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TESTING THE APPLICABILITY OF DENSITY FUNCTIONAL THEORY TO ZINC DIHALIDES

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RESUM

S'ha emprat la teoria del funcional de la densitat (DFT) per calcular les geometries dels compostos ZnX_2 (X = Cl, Br, I) a l'estat fonamental, com també les seves freqüències vibracionals dins de l'aproximació harmònica. En concret, s'ha investigat la metodologia mecanoquàntica, basada tant en l'aproximació local de la densitat (LDA) com en la no local (GGA), que, a diferència de la primera, inclou correccions de gradient. S'ha fet servir una base de càlcul del tipus STO, de qualitat triple-ζ per al metall i doble-ζ amb una funció de polarització afegida per a l'halogen. Tot comparant els paràmetres calculats en relació amb dades experimentals i amb resultats obtinguts per altres models teòrics (quan ha estat possible), es fa palès que la teoria del funcional de la densitat esdevé una alternativa viable i certament avantatjosa respecte a mètodes més cars.

RESUMEN

Se ha utilizado la teoría del funcional de la densidad (DFT) para calcular las geometrías de los compuestos ZnX_2 (X = Cl, Br, I) en el estado fundamental, así como también sus frecuencias vibracionales dentro de la aproximación armónica. En concreto, se ha investigado la metodología mecanocuántica tanto en la aproximación local de la densidad (LDA) como en la no local (GGA), que, a diferencia de la primera, incluye correcciones de gradiente. Se ha utilizado una base de cálculo del tipo STO, de calidad triple-ζ para el metal y doble-ζ con una función de polarización añadida para el halógeno. Comparando los parámetros calculados en relación con los datos experimentales y con resultados obtenidos mediante otros modelos teóricos (cuando ha sido posible), se pone de manifiesto que la teoría del funcional de la densidad es una alternativa viable y ventajosa frente a métodos más caros.

ABSTRACT

Density functional (DF) calculations are reported for the ground-state geometries and harmonic vibrational frequencies of ZnX_2 (X = Cl, Br, I). Both local density approximation (LDA) and non-local generalized gradient approximation (GGA) functionals were investigated using an STO basis set of triple-ζ quality for the metal and double-ζ plus polarization function quality for the halogen. Comparison of calculated parameters with experiment and with results from other theoretical models (when available) shows that DF theory is a viable and advantageous alternative to more expensive methods.

Keywords: Density functional theory, linear triatomic molecules, molecular structures, transition-metal complexes, vibrational frequencies, zinc dihalides.

INTRODUCTION

Group IIB dihalides MX_2 are of considerable interest for discussing chemical bonding (1). Among the three binary zinc dihalides (X = Cl, Br, I), extensive literature (both experimental and theoretical) is found only for the smallest member of the set (2,3), whereas the dibromide and diiodide have received much more less attention (4). Some important conclusions can be drawn when studying such a series. In addition to the nature of the bonding in any given MX_2 species, one can assess the trends on going from Cl to I, the role of the d-electrons, implications of electronegativity, and so forth.

One of the central tasks in computational chemistry is the accurate and efficient prediction of molecular geometries, vibrational frequencies, and energies involved in chemical reactions. From a great number of systematic calculations, mostly on organic molecules, it has been established that useful energetic, structural, vibrational and electronic properties can be obtained from Hartree-Fock theory, even at the single-configuration self-consistent field (SCF) level (5). Nowadays, molecules having *ca.* 10-20 carbonlike atoms are being investigated routinely at that level of theory using large basis sets.

Recent advances in the implementation of direct SCF schemes (6,7), combined with the increasing performance of computer hardware are moving the frontier to molecules of increasing size and complexity. Novel algorithms for two-electron integral evaluation have been pursued and implemented successfully (8-10). Nevertheless, the calculation of four-index, two-electron integrals remains a major computational bottleneck. Recent developments of pseudospectral methods allow to carry out Hartree-Fock calculations with an algorithm that scales with the third power of the number of basis functions (11).

However, these advances do not address the key issue of electron correlation and the need for multireference calculations, which are known to be important for many systems such as transition-metal complexes. Inclusion of correlation energy usually increases dramatically the computational requirements, thus limiting the applicability of correlated methods to rather small molecules.

In particular, the structure of coordination compounds has proven to be a challenge for conventional molecular orbital methods based on Hartree-Fock theory (12-14). Besides the drawback of size limitation and the problems inherent in applying this method to transition-metal systems, there is the additional problem of the existence of many possible hybridization schemes for block d elements.

Therefore, there is a fairly urgent need to explore and develop new theoretical and computational methods that include electron correlation and, at the same time, are practical enough for large systems. One method that has been applied with great success by the solid-state physics community to treat the electronic structure of metallic systems (including transition metals) is density functional theory (DFT) (15-20). The recently acquired popularity of DFT stems in large measure from its computational speed, which makes it suitable to real-life molecules, which can be studied at a fraction of the time required with HF or post-HF calculations. More important, perhaps, is the fact that expectation values derived from DFT in most cases are better in line with experiment than results obtained from HF calculations. This is especially the case for systems involving transition metals. Literally hundreds of DFT calculations have been performed on molecules comprising hydrogen and first-row elements (21,22). Far fewer calculations have been reported for molecules containing second-row atoms (23), and fewer yet for compounds incorporating heavier elements. In this latter class, very few DFT computations which involve transition metals had been undertaken until the nineties. Efforts in this direction, however, have been made in recent years (20,24). Sosa et al. (25) and Deeth (26) reported geometries and vibrational frequencies of several first and second-row coordination compounds and found good agreement with experimental data. Density functional computations have also been performed on transition-metal dimers such as Cr_2 and Mo_2 with encouraging results (27-29).

While a great amount of effort has been spent in this area, much further systematic work is certainly required. The prevailing belief that adequate descriptions of the bonding in transition-metal complexes can be achieved by DFT (outperforming methods based on HF theory) still stems from relatively few comparisons.

In the present study, a set of zinc compounds have been examined in order to obtain a more complete understanding of the performance and future applicability of DFT for use in the study of transition-metal systems. Thus, the aim of the present work is to provide a hint on the sort of accuracy that is achievable using DF methodology to reproduce ground-state geometries and vibrational frequencies of molecules containing block d elements. To make a proper comparison, experimental data have been taken as reference.

METHODOLOGY

Calculations described below were done by means of the Amsterdam Density Functional program (30-35). Molecular orbitals were expanded into two different uncontracted sets of Slater type orbitals (STOs), i.e. the DZP and the TZ basis. The DZP basis set, used for the two smaller halides, is of double-ζ quality (two STOs per nl shell), with a 3d polarization function added on each atom. The TZ basis set, used for zinc and iodine, is of triple-ζ quality. The $1s^2 2s^2 2p^6$, $1s^2 2s^2 2p^6 3s^2 3p^6$ and $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ configurations, assigned to chlorine, bromine and iodine cores, respectively, were treated by the frozen-core approximation (30). For the metal, the inner atomic shells ($1s^2 2s^2 2p^6$) were also considered under this approximation.

Geometries were optimized using gradient techniques (35) with two different methods: GGA, which includes non-local corrections, and the simple LDA. At the non-local level, exchange was described with Slater's potential (36), with a non-local correction due to Becke (37-39). In the GGA method, correlation was introduced through local corrections using electron gas data in the Vosko-Wilk-Nusair (VWN) parameterization (40), with a non-local correction due to Perdew (41). At the LDA level, formulas given by VWN were used including no gradient corrections.

RESULTS AND DISCUSSION

In this section, we analyze separately the results of geometries and the results of vibrational frequencies. The first part includes symmetry considerations as well, together with a discussion on the chemical bonding. In the second part, besides spectroscopic data, a related thermodynamic parameter will be examined.

MOLECULAR STRUCTURES

Table 1 lists the optimized geometries, atomic charges and bond energies for the ZnX_2 complexes (X = Cl, Br, I). As far as equilibrium distances are concerned, the first observation is that the GGA results with the Becke-Perdew (BP) gradient corrections give bond lengths that are 0.031-0.040 Å longer than the distances obtained with LDA. This arises from the fact that gradient corrections reduce the overbinding of molecules by LDA, thus leading to a weaker bond and a larger interatomic distance. Another observation is that the heavier the halogen atom bonded to the central zinc, the bigger the difference between LDA and GGA equilibrium distances (Cl 0.031, Br 0.039, I 0.040 Å).

Full geometry optimizations have yielded an unambiguous bond angle of 180° for the species studied ($D_{\infty h}$ symmetry). From a theoretical point of view, the linear configuration of zinc dihalides is not surprising at all in view of the [Ar] $3d^{10}$ $4s^2$ electronic configuration of zinc, and is also in agreement with the discussion of MX_2 structures including ZnX_2 molecules by Drake and Rosenblatt (42) and by Coulson (43).

However, when the structures of binary zinc dihalides were first studied by electron diffraction nearly 40 years ago (44), the authors were not sure whether the equilibrium configuration of the molecules was linear or bent. Later improvements in the method allowed for more accurate analyses of such systems. The molecular structures of zinc dichloride, zinc dibromide and zind diiodide were reinvestigated by Hargittai et al. (45) and determined at *ca.* 656, 614 and 580 K, respectively, by gas-phase electron diffraction. All molecules displayed linear configurations with the following bond lengths (in Å):

Zn-Cl	2.072 ± 0.004
Zn-Br	2.204 ± 0.005
Zn-I	2.401 ± 0.005

These values can be taken as reference in order to check the relative validity of local and non-local approximations. According to these values, the best DFT geometrical parameters of table 1 appear to arise from the local method, possibly indicating that LDA is accurate enough to reproduce molecular structures so no gradient corrections are required here. Similar results were obtained earlier by several authors (46,47). In a previous work on H_2, N_2, F_2, hydrogen fluoride and formaldehyde by Murray et al. (48), the BP method was found to consistently overestimate bond lengths by up to *ca.* 0.02 Å. Those results appeared to be comparable with MP2 bond lengths, and they were generally slightly longer than the experimental values.

It is interesting to compare our DFT geometries with others reported in the literature which use molecular orbital methods based on HF theory. Thus, previous theoretical calculations on $ZnCl_2$ include the work by Strömberg et al. (49), who studied a number of species containig Hg, Cd and Zn at the CI level using non-relativistic and relativistic techniques, and who calculated equilibrium distances and binding energies. For $ZnCl_2$, the following bond lengths were reported: 2.15 Å (SCF), 2.16 Å

(CASSCF) and 2.14 Å (CI). All these computed HF and post-HF equilibrium distances are slightly too long, by 0.07-0.09 Å, whereas the deviation of LDA and GGA results in the present paper falls below 0.02 and 0.05 Å, respectively. To our knowledge, neither $ZnBr_2$ nor ZnI_2 have been studied yet using HF and post-HF methods to predict their gas-phase geometries.

Bond energies and atomic charges collected in table 1 provide some elements to discuss the chemical bonding in these complexes. On simple chemical grounds, one expects the bonding in ZnX_2 to consist largely of sp hybrids on the X atom overlapping with the 4s orbital on Zn. There should be some contribution from the $3d_{z2}$ Zn orbital. Polarization functions on X^- do not actually bind the molecule, but do permit a more acccurate description of the bonding X function. One also suspects that some π bonding may arise from the Zn 4p and 3d functions. Finally, one expects that iodide should be less ionic than bromide, the latter less than the chloride, and that, overall, Zn 3d-electrons will play only a minor role in the bonding. Kohn-Sham orbitals and atomic charges we have obtained bear out these expectations. Since electronegativity is defined as the relative ability of a certain atom to draw electron density to itself within a molecule, the actual assignment of electronegativities might be checked by molecular orbital calculations in which one finds either a relative population (Mulliken, Löwdin or similar), or an actual electron density distribution within a molecule.

Table 1 gathers the atomic charges calculated by LDA and GGA methods, both reporting very similar results. Taking for instance the GGA charges, the gross Mulliken population corresponds to a total charge of $Zn^{+0.10} (I^{-0.05})_2$, as compared to $Zn^{+0.64} (Br^{-0.32})_2$ or $Zn^{+0.81} (Cl^{-0.41})_2$; thus, iodide is indeed considerably less ionic. An explanation can be given in terms of Pauli electronegativity for the halogen group (Cl 3.0, Br 2.8, I 2.5), which decreases in a similar way.

Equally important turns out to be the analysis of bond energies referred to atomic systems. Experience so far suggests that Becke's gradient correction to the exchange is very important to improve the bonding energy (22). From the energy values of table 1 and in the light of other researchers reports (24,48), it can be expected than GGA predictions are more reliable than values estimated by LDA. The latter method yields energies that are systematically higher by an amount of *ca.* 0.8 eV, irrespective of the halogen atom. Further attention will be paid to this point in the next subsection.

VIBRATIONAL FREQUENCIES

The three normal modes of linear XMX ($D_{\infty h}$) triatomic molecules are shown in table 2, corresponding the first (υ_1) and the third (υ_3) vibrations to symmetric and antisymmetric stretchings, respectively. The υ_2 bending mode is a doubly degenerate vibration. Apparently, there are an infinite number of normal vibrations of this type, which differ only in their directions perpendicular to the molecular axis. Any of them, however, can be resolved into two vibrations, which are perpendicular to each other.

Furthermore, υ_1 is Raman active but not infrared active, whereas υ_2 and υ_3 are infrared active but not Raman active (the so-called mutual exclusive rule) (50). The calculated double-harmonic intensities (I_i) confirm this fact.

Both LDA and GGA methods yield frequencies in good agreement with experiment (51). The first approximation tends to overestimate frequencies by less than 15% (ZnI_2), 13% ($ZnBr_2$) and 3% ($ZnCl_2$). Even better results are obtained with the non-local method, as observed by Murray et al. in calculations on diatomic molecules (48). Thus the GGA method overestimates the vibrational frequency by less than 9% and 8% for ZnI_2 and $ZnBr_2$, respectively, the exception being for $ZnCl_2$, whose frequencies are underestimated between 1% and 5%.

In contrast to geometries, the LDA method appears here to be less reliable than the method using non-local corrections in the functional (when usually the trend for frequencies is a reflection of the accuracy reached for bond lengths).

As mentioned above, it has been found that applying corrections to the simplest LDA method usually gives better results for comparison with experimental data, especially as regards to bonding energies and the spectra computed from one-electron energies (22). Geometries are also reproduced better, but here the difference appears to be less pronounced.

Our calculations show a similar behaviour for the case of ZnX_2 frequencies, *i.e.*, non-local corrections do work. However, as reported by Van Leeuwen et al. (52), this improvement may be due possibly to a cancellation of errors. These authors investigated the question why the use of GGA gives energy results better than LDA, and found that gradient corrected functionals replace a region of high gradients in the sum of atomic exchange-correlation energy densities by a region of low gradients in the molecular exchange-correlation energy density around the bond midpoint. This region of zero gradients arises purely due to the topological properties of the molecular density, and is unrelated to atomic density changes upon bond formation.

In order to rationalize the declining tendency of vibrational frequencies on going from Cl to I, the metal-halide bond can be represented by the simple harmonic oscillator model for diatomic systems. According to this assumption, the frequency of the vibration is then inversely proportional to the square root of the reduced mass. As a result, the higher the atomic number of the halogen, the lower the frequency. This point is illustrated by any of the calculated normal modes shown in table 2. It is worth noting that the zero point energies follow the same trend, since they are closely related to the spacings of electronic levels involved in these transitions.

Another interesting property related to thermodynamic functions and for which experimental data are available (51) is heat capacity. Table 2 gathers calculated and measured parameters (both at 298.15 K). The accurate Cv evaluated by LDA for zinc dichloride is noteworthy. This notwithstanding, when all values considered, GGA seems to be again more favourable in predicting a trend along the series ($ZnCl_2 < ZnBr_2 < ZnI_2$). Thus, non-local approximation gives quantitative values that are slightly too small yet predicts a qualitatively correct result.

CONCLUSIONS

In this study, we have examined the accuracy of density functional theory at both the local density approximation and non-local gradient corrected levels of theory for binary zinc dihalides. These calculations have been motivated by a wish to test the quality of DFT for calculating some molecular properties and geometrical structures of coordination compounds. The need of using non-local corrections when calculating vibrational frequencies and molecular properties different from geometries has also been assessed.

The results obtained are extremely satisfactory, as judged by comparison to experimental data. The LDA method gives excellent bond lengths, with the worst case being zinc diiodide, where the error is *ca.* 0.036 Å. Non-local DF calculations have been able to correct slightly LDA results for the vibrational frequencies in some cases, and the gradient corrected values are in better compliance with experimental results. However, non-local corrections have not improved the agreement with experimental geometries obtained using the simple local density approximation.

A final remark on computational requirements can be inferred from our results. The incorporation of gradient corrections during the SCF procedure significantly increases the computing effort (CPU time and I/O). Consequently, it is better to perform molecular optimizations at the cheaper LDA level, because geometries are not very depending on the inclusion of non-local corrections (being even better with only LDA as in the case studied here), and then, to evaluate molecular properties by means of a GGA method. This procedure is an alternative way worth considering. It saves a great amount of time and the effects are small as regards the reliability of calculated parameters.

Here we have only provided a hint on the potential usefulness of density functional theory and have demonstrated the good accuracy for the prediction of structures involving transition metals for both the LDA and GGA methods. However, the optimum density functional must still be the subject of further, extensive research.

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Table 1. Equilibrium distances (in Å), charges (in a.u.) and bond energies referred to atomic systems (in eV) for the ZnX_2 compounds (X = Cl, Br, I).

Compound	r(Zn-X)	q(Zn)	q(X)	ΔE
LDA				
$ZnCl_2$	2.091	0.7501	-0.3751	-7.6474
$ZnBr_2$	2.201	0.5892	-0.2946	-6.7133
ZnI_2	2.365	0.0245	-0.0123	-5.6024
GGA				
$ZnCl_2$	2.122	0.8136	-0.4068	-6.7718
$ZnBr_2$	2.240	0.6407	-0.3203	-5.8294
ZnI_2	2.405	0.1014	-0.0507	-4.7376

Table 2. Vibrational frequencies, υ (in cm^{-1}), intensities, I (in km mol^{-1}), zero point energies, ZPE (in eV) and heat capacities, Cv (in cal mol^{-1}K^{-1}) for the zinc dihalides.

	$ZnCl_2$	$ZnBr_2$	ZnI_2
Exp.[a]			
υ_1	352	223	163
υ_2	103,100	71	61
υ_3	503	404	346
Cv	11.677	12.180	12.391
LDA			
υ_1	356.2	233.6	182.0
υ_2	100.8	79.9	67.9
υ_3	515.8	432.6	394.7
I_1	0.0	0.0	0.0
I_2	9.9	4.3	2.4
I_3	70.5	56.0	63.6
ZPE	0.067	0.051	0.044
Cv	11.643	8.157	8.314
GGA			
υ_1	341.6	222.6	172.9
υ_2	94.9	76.0	66.4
υ_3	497.5	412.0	375.7
I_1	0.0	0.0	0.0
I_2	11.4	5.0	3.0
I_3	73.7	58.5	63.3
ZPE	0.064	0.049	0.042
Cv	7.816	8.219	8.366

[a] From ref. (51)