2	0.8
cc-pCVTZ	101.6	411.8	13.1	5.3	353.3	0.8
cc-pwCVTZ	101.5	412.3	13.0	4.8	351.1	0.9
aug-cc-pVTZ	101.4	438.6	14.3	5.3	347.7	0.9
aug-cc-pCVTZ	101.6	437.0	15.1	4.9	347.6	0.8
aug-cc-pwCVTZ	101.4	437.0	15.2	4.9	347.0	0.9
cc-pVQZ	103.9	432.3	13.0	—	—	—
aug-cc-pVQZ	103.4	443.1	12.2	—	—	—
cc-pV5Z	103.9	442.9	11.6	—	—	—
Experimental	74.4	368.5	10.7	1.5	115.6	0.4

triple-zeta results a trend can be noticed for Q_3 as a decrease in the intensity values occurs when core–valence correlation is added. Nevertheless, this effect is still much less pronounced than the effect of the augmented functions.

It is clear that the agreement is not as good as expected with such levels of theory in any of the cases, and this observation has already been reported in our previous works [19, 27]. Indeed, the best result yet achieved for the infrared intensities of BF_3 was obtained with the 6–31G(2d,2p) basis set, a quite surprising result since the inclusion of diffuse functions was reported as essential to give the wave function the necessary flexibility to describe the behavior of the electronic density during vibrational motion [9]. Moreover, for BCl_3 the agreement was not satisfactory at any of the tested levels, as was observed before [27], mainly due to the lack of experimental agreement for the Q_3 degenerate band. The recurring discrepancy between the calculated and experimental values of the Q_3 band reinforces the suspicion that an error might have occurred during the experimental measurement of BCl_3 intensity. This discrepancy is much larger than any observed so far in more than thirty molecules for which standard modest basis sets were used at the MP2 level [28]. Moreover, calculated intensities obtained by different groups with several different levels of theory including perturbation theory (MP2(FULL)/aug-cc-pVDZ: 732.3 $\text{km}\cdot\text{mol}^{-1}$), configuration interaction (CISD/6–31G(d): 822.5 $\text{km}\cdot\text{mol}^{-1}$), quadratic configuration interaction (QCISD/cc-pVTZ: 721.7 $\text{km}\cdot\text{mol}^{-1}$) and density functional theory (PBE/PBE/aug-cc-pVTZ: 648.2 $\text{km}\cdot\text{mol}^{-1}$), among others, are available online in the Computational Chemistry Comparison and Benchmark Database (CCCBDB) (<http://cccbdb.nist.gov/>), and all these values are also far from the experimental one reported by Mandirola. As pointed out by Nxumalo, “because of the experimental difficulty of separating

the bands due to the molecules containing ^{10}B and ^{11}B , however, these observed intensities may themselves be subject to serious error” [20]. The observations regarding the agreement between theoretical and experimental results for Q_3 are summarized in Fig. 1.

The theoretical results for BF_3 and BCl_3 do not vary drastically, but only for the BF_3 molecule there is a satisfactory agreement between the calculated intensities and the experimentally measured data.

The difficulties faced in obtaining theoretical and experimental agreement seem to be part of a more complex problem. In fact, when any molecule with more than one normal coordinate is analyzed focusing on its infrared intensities, often trends and systematic differences between theory and experiment are not present. Furthermore, when trends are observed, they are not necessarily proportional to the increase of the complexity of the basis set. In other words the intensities of the different normal coordinates from the same molecule do not converge simultaneously toward the experimental values. Indeed, it is possible for one of the intensities to reach the best possible agreement with its experimental value, while others are still far from theirs. As the level of theory increases some bands could be converging to their experimental values while others are diverging. Furthermore it is possible to measure the quality of a calculated IR intensity using several criteria (error percentage, root-mean-square error, absolute error, etc.), each one providing different results regarding relative agreement with experiment. Moreover, even if the intensities are approaching a specific value, there is no guarantee that this final value will be similar to the experimentally measured data.

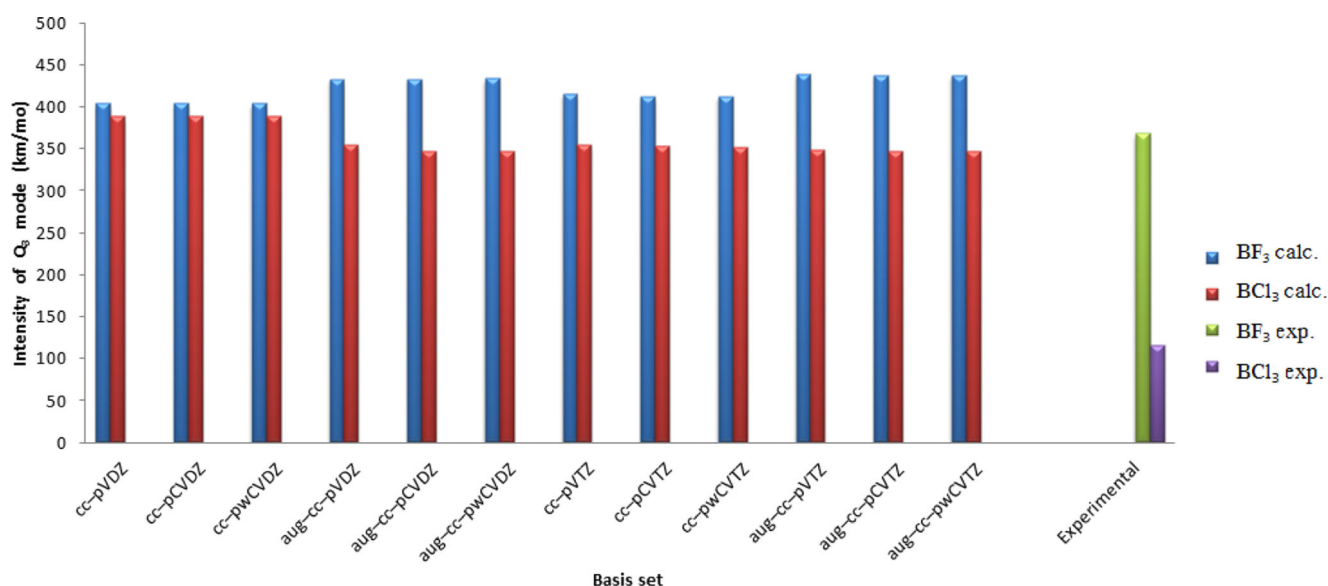


Fig. 1 Theoretical and experimental values for Q_3 band of BF_3 and BCl_3

Conclusions

One can conclude that the inclusion of high-level core-valence correlation effects on infrared calculations does not improve the agreement between theoretical and experimental infrared intensities nor their infrared frequencies. Some tendencies can be found in the BF_3 and BCl_3 data, as the calculated values change, although these tendencies seem to be more dependent on the presence of augmented functions than core-valence correlation functions. Nevertheless, the computational cost and necessary hardware to run these jobs are significantly more expensive when core-valence correlation effects are included. Thus, even though the infrared intensity is a property directly related to electronic structure, the calculation of this property does not seem to be particularly dependent on a high-level description of the electronic environment. Since the BF_3 and BCl_3 molecules contain atoms with shells that might be influenced by core-valence treatments and this was not confirmed, there is no reason to believe that different results would be obtained for smaller atoms for which electronic core description is not expected to be so important. It is troubling that none of these tendencies seem to be converging toward the experimental values for Q_3 for BCl_3 . Recent relative intensity measurements [19] concerning our theoretical data with the experimental ones reported by the Pacific Northwest National Laboratory indicate that Q_3 stretching bands of BF_3 and BCl_3 have comparable intensity values in agreement with the theoretical results reported here.

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