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# ***Ab initio* study on the spectroscopy of CuCl<sub>2</sub>.**

## **II. Benchmark calculations on the $X^2\Pi_g - C^2\Delta_g$ and $X^2\Pi_g - D^2\Delta_g$ transitions.**

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### **ABSTRACT**

The  $X^2\Pi_g - C^2\Delta_g$  and  $X^2\Pi_g - D^2\Delta_g$  transitions on CuCl<sub>2</sub> have been studied using the most sophisticated non-dynamic and dynamic electronic correlation treatments. We report here *ab initio* benchmark calculations using especially developed basis sets to study, at the CASSCF+CASPT2 and CASSCF+ACPF levels, the transition energies as well as the corresponding equilibrium geometries. The spin-orbit (SO) effects of both atoms were included in a second step through the effective hamiltonian formalism, using the calibrated SO effective potentials developed by the Stuttgart group. Without SO at the CASSCF+ACPF level, the vertical excitation energy for the  $^2\Delta_g$  state is 6711 cm<sup>-1</sup> and the symmetric stretching equilibrium Cu-Cl distance is 4.04 a.u. The inclusion of the SO effects leads to a pure  $^2\Delta_g$   $\Omega=5/2$  C state and a  $\Omega=3/2$  (0.7%  $^2\Pi_g$ , 99.3%  $^2\Delta_g$ ) D state. The calculated transition energies for the C and D states are 6340 and 8020 cm<sup>-1</sup>, in good agreement with the spin-orbit splitting recent values from gas-phase and rare-gas matrix isolation laser induced fluorescence experiments. The present benchmark results show, as was recently done for the  $X^2\Pi_g - ^2\Sigma_g$  transition, the rather poor performance of all the DFT-based descriptions for the  $^2\Delta_g$  state, which largely overestimate its  $T_e$ , systematically placing it around 19,000 cm<sup>-1</sup>. The CASSCF+CASPT2 method also overestimates, by around 50%, the  $X^2\Pi_g - ^2\Delta_g$  transition energy, showing that only large variational calculations can produce reliable spectroscopic results for this kind of complex systems where delicate electronic correlation effects have to be carefully dealt with.

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## I. Introduction

We have recently published the first study of a research program on the spectroscopy of  $\text{CuCl}_2$  where attention was focused on the nature of the ground state [1] since, despite numerous and recent works dedicated to the experimental and/or theoretical study of  $\text{CuCl}_2$ , there are still many unsolved questions concerning several aspects of the spectroscopy of this apparently simple molecule. The first reported optical absorption spectra [2,3] show two broad bands with maxima at around  $9000\text{ cm}^{-1}$  and  $19000\text{ cm}^{-1}$ . More recently, there have been several high resolution spectroscopic studies that allowed to obtain rotationally resolved information of the excitation spectra [4-8].

A supplementary interest in this system lies in the possibility to use gaseous  $\text{CuCl}_2$  as a chemical laser, since this molecule has shown laser oscillations when metastable molecular oxygen ( $^1\Delta_g$ ) is passed over heated copper in the presence of chlorine.

Very recent laser induced fluorescence (LIF) experiments were performed [9] on the  $E^2\Pi_u-X^2\Pi_{g(3/2)}$  transition to explain the rovibronic structure of the ground state up to  $4000\text{ cm}^{-1}$ . Also some spectroscopic studies of  $\text{CuCl}_2$  have been done in rare gas matrices [10] that provide accurate transition energies for the lowest excited states.

From the theoretical point of view, the first studies of this molecule were done by using the simple ligand field approach [11] and the SCF method [12]. A more refined theoretical analysis including electronic correlation effects was made by Bauschlicher and Roos [13]. They determined the  $^2\Pi_g$  state as the ground state, in contradiction with the ligand field theory and SCF predictions. They showed that it was necessary to use very large and flexible basis sets and to introduce a large fraction of the electronic dynamic correlation effects, via the Coupled Pair Functional (CPF) method, in order to

get the right energetic ordering of the two lowest-lying states. It must be stressed that their calculations were of all-electron type and that they did not include the main scalar relativistic effects (the Darwin and the mass-velocity corrections) which are important, especially for the copper atom. Their approximate treatment of spin-orbit effects lead to the wrong prediction regarding the  $\Omega$  value of the ground state, finding the 1/2 component lower than the 3/2 one by a very small amount ( $178\text{ cm}^{-1}$ ); however, we have recently shown [1] that this inversion is due to a not precise enough calculation of the purely electronic energies.

All of the density functional theory-based (DFT) calculations [14-16], with different types of functional forms for the exchange-correlation part, placed the  $^2\Pi_g$  state as the ground state, but the transition energy to the  $^2\Sigma_g^+$  state was largely overestimated ( $5565\text{ cm}^{-1}$  [14],  $5887\text{ cm}^{-1}$  [15] and  $4758\text{ cm}^{-1}$  [16]), as compared to the very recent value of  $1050\text{ cm}^{-1}$  from anion photoelectron spectroscopy (PES) [17], such value being in fair agreement with *ab initio* results ( $659\text{ cm}^{-1}$  without spin-orbit (SO) coupling and  $1576\text{ cm}^{-1}$  with SO effects [13], and  $1609\text{ cm}^{-1}$  without SO coupling [17]). As was stated in [1], the present investigation is focused on the ground state transition energy to the  $^2\Delta_g$  state, which has been dramatically overestimated by all the DFT approaches ( $21370\text{ cm}^{-1}$  [14],  $18630\text{ cm}^{-1}$  [15] and  $17904\text{ cm}^{-1}$  [16]) compared to the experimentally obtained value of  $7100\text{ cm}^{-1}$  through gas-phase PES [17]. This overestimation along with the underestimation of the transition energy to the  $^2\Pi_u$  state, leads to an incorrect ordering of the low-lying states predicted by all the DFT-based methods. However, it must be stressed that the DFT approaches have obtained some important points correctly for this complex molecule: a) in contrast to naïve LFT, DFT has provided the right order of the Cu-d splitting; b) it has given reasonable structural

and vibrational parameters for the ground state and c) reasonable atomic effective charges .

The  $\text{CuCl}_2$  spectrum is a very good example where the  $\Delta\text{SCF}$  approximation of the DFT method can, in principle, be applied, since the five lowest states differ by their spatial symmetry; therefore, the electronic complexity of  $\text{CuCl}_2$  represents an excellent case for further research in this area [18].

It is now well documented that relativistic effects must be included even for first row transition metals like Cu in order to reach spectroscopic accuracy. These relativistic effects are either scalar relativistic or spin-orbit (SO) effects. It must be stressed that in order to achieve a reasonable zeroth-order description of molecules including these metals, it is necessary to take into account at least the scalar effects, while the spin-orbit effects can be treated separately in a second step; see section IV.C of [1].

As concerns the experimental measurements, it is almost clear that there is no possibility for giving an estimation of the scalar relativistic effects but, for the spin-orbit ones, there are some results.

For the  $^2\Delta_g$  state that interests us here, fortunately, there is accurate information concerning the SO effects, since the two fine-structure components ( $\Omega=5/2, 3/2$ ) generated by this state have been clearly identified in neon and argon matrix isolation experiments; the corresponding transition energies are  $7893\text{ cm}^{-1}$  ( $\text{C}^2\Delta_g$ ),  $9568\text{ cm}^{-1}$  ( $\text{D}^2\Delta_g$ ) in neon matrix [10a]. However, the recent gas-phase PES experiments [17] were not precise enough to provide reliable values for the C and D states.

Among the few calculated values, we already mentioned that Bauschlicher and Roos obtained the wrong  $\Omega$ -ordering for the ground state, but they were able to predict the  $\text{X-C}^2\Delta_g(5/2)$  and  $\text{X-D}^2\Delta_g(3/2)$  transitions as  $7514$  and  $9656\text{ cm}^{-1}$  respectively, using an approximate estimation of the SO effects. None of the DFT calculations went beyond

the purely electronic Hamiltonian, so no SO effects have been reported using the DFT  $^2\Delta_g$  wavefunctions.

The complexity of the electronic structure of  $\text{CuCl}_2$  arises since, at the doubly ionic limit, is described by the  $\text{Cl}^-\text{Cu}^{2+}(3d^9)\text{Cl}^-$  structure, while in the covalent  $\text{ClCuCl}$  description, the copper atom is promoted to the  $3d^94s^2$  excited state, undergoes 4s-4p hybridization and can establish covalent bonds with both Cl atoms. An intermediate situation arises when one considers the resonant  $\text{Cl}^-\text{Cu}^+(3d^94s^1)\text{Cl}$  and  $\text{ClCu}^+(3d^94s^1)\text{Cl}^-$  ionic structures. Near the equilibrium distance, the exact electronic structure for all states is a mixture of these three valence situations. The first three (LF) states correspond to d-d transitions on the copper atom and they can be described by different orientation ( $\sigma$ ,  $\pi$  or  $\delta$ ) of the singly occupied 3d orbital. The two next higher-lying states correspond to charge transfer (CT) states from the Cl atoms to the Cu one; these states are indeed less ionic than the lower lying LF ones. It is well known that a correct description of electronic structures, and even more with such close lying states, must include a correct description of correlation effects especially important for the d shell, but also must allow for large repolarization differential effects between localized d-d states and charge transfer states. Some other complications arise if one aims at providing a theoretical description which could be useful for helping to interpret high-resolution spectroscopic results (SO, Renner-Teller effects, K-doubling, etc).

Due to the broad interest in this system which can be considered as a prototype for  $\text{MX}_2$  (M=transition metal, X=halogen) molecules, we decided to make a new series of accurate *ab initio* calculations, dealing with all the difficult points previously mentioned in order to provide the most accurate and reliable transition energies for the C and D states of  $\text{CuCl}_2$ .

## II. Method and Computational Details

### A. Basis sets and RECP

The complex spectroscopy of  $\text{CuCl}_2$  requires the use of basis sets adapted to properly describe the ionic and covalent asymptotic limits including some excited states of Cu and  $\text{Cu}^+$ . We have chosen to reduce the number of explicit electrons by using the energy-adjusted Relativistic Effective Core Potentials (RECP) of the Stuttgart group, from refs. [19] for Cu and [20] for Cl, which can describe in a balanced manner the lowest-lying electronic states and include the main scalar relativistic effects. However, the corresponding gaussian basis sets originally developed for these RECP are not sufficiently flexible for the spectroscopic purposes we are aiming at and must therefore be uncontracted and augmented with diffuse functions. Thus, we developed [1] the extended and optimized basis sets at the Complete Active Space SCF plus Averaged Coupled Pair Functional (CASSCF+ACPF) level for both atoms, trying to reproduce at best the relevant IP and atomic transitions in Cu, as well as the EA for Cl. The atomic J-averaged spectra appear in table II of ref. [1] and the energy differences thus obtained between the Cu and Cl atomic states are in excellent agreement with the known transitions.

One could ask what is extent of the role of the semicore 3s-3p shells in the correlation effects for the lowest excited states of Cu. The answer can be found (see table II of ref. 1) in the relative accuracy for the  $^2\text{D}$  and  $^2\text{P}$  states, where as expected, we have a larger error of  $170\text{ cm}^{-1}$  within  $12000\text{ cm}^{-1}$  from the J-averaged energy for the  $^2\text{D}$  state, while for the  $^2\text{P}$  state the same error is only of  $200\text{ cm}^{-1}$  within almost  $31000\text{ cm}^{-1}$ . This is natural since the semicore-valence differential correlation is much larger due to fact of the changing occupation number in the 3d shell for the  $^2\text{D}$  state ( $3\text{d}^9$ ).

However, since all the ligand field states of  $\text{CuCl}_2$  arise from the same valence configuration with only a change in the orientation of the 3d hole on Cu or  $\text{Cu}^+$ , we expect the relative error of not explicitly including the semicore-valence correlation to be almost identical for the states we are currently studying.

A last especially relevant atomic result for the problem at hand was that our optimized basis with the CASSCF+ACPF method produced a copper IP of 7.62 eV [1], much closer to the experimental value (7.72 eV) than the one reported in ref. [13] of 7.27 eV using an all-electron basis and without scalar relativistic effects.

#### *B. Non-dynamic and dynamic electronic correlation treatments.*

The non-dynamic correlation effects were introduced via the complete active space SCF method (CASSCF) while the dynamic correlation effects were taken into account either variationally, with the averaged coupled pair functional (ACPF) method, or perturbationally with the second-order multireference Möller-Plesset algorithm (CASPT2). As has been done in [1], we used the CASSCF+CASPT2 or CASSCF+ACPF approach with the whole valence CAS in each atom, that is, for Cu we included 11 active electrons in 9 active orbitals (the 4s, 4p and 3d shells), while for each Cl we included 7 active electrons in 4 valence orbitals (the 3s and 3p shells). For the molecular calculations we excluded the 3s orbitals of the Cl atoms, thus eliminating 4 active electrons in the CAS and even doing so, rather large CASSCF(21,14) calculations have been performed; the resulting wavefunctions were then used as references for the CASPT2 or ACPF methods. Table I shows the technical details of these CASSCF, CASPT2 and ACPF calculations, along with the number of configuration state functions (CSF) dealt with at each level. As previously reported, each single-point ACPF calculation with these huge variational spaces took



60 CPU hours and 6GB of RAM on a single Power4 processor of the IBM p690 supercomputer at UAEM. All the calculations were performed within the  $D_{2h}$  point group (the highest symmetry available) with the Molpro-2002.3 program [21].

*C. Inclusion of the spin-orbit couplings.*

As has been done before [1], we shall first determine very precise purely electronic eigenstates and, in a second step, build an effective hamiltonian to couple these through the SO operator to obtain the fine-structure states. In this method we still have one degree of freedom for the choice of the diagonal matrix elements. Again we will present results with diagonal elements directly taken from the ACPF energies and, in this two-step approach, a single set of molecular orbitals should be used for calculating the SO matrix elements; in this case we have chosen the  ${}^2\Delta_g$  CASSCF(21,14) orbitals, since we are particularly interested in obtaining a precise value for the SO splitting for this excited state.

The spin-orbit effects have been included using the effective hamiltonian (EH) approach as programmed in the Molpro-2002.3 code. We have followed the same procedure as reported in [1] but shall briefly recall here the basic ideas. The spin-orbit interactions were introduced using the effective spin-orbit potentials (ESOP) for Cu [23] and Cl [24] and the electronic CASSCF+ACPF energies replace the diagonal elements in the effective hamiltonian. This EH is constructed at every geometry in the CSF basis spanned by the union of sets describing each  $\Lambda\Sigma$  SDCl wavefunction for the  ${}^2\Sigma_g$ ,  ${}^2\Pi_g$  and  ${}^2\Delta_g$  states (around 1,320,000 CSF). Care has to be taken in order to produce both degenerate components of the  ${}^2\Pi_g$  and  ${}^2\Delta_g$  states. The production of completely degenerate ( $x^2-y^2$ ) and  $xy$  components of the  ${}^2\Delta_g$  state at the CASSCF level is far from being obvious; we had to proceed through the minimal CASSCF wavefunction for the  $\text{CuCl}_2^-$  anion and then, to perform a state-averaged CASSCF for

the second root of the first irrep with the first root of the fourth irrep for the neutral molecule with the same minimal CAS; finally, several increasingly large CASSCF calculations with more active orbitals were done until the CASSCF(21,14) was equally converged for both  $^2\Delta_g$  states.

Since these single- or multireference-SDCI wavefunctions already contain all of the physically relevant ionic and neutral valence structures for the molecule, we are confident that the EH thus built is an excellent representation with this rather large CSF basis . The fine-structure states resulting from the diagonalization of this EH are thus expressed in the form of a linear combination of parent  $\Lambda S \Sigma$  states.

### III. Results and discussion

#### A. General

Both  $X^2\Pi_g$  and  $^2\Delta_g$  (LF) states are rather ionic, the ground state presents a CASSCF(21,14) Mulliken net charge (at the equilibrium geometry) of +0.69(Cu) – 0.345(each Cl), while the  $^2\Delta_g$  state shows a net charge of +0.66(Cu) –0.33 (each Cl). We stress the fact that both states show a formal configuration that roughly corresponds to  $\text{Cu}^+(3d^9 4s^1)$  and not to  $\text{Cu}^{2+}(3d^9)$ , as generally accepted.

As was pointed out in [1], an important factor that must be taken into account for later correlated descriptions is that the 3d-hole in copper, that is the open-shell orbital in each of the three lowest-lying ligand field states, is strongly localized, which means that the transitions between these states can almost be described by d-d intra-atomic transitions in  $\text{Cu}^+(3d^9 4s^1)$ , simply changing the orientation of the 3d hole. We recall again here that simple ligand field theory applied to the present case would predict the well known  $^2\Sigma_g^+ < ^2\Pi_g < ^2\Delta_g$  energetic ordering based on the  $\text{Cl}(3p)\text{-Cu}(3d_{\sigma,\pi,\delta})$  overlaps. The two next,  $^2\Sigma_u^+$  and  $^2\Pi_u$  higher-lying states, are charge transfer states

that restore the basic  $\text{Cu}^+(3d^{10})$  nature of the central atom, and the  $\sigma_u$  or  $\pi_u$  open-shell orbitals are mainly localized on the Cl atoms. For all the states, the Hartree-Fock description represents a good starting point, since even for our large CASSCF wavefunctions, the HF weights were always larger than 0.93. All these facts are in agreement with the previous theoretical studies and represent the conceptual basis for the single-reference calculations performed at the CPF and CCSD(T) levels [13,17].

We recall here that both the CASSCF+CASPT2 and the CASSCF+ACPF methods produce a  $^2\Pi_g$  ground state [1], however the corresponding adiabatic  $X^2\Pi_g$ - $^2\Sigma_g^+$  transition energies were found to be quite different, since the CASPT2 method gives  $3861\text{ cm}^{-1}$ , while the ACPF predicts an almost degenerate  $^2\Sigma_g^+$  state at only  $99\text{ cm}^{-1}$  above the ground state. These facts are of relevance since the  $^2\Sigma_g^+$  and  $X^2\Pi_g$  energies are needed to define the effective hamiltonian for the present spin-orbit calculations.

#### *B. The purely electronic $X^2\Pi_g$ - $^2\Delta_g$ transition energy*

As was found to be the case for the  $X^2\Pi_g$ - $^2\Sigma_g$  transition, the CASSCF(21,14)+CASPT2 and CASSCF(21,14)+ACPF methods also produced very different  $X^2\Pi_g$  -  $^2\Delta_g$  transition energies, the former yielding a vertical value of  $11250\text{ cm}^{-1}$  while the ACPF value is only  $6910\text{ cm}^{-1}$ , in much better agreement with the experimental information; this shows again the poor performance of the multireference perturbational approach for this highly complex problem in the electronic structure of  $\text{CuCl}_2$ ; however, even the CASPT2 estimation is much closer to the experimental values than all of the DFT predictions (around  $19,000\text{ cm}^{-1}$ ).

Figure 1 shows the potential energy curves for the  $X^2\Pi_g$  and  $^2\Delta_g$  electronic states at the CASSCF+ACPF level.

Before starting the discussion on the transition energies, note that in figure 4 of ref. [10a] the authors show the type (emission or absorption) of the various observed transitions between the ground and the lowest excited states of  $\text{CuCl}_2$ . It is worth noting that, experimentally, the  $X^2\Pi_g\text{-}C^2\Delta_g$  and  $X^2\Pi_g\text{-}D^2\Delta_g$  transitions have been observed as strong absorptions and weak emissions in neon matrix, while in argon matrix only the  $X^2\Pi_g\text{-}C^2\Delta_g$  transition has been observed as weak absorption and weak emission. These transitions are made possible via vibronic coupling (with a single  $\nu_2$  quantum) in the symmetric bending mode, which is the only possible radiative channel due to the symmetry-forbidden transition rule between two gerade states.

It should be pointed out that the experimental excitation energies of ref. [17] obtained through vertical detachment energies (VDE), have been questioned in ref [10b]; there are two problems with the VDE indirect measurements. The first one is that they show a rather poor agreement when compared with the neon and argon matrix measurements to be credible; the second one arises from the fact that the bands in the photodetachment spectrum are rather broad, exhibit different intensities and shapes and, in some cases, are not clearly resolved; thus the transition energies reported in ref. [17] should be taken cautiously.

Table 2 shows the purely electronic transition energies at the CASSCF, CASSCF+CASPT2 and CASSCF+ACPF levels, compared with the previous experimental as well as theoretical values obtained using several DFT-derived and *ab initio* methods. A very rich discussion can be extracted from the extremely wide range of theoretical values obtained for this transition energy, going from 5273 at the SCF level to 21372  $\text{cm}^{-1}$ , corresponding to the first DFT-based calculation. Our CASSCF(21,14) values are slightly above both SDCI values from ref. [13] correlating 21 or 25 valence electrons, around 5800  $\text{cm}^{-1}$ . The second column of table 2 shows

that our CASSCF-CASPT2 value is around  $11000\text{ cm}^{-1}$ , which overestimates by 50% the experimental value, but which is still much closer to it than any of the DFT-based predictions, ranging from  $18,000$  to  $21350\text{ cm}^{-1}$ . The third column gives our CASSCF-ACPF values ( $6711\text{ cm}^{-1}$  for the vertical transition) which are above the SDCI+Q results ( $6174$  and  $6000\text{ cm}^{-1}$ ) of ref. [13] but below the CPF values ( $7272$  and  $7432\text{ cm}^{-1}$ ) of that same reference.

One important point that has not been discussed anywhere is the non-monotonic behavior of the transition energies calculated at the SDCI, SDCI+Q and CPF levels in ref. [13] when going from the 21 to 25 correlated electrons. It is only for the CPF method than the value calculated using 25 correlated electrons is larger than that calculated using 21 active electrons; exactly the opposite happens for the SDCI and SDCI+Q descriptions. This different behavior can be explained by the fact that the CPF approach and its multireference version, the ACPF approach, are true size-extensive methods, whereas the SDCI and SDCI+Q are not. Therefore we feel that we can, making an educated guess, predict that the CASSCF(25,16)+ACPF method, if it could be done (a calculation which is still practically unfeasible even in the largest supercomputers) would produce a transition energy around  $300$  to  $500\text{ cm}^{-1}$  larger than our present calculation, where both  $3s$  orbitals on the chlorine atoms were excluded from the active space, leading to a value around  $7400\text{ cm}^{-1}$ . This shows that even though the  $3s$  semi-core orbitals of chlorine are not crucial to define electronic state orderings, they do play a role on the quantitative definition of the transition energies in  $\text{CuCl}_2$ .

#### *D. Spin-orbit effects*

Before going into the details of the SO EH calculations, we recall that both  $^2\Delta_g$  states can be coupled through the SO operator with both components of the  $^2\Pi_g$  ground

state. All the EH results reported from here onwards were obtained including the  $^2\Sigma_g^+$  and  $X^2\Pi_{g(x,y)}$  states, which means that our EH produces 10 different eigenvalues, the last couple of them being doubly degenerate, two  $\Omega=5/2$  (whose eigenvectors are pure of  $^2\Delta_g$  nature) and two  $\Omega=3/2$ , whose eigenvectors are  $^2\Delta_g$ - $^2\Pi_g$  mixtures. The EH is built on the SDCI wavefunctions arising from the minimal CAS that allows an SCF construction of the  $^2\Sigma_g^+$ ,  $^2\Pi_g$  and  $^2\Delta_g$  states; given the optimized and extended gaussian basis sets used for the present calculations, even this small CAS produces SDCI wavefunctions expanded on 227,300 (1,270,000) contracted (uncontracted) CSF.

The spin-orbit matrix elements calculated using the state averaged minimal CASSCF+SDCI wavefunctions (at 4.05 a.u.) are as follows:  $\langle ^2\Delta_g | H_{SO} | ^2\Pi_g \rangle = 101 \text{ cm}^{-1}$  and  $\langle ^2\Delta_{g(x^2-y^2)} | H_{SO} | ^2\Delta_{g(xy)} \rangle = 826i \text{ cm}^{-1}$ . Of course, such large value for this last matrix element produces a large spin-orbit splitting between the two components of  $1680 \text{ cm}^{-1}$ . Figure 2 shows the potential energy curves for the totally symmetric stretching mode, of the the C and D fine-structure states using the corresponding CASSCF+ACPF  $\Lambda\Sigma$  splittings as diagonal energies of the effective hamiltonian for each Cu-Cl distance.

One important result is that the dependence of the  $\Omega=3/2$  -  $\Omega=5/2$  splitting on the purely electronic  $\Lambda\Sigma$  energies that define the diagonal matrix elements of the effective Hamiltonian is very small, always around  $1700 \text{ cm}^{-1}$ . This is a different situation from what was found for the  $\Omega=3/2$  -  $\Omega=1/2$  splitting of the lowest-lying states. However, this is easily understood because, in this case, this value corresponds to the almost atomic  $\text{Cu}^+(3d)$  splitting since, as noted before, the  $^2\Pi_g$  -  $^2\Delta_g$  SO coupling is only around  $100 \text{ cm}^{-1}$ .

#### *E. Comparison with previous theoretical and experimental results.*

Table 3 shows the X-C and X-D transition energies at the CASSCF, CASSCF+CASPT2 and CASSCF+ACPF levels, compared with the previous experimental as well as theoretical values obtained using several DFT-derived and *ab initio* methods. Table 4 presents the optimized Cu-Cl equilibrium geometries following the totally symmetric stretching vibrational mode, also at different levels of theory. The ACPF-SO values are in very good agreement with the experimental figures for both states.

Our more accurate effective hamiltonian SO calculation leads to a  $\Omega=5/2$ - $\Omega=3/2$  splitting ( $1680\text{ cm}^{-1}$ ) that is in much better agreement with the experimental C-D energy difference than the results obtained using the approximate inclusion of the SO effects reported in ref [13], where the authors report a SO  $C^2\Delta_g$ -D  $^2\Delta_g$  difference of  $2206$ ,  $2192$  and  $2140\text{ cm}^{-1}$  at the SDCl, SDCl+Q and CPF levels, respectively. If one translates their intermediate normalization coefficients to percentual composition, it is easy to see that they obtained a D( $\Omega=3/2$ ) state with CPF (99.2%  $^2\Delta_g$ , 0.8%  $^2\Pi_g$ ) weights and a pure C( $\Omega=5/2$ ) state, in close agreement with our more accurate results.

We have proved that the crucial factor for a truly reliable theoretical prediction of the spectroscopy of  $\text{CuCl}_2$  actually lies in the extremely accurate electronic description that is needed before the inclusion of the SO effects, since the latter can be very well accounted for using the ESOP-EH method.

## V. Conclusions

Perturbative and variational multireference benchmark calculations have been performed on the  $X^2\Pi_g$ - $^2\Delta_g$  transition energy of the  $\text{CuCl}_2$  molecule. The spin-orbit effects were introduced in a second step through the effective hamiltonian approach using the Stuttgart effective spin-orbit potentials for both atoms. The

CASSCF+CASPT2 method provides a much larger value for this transition, but still around half of the DFT predictions based on the  $\Delta$ SCF approximation; therefore, even though all the relevant non-dynamic electronic correlation effects have been correctly included through the large CASSCF(21,14) reference wavefunctions, this perturbative approach cannot provide reliable enough results for such a complex problem.

Our most accurate estimation, the CASSCF+ACPF result, the  $^2\Pi_g$ - $^2\Delta_g$  transition energy falls  $800\text{ cm}^{-1}$  below the previous non-relativistic CPF value, at  $6711\text{ cm}^{-1}$ .

Inclusion of the spin-orbit effects leads to a  $\Omega=3/2$  D state that is a (0.7% $^2\Pi_g$ ,99.3%  $^2\Delta_g$ ) mixture, while the  $\Omega=5/2$  ( $^2\Delta_g$ ) C state lies  $1700\text{ cm}^{-1}$  below the D one, both of them with a longer  $R_e$  (around 3.99 a.u.) than the  $X^2\Pi_g$  ground state.

Contrary to what happens for the  $X^2\Pi_g - ^2\Sigma_g^+$  transition, where less sophisticated methods provide results which are, apparently, in better agreement with experimental figures, for the  $X^2\Pi_g - C^2\Delta_g$  and  $X^2\Pi_g - D^2\Delta_g$  transitions the CASSCF+CASPT2 results overestimate (around 50%) the position of the excited states. In spite of the fact that we have been able to produce true benchmark variational multireference calculations at the CASSCF+ACPF level using especially optimized RECP gaussian basis sets for both atoms, the X-C and X-D transition energies are found to be somewhat smaller than those previously obtained with the single-reference CPF method [13], where no scalar relativistic effects were included, but which seem in better accordance with the available gas-phase and matrix isolation experimental values. The role played by the inclusion of 4 extra electrons on the 3s orbitals on both chlorine atoms seems to be responsible for the increase in the transition energies at the single reference CPF level when going from 21 to 25 correlated electrons. We predict that the translation of this effect to our multireference ACPF result would produce transition energies around  $400\text{-}600\text{ cm}^{-1}$  larger than the present values;



however, this effect cannot be proved with our present methods given the size of the CASPT2 and ACPF spaces already attained with 21 active electrons. As has been pointed out in Ref. [1], the solution of this dilemma will imply either much larger calculations (orders of magnitude larger) or, a different way to deal with the dynamic electronic correlation effects that are at the root of this fundamental problem .

Finally, our more accurate effective hamiltonian SO calculation leads to a  $\Omega=5/2$ - $\Omega=3/2$  splitting ( $1680\text{ cm}^{-1}$ ) that is in much better agreement with the experimental C-D energy difference than the results obtained using the approximate inclusion of the SO effects reported at the CPF level.

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**Table 1.** Details of the CASSCF(21,14) and ACPF calculations.  $N_{\text{elec}}$  is the number of active electrons. Increasingly large CASSCF calculations were done but ( $N_1, N_2, N_3, N_4, N_5, N_6, N_7, N_8$ ) denote the final number of active orbitals per irreducible representation (in the  $D_{2h}$  point group) used for the CASSCF wavefunctions. CSF is the number of configuration state functions generated by the CAS using the given  $N_{\text{elec}}$  and ( $N_1, N_2, N_3, N_4, N_5, N_6, N_7$ ) values; uCSF (cCSF) is the number of un(contract)ed CSF in the ACPF diagonalization.  $C_0$  is the weight of the CASSCF reference wavefunction in the overall ACPF wavefunction.  $E_{\text{ACPF}}$  is the ACPF energy (+226 a.u.) at the minimum of each potential energy curve.

State	$^2\Sigma_g^+$	$^2\Pi_g$ (*)	$^2\Delta_g$ (+)
$N_{\text{elec}}$	21	21	21
$N_1, N_2, N_3, N_4,$ $N_5, N_6, N_7, N_8$	4,2,2,1,1,2,2,0	4,1,1,1,1,3,3,0	4,1,1,1,1,3,3,0
CASSCF (CSF)	22920	22768	22988
CASPT2(cCSF)	13,198,981	13,193,466	13,189,594
(uCSF)	3,157,545,950	3,096,354,828	3,153,885,712
ACPF (cCSF)	39,337,683	39,254,147	39,306,829
(uCSF)	7,032,258,232	6,808,263,229	6,972,361,149
$C_0$	0.90	0.93	0.93
$E_{\text{ACPF}}$ a.u.	-0.700457	-0.700910	-0.669424

(\*)State-specific x-y symmetrized CASSCF reference: weights (1,1)

(+) Symmetrized  $\delta(+2)$  and  $\delta(-2)$  components as CASSCF references.

**Table 2.** Transition energies (in wavenumbers) at the purely electronic approximation compared with previous theoretical and experimental results. Theoretical values in parentheses. No experimental spin-orbit deconvoluted values available yet.

Transition	CASSCF(21,14)	CASSCF + CASPT2	CASSCF+ACPF	Exp.
$X^2\Pi_g - ^2\Delta_g$	5984 Vertical	11270 Vertical	6711 Vertical	
	5930 Adiabatic	11090 Adiabatic	6580 Adiabatic	7100 <sup>i</sup>
	(5273) <sup>a</sup>	(21372) <sup>c</sup>	(6174, 6000) <sup>f</sup>	7780 <sup>j</sup>
	(5835, 5772) <sup>b</sup>	(18630) <sup>d</sup>	(7272, 7432) <sup>g</sup>	7893 <sup>k</sup>
		(17904) <sup>e</sup>	(7768) <sup>h</sup>	7753 <sup>l</sup>

<sup>a</sup>Non-relativistic SCF value from ref [13].

<sup>b</sup>Non-relativistic SDCl values from ref [13] with 21 and 25 electrons correlated.

<sup>c</sup> DFT value from ref [14].

<sup>d</sup> DFT, Perdew-Wang functionals value from ref [15].

<sup>e</sup> DFT, VWN-BP functionals with atomic cores from ref [16].

<sup>f</sup> Non relativistic SDCl+Q values from ref [13] with 21 and 25 electrons correlated.

<sup>g</sup> Non relativistic CPF values from ref [13] with 21 and 25 electrons correlated.

<sup>h</sup> RECP-CCSD(T) value from ref [17].

<sup>i</sup> Anion VDE-PES from ref. [17].

<sup>j</sup> Corrected gas phase VDE-PES value from ref. [10b]

<sup>k</sup> For the  $\Omega=5/2$  C state in neon matrix from ref. [10a].

<sup>l</sup> For the  $\Omega=5/2$  C state in argon matrix from ref. [10a].

**Table 3.** X-C and X-D transition energies including spin-orbit effects (wavenumbers) at different levels of theory. Previous theoretical values in parentheses.

Transition	CASSCF+CASPT2	CASSCF+ACPF	Exp.
$X^2\Pi_g - C^2\Delta_g^+$	10115	6340 Vertical	7100 <sup>f</sup>
	(21372) <sup>a</sup>	(4714, SCF) <sup>d</sup>	7780 <sup>g</sup>
	(18630) <sup>b</sup>	(5243, SDCI) <sup>d</sup>	7893 <sup>k</sup>
		(5498, SDCI+Q) <sup>d</sup>	7753 <sup>l</sup>
		(7514, CPF) <sup>d</sup>	
		(7768) <sup>e</sup>	
$X^2\Pi_g - D^2\Delta_g^+$	11840	8020 Vertical	8700 <sup>f</sup>
	(17743) <sup>c</sup>	(6948, SCF) <sup>d</sup>	9450 <sup>g</sup>
		(7449, SDCI) <sup>d</sup>	9567 <sup>k</sup>
		(7692, SDCI+Q) <sup>d</sup>	9427 <sup>l</sup>
		(9656, CPF) <sup>d</sup>	

<sup>a</sup> DFT value from ref [14].

<sup>b</sup> DFT, Perdew-Wang functionals value from ref [15].

<sup>c</sup> DFT, VWN-BP functionals with atomic cores from ref [16].

<sup>d</sup> Approximate SO non-relativistic values from ref [13].

<sup>e</sup> Spin-orbit averaged CCSD(T) from ref. [17]

<sup>f</sup> Experimental VDE value from ref [17]; see discussion about this value in sect. IV.C.

<sup>g</sup> Gas phase corrected values [10b] using VDE data from ref. [17].

<sup>k</sup> LIF in neon matrix from ref. [10a].

<sup>l</sup> LIF in argon matrix from ref. [10a].

**Table 4.** Equilibrium Cu-Cl geometries for the symmetric stretching mode of CuCl<sub>2</sub> in bohr. Previous theoretical values in parentheses. No experimental values available yet.

State	CASSCF+ACPF
<b>C</b> $^2\Delta_g^+$	3.99 (3.98) <sup>a</sup>
<b>D</b> $^2\Delta_g^+$	4.00 (3.95) <sup>b</sup> (3.98) <sup>c</sup>

<sup>a</sup> Non-relativistic CPF value from ref. [13].

<sup>b</sup> Same value from ref. [14,15,16] for the  $^2\Delta_g$  state.

<sup>c</sup> B3LYP value for the  $^2\Delta_g$  state from ref. [17].

### Figure Captions

Figure 1. CASSCF(21,14)+ACPF potential energy curves of the  $^2\Delta_g$  (triangles),  $^2\Sigma_g^+$  (circles) and  $X^2\Pi_g$  (squares) states.

Figure 2. Potential energy curves of the  $\Omega=5/2$  (up-triangles) and  $3/2$  (down-triangles) fine-structure states. CASSCF+ACPF diagonal energies used at each geometry. The  $X(\Omega=3/2)$  ground state curve is also shown (squares).