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A coupled-cluster study of lanthanum trihalide structures

Branislav Jansik,[a] Alfredo M. J. Sanchez de Meras,[b] Bernd Schimmelpfennig[a] and Hans Ågren[a]

[a] *Laboratory of Theoretical Chemistry, Department of Biotechnology, Royal Institute of Technology, SCFAB, SE-10691 Stockholm, Sweden*
[b] *Department de Quimica Fisica, Universitat de Valencia, Dr. Moliner, 50, 46100 - Burjassot (Valencia), SPAIN*

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Coupled-cluster calculations were carried at the CCSD(T)-level in order to determine the structures and vibrational spectra of the lanthanum trihalides LaF_3 and $LaCl_3$. Two different approaches were employed to describe scalar relativistic effects; the quasi-relativistic Effective Core Potential approach and the all-electron Douglas–Kroll approach. We find LaF_3 to be of pyramidal structure and $LaCl_3$ to be planar. The obtained vibrational frequencies accord well with experimental measurements except for the ν_2 mode. This disagreement is attributed to the intrinsic uncertainty of harmonic frequencies of this fluxional mode as extracted from spectra which were obtained at high temperature and for matrix isolated species.

1 Introduction

During the last decade much attention has been focused on lanthanide trihalides, mainly due to the particular properties of these 4f molecular systems relevant for several fields of applied chemistry and physics.[1–4] Recent advances in quantum chemistry have made it possible to study this type of compound by means of *ab initio* methods in order to predict their structures and properties as well as to use them for benchmarking various theoretical models. An example of that was recently given by the extensive multi-configurational self-consistent field study of lanthanide trihalides by Taketsugu and coworkers,[5] and by the work of Di Bella *et al.* who also considered dynamic correlation effects.[6] These authors studied lanthanum trifluoride and trichloride at several levels of calculation (SCF, CASSCF and SDCI). Other related studies have been carried out by Lanza and Fragalà[7] who investigated the corresponding gadolinium and lutetium trihalides and cerium tri- and tetrahalides[8] at the Hartree–Fock, CASSCF and MP2 levels of theory, by Adamo and Maldivi who used DFT theory[9] with different exchange and correlation potentials to examine the geometry and bonding of the various lanthanide trihalides, and by Dolg *et al.*[10] who investigated selected dihalides and trihalides of the rare earth elements using SCF and SDCI calculations. The same methodology with the Davidson correction for quadratic excitations has been used by Solomonik and Marochko.[11] Despite all these efforts there are still questions to be answered. In particular, the geometric structure of LaF_3 has not been unambiguously characterized. Thus, planar D_{3h} geometries were proposed for all lanthanide trihalides in the CASSCF studies of Taketsugu and coworkers[5] mentioned above and of Cundari *et al.*,[12] who, however, did not explicitly consider LaF_3. By contrast, the results of Di Bella *et al.* indicated a pyramidal C_{3v} structure in agreement with the DFT results of Adamo and Maldivi[9] and with those of an earlier *ab initio* study[13] and also with the recent SDCI+Q calculation in ref. 11. The difference between the two structures is thought as small as 0.05 kcal mol^{-1} at the DFT/BP level.[9] In general terms, it seems that dynamic correlation tends to favour the pyramidal conformation. Basis set effects are also important as well as the number of electrons represented by the pseudopotential.[14] The planar form is usually the equilibrium configuration for heavier halides and in particular for $LaCl_3$, although even in that case experiments are non-conclusive. The experimental information referring to LaF_3 is also somehow contradictory, with both D_{3h} and C_{3v} structures having been deducted from the observed data. In this way, the infrared spectrum has been interpreted as coming from a planar structure[15] but also from the pyramidal geometry.[16,17] Molecular beam electric deflection experiments[18] give also a C_{3v} structure. Anyway, it seems that the majority of experimental data support a slight pyramidal form for these molecules. In this communication we take account of recent progress in combining highly correlated methodology with the use of effective core potentials as well as with the use of approximate schemes to treat relativistic effects, and readdress the question of the quantum chemical determination of the equilibrium geometries of LaF_3 and $LaCl_3$ in the gas phase as well as their harmonic frequencies of vibration. We will analyze results obtained with the coupled-cluster CCSD(T) model using relativistic effective core potentials or the scalar relativistic Douglas–Kroll[19,20] Hamiltonian and compare with previous results and with experimental data. We focus most effort on the fluoride system due to the controversy related to its structure.

2 Calculational details

Calculations were carried out using the coupled cluster approach at the CCSD(T) level[21] in the implementation[22,23] available in the DALTON code.[24] Vibrational frequencies were determined from a fourth degree polynomial fitting of the computed points by means of the Survib program.[25–27] The Relativistic Effective Core Potential (RECP) calculations were carried out using a generally contracted basis set of the atomic natural orbital (ANO) type[28] for fluorine (4s3p1d) and chlorine (5s4p2d1f) and the relativistic pseudopotential and basis set proposed by Cao and Dolg[29] for lanthanum (4s4p3d2f) in which 28 electrons are considered inside the atomic core while the remainder are treated in the valence shell according to the prescriptions of Lanza and Fragalà for other lanthanides.[8] Performance of the basis set has been systematically tested for the LaF_3 molecule by extending the florine basis set up to F(4s4p2d1f). The C_{3v}–D_{3h} inversion barrier for geometries optimized with F(4s3p1d) and F(4s3p2d1f) basis set was found to decrease by only 1.7 cm^{-1}, which justified the choice of the

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Table 1 Experimental and theoretical geometries of LaF_3. ED: Electron diffraction, MBED: molecular beam electron deflection, NR: non-relativistic, RECP: relativistic electron core potential, QR: quasi-relativistic, DK: Douglas–Kroll)

Method	R/Å	Θ/°	Ref.
ED	2.22	120	31
IR		120	15
IR		117	16,17
MBED		120	18
Extended Hückel		91.0	32
NR SCF	2.08	116.3	13
RECP SCF	2.16	118.3	6
RECP SDCI	2.16	117.6	10
RECP SDCI	2.18	118.6	6
RECP SDCI+Q	2.13	117.5	11
RECP UHF	2.21	120.0	5
RECP CASSCF	2.16	118.2	5
DFT BP/QR	2.12	114.8	9
DFT BP3/RECP	2.18	116.5	9
DFT BP/RECP	2.17	112.7	9
RECP SCF	2.14	120.0	This work
RECP MP2	2.14	118.5	This work
RECP CCSD(T)	2.14	118.5	This work
DK CCSD(T)	2.15	117.4	This work

F(4s3p1d) basis set for actual calculations on the LaF_3 molecule. Douglas–Kroll calculations were performed using the large component of a four-component basis set by Faegri,[30] which after augmentation with the f-functions taken from the ECP basis set was generalized contracted at the SDCI-level to a basis set of ANO-type (7s6p4d1f). The ANO basis set for fluorine was also recontracted using the Douglas–Kroll approach. Indeed, we used smaller basis sets and pseudopotentials in preparatory calculations not collected here and which were used to obtain a convergent pattern to the ones from which results are presented.

3 Results and discussion

3.1 LaF_3 geometry

As already indicated in the introduction there has been a big controversy about the equilibrium geometry of lanthanum trifluoride, as various methods and experiments have delivered disparate results. Following Hargitai[14] some caution must be taken when comparing theoretical and experimental data, especially those derived from electron diffraction experiments at high temperature as required by the low-volatile lanthanum trifluoride. As an immediate consequence, the computed distances are normally shorter than the experimental ones. In addition, the large anharmonicity of the potential hypersurfaces of these trihalides can make the thermally averaged bond distance considerably different from the equilibrium distance. It is therefore not strange that most of the calculated values of the La–F distance presented in Table 1 are too small compared to the experimental measurement by Akishin and Naumor. Our results are, in fact, in the same interval as some other theoretical numbers. It is notable that correlation effects are not essential in this context as can be seen by comparing the HF distance (2.143 Å) with the correlated results from MP2 and CCSD(T), (2.141 Å). The effect of replacing the innermost electrons by a pseudopotential may be understood by taking into account the value of 2.154 Å obtained when carrying out an all-electron calculation with the Douglas–Kroll Hamiltonian. Probably the most important discrepancies for the lanthanide halides concern its structure, as both C_{3v} and D_{3h} symmetries have been found. As already mentioned, inclusion of correlation favours pyramidal structures.[14] We have determined a planar conformation at the SCF level of theory, and, conversely, both at the MP2 and the CCSD(T) levels we find C_{3v} geometries, more precisely with angles F–La–F of 118.5 and 114.5°, respectively. However, in ref. 6 also a non-planar form is proposed even with the Hartree–Fock formalism, probably because of the use of a different ECP. We have also found a planar conformation at the CCSD(T) level only slightly above in energy with respect to the encountered C_{3v} minimum. This planar form falls into the pyramidal structure after a very small deformation, thus rendering the planar conformation to be a transition state. It should be noticed that all the methods predicting a pyramidal conformation are essentially monoreferential. In contrast, Taketsugu and coworkers state a planar D_{3h} molecule from their CASSCF calculations. Indeed, it has been suggested that pyramidalization can be an artifact of the MP2 method,[8] so it is therefore motivated to try to go beyond the MP2 level of theory to find out if the prediction at this level of correlation still can be maintained. We have used the singles and doubles coupled cluster method corrected with a perturbative estimation of the contribution of linked triple excitations for this purpose. This CCSD(T) model has proven able to reproduce molecular geometries, as well as vibrational frequencies in general,[38] even for systems with a pronounced multireference character, such as, for instance, ozone and for lanthanide compounds.[29] In the case of LaF_3, the singles contribution to the CCSD wave function is of the order of 10%. This means that even if it is slightly too large for a pure single reference description, it is not sufficiently large to invalidate the CCSD(T) results, making unnecessary the use of CAS reference wavefunctions. In any case, as pointed out among others by Cumari *et al.*,[12] the difference (10.985 cm^{-1} according to our calculations) between the two possible conformations is even smaller than the corresponding zero point energies, so in the gas phase this type of compound can probably be considered as highly fluxional.

In order to measure basis set effects we have enlarged the fluorine basis by adding one set of d functions and one set of f functions, to reach a triple zeta quality basis 4s3p2d1f. The obtained results confirmed those with the smaller basis previously discussed. Thus, the planar structure is again higher in energy, with an inversion barrier with respect to the pyramidal form of 12.72 cm^{-1} to be compared to the 10.99 cm^{-1} barrier found with the 4s3p1d basis with the same geometry. Geometry optimization causes only insignificant changes, predicting a bond length of 2.138 and an angle of 118.8, while the inversion barrier falls to 12.71 cm^{-1}. It is important to mention that suppression of the f function, what actually gives a less balanced description, reduces the inversion barrier to 6.02 cm^{-1}, but still the pyramidal form represents the most stable conformation.

3.2 LaF_3 vibrational frequencies

A molecule such as LaF_3 has the following IR modes: symmetric stretching (ν_1), double degenerate asymmetric stretching (ν_3), double degenerate asymmetric deformation (ν_4) and fluxional bending towards inversion (ν_2). In Table 2 we present our results on the vibrational frequencies of LaF_3, together with other theoretical results and with experimental frequencies. Again, experimental numbers must be examined with caution, especially the very small fluxional frequency ν_2, due to probable interactions with the matrix in which the infrared spectrum is produced.[6,14] Referring to the theoretical calculations it must be noted that because of the extreme flatness of the potential energy hypersurface, the calculation of derivatives by the finite differences method is probably not efficient as significant variations in energy will require too big increments in the molecular coordinates. In addition, as no analytic Hessian is available, we have chosen to compute the molecular Hessians from a weighted fitting to a fourth-degree polynomial. The first point to note is that all theoretical calculations predict ν_2 to be significantly smaller than the experimental value, for instance our ECP result is 47 cm^{-1} below the experimental value. A similar, although not as pronounced behaviour is encountered for ν_4,

Table 2 Experimental and theoretical vibrational frequencies of LaF_3

Method	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}	ν_4/cm^{-1}	Ref.
Experimental	528	81	497	130	16,17
RECP-SCF	560	42	561	130	6
RECP-SDCI+Q	535	46	511	120	11
RECP-CASSCF	542	53	545	129	6
DFT-BP3/RECP	517	83	485	127	9
DFT-BP/RECP	521	63	496	113	9
RECP-CCSD(T)	517	34	489	116	This work
DK-CCSD(T)	502	43	474	115	This work

Table 3 Experimental and theoretical geometries of $LaCl_3$. ED: Electron diffraction, MBED: molecular beam electron deflection, NR: non-relativistic, RECP: relativistic electron core potential, QR: quasi-relativistic, DK: Douglas–Kroll)

Method	R/Å	Θ/°	Ref.
ED	2.6	120.0	33
ED	2.59	112.5	33
ED	2.56	116.5	34,35
Extended Hückel		101.0	32
NR-SCF	2.62	120.0	13
RECP-SCF	2.66	120.0	6
RECP-SDCI	2.62	120.0	10
RECP-SDCI	2.64	120.0	6
RECP-SDCI+Q	2.60	120.0	11
RCP-UHF	2.70	120.0	5
RECP-CASSCF	2.66	120.0	6
DFT-BP/QR	2.59	116.5	9
DFT-BP3/RECP	2.61	118.2	9
DFT-BP/RECP	2.64	114.1	9
RECP-CCSD(T)	2.61	120.0	This work

which is predicted by the ECP-CCSD(T) method to be 116 cm^{-1} compared to the experimental value of 130 cm^{-1}. This value is in complete agreement with the DFT-BP/RECP result from ref. 9. Actually, except for the already mentioned prediction of ν_2, CCSD(T) results are quite similar to DFT numbers. On the other hand, the CCSD(T) results are very different with respect to the SCF and MCSCF results, which clearly overestimate the stretching frequencies. It is notable that the ECP results compare better with experiment than those obtained with the more elaborated Douglas–Kroll Hamiltonian, possibly due to the adequate parameterization of the pseudopotential.

3.3 $LaCl_3$ results

In Tables 3 and 4 we have collected experimental and theoretical information related to geometry and harmonic frequencies of lanthanum trichloride. Referring to the geometry it is important to realize that almost all methods predict a planar geometry in accordance with the earlier experimental evidence, but not with the more recent experimental results. Only the DFT results in ref. 9 and extended Hückel calculations[32] suggest a pyramidal structure. It is thus interesting that while the correlated *ab initio* methods basically agree with DFT on a pyramidal structure for LaF_3, they disagree on that for $LaCl_3$. It would therefore be very valuable to obtain a more conclusive evidence by experiment on this issue. Bond lengths are systematically calculated to be longer than the experimental ones, especially when CASSCF wave functions are employed. This is an already known feature characteristic of the CASSCF method. Our result on the D_{3h} structure with a bond distance of 2.61 Å is best met by the older electron diffraction results from Akishin and Naumor.[31] Of course, bond distances are to be predicted shorter when a pyramidal structure is suggested as in the other ED experiments.[33–35] The vibrational frequencies, presented in Table 4, display trends similar to those of LaF_3. The largest differences between experiment and theory appear when comparing the fluxional frequency ν_2. Again, the probable interference by the matrix in which the sample is measured must be considered. Our results (last row in the table) are somewhat too low, but still comparable to other recent theoretical results. An important feature to be mentioned is that most of the theoretical methods predict an ordering of the stretching frequencies that disagrees with the experimental result. Thus, the electron diffraction method of Spiridonov *et al.*[34,35] predicts the symmetric stretch at a frequency higher than the asymmetric one, while SCF, SDCI, CASSCF and CCSD(T) methods predict a frequency lower for the symmetric stretching than for the asymmetric one. The opposite behaviour of one of the DFT calculations shown in Table 4 is thus notable. Nevertheless, let us recall that DFT methods have predicted a pyramidal C_{3v} structure in accordance with refs. 34 and 35 but opposite to ref. 31. The need for new additional experimental information is again evident.

4 Conclusions

In this article we have used the CCSD(T) approximation and relativistic effective electronic core pseudopotentials to compute the geometries and harmonic frequencies of LaF_3 and $LaCl_3$. Our results using what is maybe the most accurate theoretical method to date to optimize molecular geometries indicate a pyramidal C_{3v} structure for the fluoride (r_e = 2.14 Å, θ_e = 118.5°) and a planar D_{3h} structure for the chloride (r_e = 2.62 Å). Harmonic frequencies were also computed, with good experimental agreement except for the fluxional mode ν_2 which

Table 4 Experimental and vibrational frequencies of $LaCl_3$

Method	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}	ν_4/cm^{-1}	Ref.
Electron diffraction	337	52	333	73	34,35
IR	335[a]	52	316	74	36
RECP-SCF	305	26	326	71	6
RECP-SDCI+Q	314	6	332	67	11
RECP-CASSCF	301	26	323	72	6
DFT-BP3/RECP	331	45	323	80	9
DFT-BP/RECP	320	30	309	65	9
RECP-MP2	332	35	321	70	37
RECP-CCSD(T)	308	20	323	66	This work

[a] Estimated value.

probably is due to the extreme flatness of the molecular hypersurface with a related high anharmonicity and also due to the fact that measurements are carried out for matrix adsorbed species. Aside from this, the results compare well with some other modern theoretical results, and together with the encountered geometries of LaF_3, they represent an additional proof of the extreme fluxionality of these systems.

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