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On the electronic structure and spectrum of CuF_2 and CuCl_2

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The ground and low-lying states of CuF_2 and CuCl_2 have been studied using the single and doubles configuration interaction (SDCI) and coupled pair functional (CPF) methods in a large Gaussian basis set including up to g -type functions. The results include a determination of the bond distances for all the ligand field states (the three states with one hole in the $3d$ shell) and charge transfer (CT) states, and force constants for the ligand field states. Overall the SDCI (with or without the Davidson correction for higher excitations) and CPF results are in good agreement. The CPF results, which we believe to be the most accurate, can be summarized as follows. The computed value for the asymmetric stretching frequency in the $^2\Sigma_g^+$ ground state of CuF_2 is 740 cm^{-1} , compared to the experimental value of 765 cm^{-1} . The $d-d$ transition energies for CuF_2 are 2500 and $10\,800\text{ cm}^{-1}$. The two lowest charge transfer states are at $31\,200$ and $33\,900\text{ cm}^{-1}$, respectively. CuCl_2 has been found to have a ground state which is an almost equal mixture of $^2\Sigma_g^+$ and $^2\Pi_g$ when an estimate of the spin-orbit interaction is included. Three $d-d$ transitions are found: 1600 cm^{-1} ($J = 1/2$), 7500 cm^{-1} ($J = 3/2$), and 9700 cm^{-1} ($J = 5/2$). The lowest charge transfer states have been computed to lie at $16\,700$ and $19\,600\text{ cm}^{-1}$. Two bands have been found in the gas-phase spectrum of CuCl_2 at 9000 and $19\,000\text{ cm}^{-1}$, in good agreement with the present results. The computed f value for the CT band is 0.017 , to be compared to the experimental value of 0.014 .

I. INTRODUCTION

The calculation by *ab initio* methods of the ligand field splitting in transition-metal complexes continues to be a challenge for quantum chemistry. The size of most of these complexes precludes highly accurate calculations. Consequently, most work has been performed at the self-consistent field (SCF) level of approximation, combined in some cases with limited configuration interaction.¹⁻⁷ Only recently has it become possible to perform more accurate calculations, which include a rigorous treatment of electron correlation.^{8,9} It is clear from an earlier study of ligand field splitting in CuF_2 (Ref. 9) that correlation effects have a profound effect on the results. It is also clear that very large basis sets are needed in order to fully account for these effects. Recent studies on transition-metal atoms and diatomics have also shown that very accurate wave functions are necessary to obtain a quantitatively correct description of spectral properties; see, for example, Ref. 10.

In this work we study the ligand field states and lowest charge transfer (CT) states of CuF_2 and CuCl_2 . The ligand field states are those which arise from a $3d^9$ occupation of Cu^{2+} and hence have a single hole in the $3d$ shell. The transitions between these states are referred to as $d-d$ excitations since they involve only a change in the orientation of the $3d$ hole. The CT states are derived from a $3d^{10}$ occupation of Cu^+ and involve the transfer of one electron from the ligand to the Cu relative to the lower-lying ligand field states. Both CuF_2 and CuCl_2 are small enough to allow for an accurate treatment of electron correlation, using extended one-particle basis sets. The earlier study of CuF_2 had shown that the

wave function is dominated by a single configuration in all electronic states of interest. Electron correlation can therefore be included by the singles and doubles configuration interaction (SDCI) method. We can, however, expect considerable contributions to the correlation energy from unlinked cluster terms in the wave function. These effects have been accounted for by the Davidson correction added to the SDCI energy, and also by performing coupled-pair functional (CPF) calculations.¹¹

The largest basis sets used were of the atomic-natural-orbital (ANO) type¹² and included up to g -type functions on the metal atom. Calculations were performed for the ground state, the $d-d$ excited states, and for the two lowest charge transfer states. The equilibrium bond distance and symmetric stretching frequency were determined for all states, and the antisymmetric stretching frequency was determined for the ground and $d-d$ excited states. Good agreement was found between the calculated quantities and limited experimental data.

II. METHODS

In the ionic limit, the molecules are $\text{X}^-\text{Cu}^{2+}(3d^9)\text{X}^-$, while in the covalent limit, the Cu atom is promoted to the $3d^94s^2$ excited state, undergoes $4s-4p$ hybridization, and forms covalent bonds with the two F or Cl atoms. The bonding in the ground and low-lying excited states is a combination of these two limits. Therefore, flexible basis sets are important to describe all states equally. In this work we use three different basis sets. The small sets are $(14s11p6d\,1f)/[8s6p4d\,1f]$ for Cu, $(9s6p1d)/[4s3p1d]$ for F, and

(13s9p1d)/[6s5p1d] for Cl. The Cu basis set is derived from Wachters' valence set,¹³ and we add his two functions to describe the 4p orbital (multiplied by 1.5 as recommended by Wachters); the diffuse 3d function of Hay¹⁴ and a 4f polarization function ($\alpha = 3.00$) are also added. The F basis set is derived from the double- ζ contraction of Dunning,¹⁵ which is supplemented with a diffuse p function ($\alpha = 0.1$) to describe F^- and a 3d polarization function ($\alpha = 1.3$). The Cl basis is the Cl^- set of McLean and Chandler¹⁶ supplemented with the d function recommended by Ahlrichs and Taylor.¹⁷ These are the same Cu and F basis sets used in the previous study.⁹

The big segmented basis set is (15s11p6d4f)/[9s7p4d3f] for Cu and (15s10p4d)/[8s7p3d] for F. The Cu basis set is derived from the same (14s9p5d) primitive set, adds an s, two p, one d, and four f functions. This Cu basis is the same as used in the CuO study and is described in more detail in Ref. 18. The F basis set is derived from the (13s8p) primitive set of van Duijneveldt.¹⁹ Two diffuse s ($\alpha = 0.093\,077$ and $0.035\,968$) and two diffuse p ($\alpha = 0.059\,326$ and $0.022\,735$) functions are added. A (62211111) contraction of the s and (4211111) contraction of the p functions are used. Four d primitive functions are added and contracted to three functions. Their exponents are the same as the most diffuse p functions in the original van Duijneveldt basis set and the contraction coefficients are obtained by scaling the p coefficients.²⁰

Our best basis sets are very large primitive sets contracted using the ANO procedure.¹² The basis sets are of the following form: (20s15p10d6f4g)/[7s6p4d2f1g] for Cu, (13s9p6d4f)/[5s4p2d1f] for F, and (19s14p6d4f)/[6s5p2d1f] for Cl. The Cu basis set is developed for the average of the Cu 3d⁹4s² and 3d¹⁰4s¹ occupations, while the F (Cl) is developed for the average of F and F^- (Cl and Cl^-). Thus these ANO basis sets are expected to be able to describe all bonding mechanisms equally. A full description of these ANO sets as well as a comparison with the results obtained in the uncontracted basis sets are given in the Appendix. In all calculations only the pure spherical harmonic components of the basis functions are used.

Each state is optimized separately using an SCF wave function that includes symmetry and equivalence restrictions. Correlation is added using either a singles and doubles CI (SDCI) approach or the coupled-pair functional method (CPF).¹¹ The CPF method is a size consistent reformulation of the SDCI approach which accounts for the effect of higher than double excitations. We also estimate the effect of these higher excitations using the Davidson correction (denoted +Q). For the small and big segmented basis sets we correlate 21 electrons: the Cu 3d and 4s and the F 2p (Cl 3p) electrons. In the calculations using the ANO basis sets, the F 2s (Cl 3s) electrons are also correlated yielding a 25-electron correlation treatment. The differential effect of the higher than double excitations on the T_e values is of modest size, and the +Q correction and CPF agree on the direction of the effect of the higher excitations. However, the CPF correction is larger, as expected when this many electrons are correlated. The good agreement between the results obtained at SDCI, SDCI + Q, and CPF levels suggests that we

have accounted for all of the important differential correlation effects. We believe that the CPF results are the most reliable, and that the correct answer probably lies between the CPF and SDCI + Q results, but closer to the CPF value. Therefore we focus on the CPF results in our discussion and in the comparison with experiment, but we report the SDCI, SDCI + Q, and CPF results in the tables to give a measure of the uncertainty in each quantity.

The calculations were carried out using the MOLECULE-SWEDEN (Ref. 21) program system on the NASA Ames Research Center Cyber 205, CRAY X-MP/48 and CRAY X-MP/14se computers.

III. RESULTS

Calculations were performed for the lowest $^2\Sigma_g^+$, $^2\Pi_g$, and $^2\Delta_g$ states, as well as the $^2\Sigma_u^+$ and $^2\Pi_u$ charge transfer (CT) states. In all cases, the Cu-X bond distance was optimized assuming a linear symmetric structure. This restriction on the geometry was lifted in the smaller basis set to allow a determination of the vibrational frequencies.

The results for the spectroscopic constants are summarized in Table I. At the SCF level the bonding is very ionic. The three states that formally arise from Cu^{2+} have 3d populations of between 9.00 and 9.14 electrons for both CuF_2 and CuCl_2 , and a net charge on Cu of 1.44 for CuF_2 and 1.10 for CuCl_2 . The magnitude of the overlaps of the 3d orbitals with the F^- or Cl^- are $3d\sigma > 3d\pi > 3d\delta (=0)$, leading to $^2\Sigma_g^+$ ground state, since this minimizes the Pauli repulsion. As the magnitude of the overlaps of the Cl 3p with the Cu 3d orbitals of Cu are smaller than corresponding F 2p overlap, the separations between the CuCl_2 d-d states are about half that of CuF_2 . The smaller ionic contribution in the CuCl_2 might also contribute to the smaller separation.

The charge transfer states have a Cu 3d population near 10, and a net charge on Cu is 0.5–0.6 smaller than the lower three states. For all states the open-shell electron is highly localized; for the three valence states the open-shell orbital is at least 97% on Cu, and for the CT states the open shell is from 95% to 99% on the F or Cl atoms.

The inclusion of correlation changes this picture somewhat, mixing in more covalent character: the population analysis shows about 0.2 electrons moving onto the Cu. In addition, the open shell is no longer completely localized on one component. The most important change takes place in the $^2\Pi_g$ state, where the F 2p (Cl 3p) orbitals mix with the Cu 3d to form a bonding and antibonding orbital. A similar mixing also occurs for the $^2\Sigma_g^+$ state, but to a smaller extent. The inclusion of higher excitations increases this effect further. The most important consequence of the correlation-induced delocalization is to lower the energy of the $^2\Pi_g$ state relative to the $^2\Sigma_g^+$ state. For CuCl_2 this reverses the order of the two lowest states, leading to the prediction of a ground state dominated by $^2\Pi_g$, but also containing a large fraction of $^2\Sigma_g^+$ through spin-orbit coupling (see below). This is an important result of the present investigation. It illustrates how important dynamical correlation effects in transition-metal compounds are, even leading in some cases to a qualitatively different prediction of the electronic structure. The

TABLE I. Summary of computed spectroscopic constants; r_e is in Å and T_e in cm⁻¹.

| | SCF | | SDCI | | SDCI + Q | | CPF | |
|--|-------|--------|-------|--------|------------|--------|-------|--------|
| | r_e | T_e | r_e | T_e | r_e | T_e | r_e | T_e |
| CuF ₂ | | | | | | | | |
| Small basis set (21 electrons correlated) | | | | | | | | |
| $^2\Sigma_g^+$ | | | 1.747 | ... | 1.748 | ... | 1.752 | ... |
| $^2\Pi_g$ | | | 1.753 | 4173 | 1.751 | 3915 | 1.749 | 3049 |
| $^2\Delta_g$ | | | 1.781 | 10 086 | 1.782 | 10 096 | 1.784 | 10 377 |
| Big basis set (21 electrons correlated) | | | | | | | | |
| $^2\Sigma_g^+$ | | | 1.731 | ... | 1.732 | ... | 1.734 | ... |
| $^2\Pi_g$ | | | 1.733 | 4115 | 1.731 | 3801 | 1.728 | 2854 |
| $^2\Delta_g$ | | | 1.710 | 10 154 | 1.727 | 10 282 | 1.749 | 10 833 |
| ANO basis set (25 electrons correlated) ^a | | | | | | | | |
| $^2\Sigma_g^+$ | 1.740 | ... | 1.722 | ... | 1.722 | ... | 1.724 | ... |
| $^2\Pi_g$ | 1.747 | 4694 | 1.724 | 4185 | 1.721 | 3863 | 1.717 | 2518 |
| $^2\Delta_g$ | 1.766 | 9806 | 1.749 | 10 159 | 1.750 | 10 223 | 1.754 | 10 885 |
| $^2\Pi_u$ | 1.962 | 52 975 | 1.896 | 39 556 | 1.884 | 35 553 | 1.894 | 31 263 |
| $^2\Sigma_u^+$ | 1.962 | 53 310 | 1.898 | 40 675 | 1.889 | 36 910 | 1.903 | 34 030 |
| CuCl ₂ | | | | | | | | |
| Small basis set (21 electrons correlated) | | | | | | | | |
| $^2\Sigma_g^+$ | | | 2.135 | ... | 2.131 | ... | 2.130 | ... |
| $^2\Pi_g$ | | | 2.079 | 2605 | 2.071 | 2440 | 2.109 | 977 |
| $^2\Delta_g$ | | | 2.151 | 5835 | 2.149 | 6174 | 2.150 | 7272 |
| ANO basis set (25 electrons correlated) | | | | | | | | |
| $^2\Sigma_g^+$ | 2.139 | ... | 2.100 | ... | 2.095 | ... | 2.091 | ... |
| $^2\Pi_g$ | 2.137 | 2495 | 2.090 | 2116 | 2.081 | 1856 | 2.056 | - 659 |
| $^2\Delta_g$ | 2.145 | 5273 | 2.109 | 5772 | 2.106 | 6000 | 2.108 | 7432 |
| $^2\Pi_u$ | 2.300 | 33 282 | 2.205 | 20 551 | 2.189 | 17 648 | 2.194 | 15 776 |
| $^2\Sigma_u^+$ | 2.308 | 35 248 | 2.208 | 22 754 | 2.191 | 19 968 | 2.191 | 18 660 |

^a If the F s and p ANOs with the small natural orbital occupation number are deleted, and the most diffuse F s and p functions uncontracted, the CPF T_e values are changed by 11, 9, 108, and 87 cm⁻¹, respectively.

present results also lead to excitation energies in excellent agreement with experiment²²⁻²⁴—this is discussed in more detail below.

The inclusion of correlation also leads to a much improved description of the CT states: The separation with the ground state decreases by up to 20 000 cm⁻¹ and the bond lengths decrease by a significantly greater amount than for the valence states. Thus the CT states are affected much more by the inclusion of correlation than the valence states.

As shown in Table I, there are only modest changes in the results as the basis set is improved. The largest change in T_e is 1600 cm⁻¹ for the $^2\Pi_g$ state of CuCl₂ at the CPF level. Therefore we feel that the ANO T_e values are probably converged to better than 500 cm⁻¹. The effect of correlation on the $d-d$ transition energies is relatively small. The difference between the SDCI and CPF is significantly larger than the difference between the SDCI and SDCI + Q . This is not unexpected considering that we are correlating up to 25 electrons, and in this case the + Q correction is expected to significantly underestimate the effect of higher excitations.

Given the trends in the correlation treatment, we expect that our CPF computed separations are accurate to about 1000 cm⁻¹ and can therefore be used to aid in the interpretation of the experimental spectra.

The vibrational frequencies have been summarized in Table II. The three valence states have very similar frequencies at all levels of treatment for both CuF₂ and CuCl₂. The CT states also have similar frequencies, but these are significantly smaller than those of the valence states. In the small basis sets we lowered the symmetry to C_{2v} and used a finite difference approach to compute the asymmetric stretch and the bend, with the assumption of no coupling between the bend and bond stretches. We consider only the bending frequency of the $^2\Sigma_g^+$ state as Renner-Teller effects greatly complicate the calculation of the bending frequencies of the degenerate states. The stretches are computed by fitting nine points, from which the symmetric stretch agrees to within 20 cm⁻¹ of that computed using a fit in $1/r$ and only the symmetric distortions. For the $^2\Sigma_g^+$ and $^2\Delta_g$ states we are able to obtain a good fit for all levels of theory; however, for the $^2\Pi_g$

TABLE II. The ground-state vibrational frequencies, in cm^{-1} . The experimental values are given in parentheses.

| | Symmetric stretch | | | | Asymmetric stretch | | | Bend |
|---|-------------------|------|------------|-------------------------|--------------------|------------|--------------------------------------|-------------------------|
| | SCF | SDCI | SDCI + Q | CPF | SDCI | SDCI + Q | CPF | CPF |
| CuF_2 | | | | | | | | |
| Small basis set (21 electrons correlated) | | | | | | | | |
| $^2\Sigma_g^+$ | | 604 | 600 | 595 | 724 | 717 | 712 | 176 |
| $^2\Pi_g$ | | 589 | 583 | 580 | 742 | 734 | ... | |
| $^2\Delta_g$ | | 539 | 536 | 533 | 685 | 682 | 681 | |
| Big basis set (21 electrons correlated) | | | | | | | | |
| $^2\Sigma_g^+$ | | 636 | 631 | 624 | | | | |
| $^2\Pi_g$ | | 616 | 612 | 607 | | | | |
| $^2\Delta_g$ | | 615 | 612 | 608 | | | | |
| ANO basis set (25 electrons correlated) | | | | | | | | |
| $^2\Sigma_g^+$ | 634 | 633 | 629 | 619 | | | 740 ^a (765 ^b) | |
| $^2\Pi_g$ | 614 | 613 | 610 | 634 | | | | |
| $^2\Delta_g$ | 610 | 611 | 608 | 602 | | | | |
| $^2\Pi_u$ | 333 | 372 | 376 | 383 | | | | |
| $^2\Sigma_u^+$ | 319 | 355 | 358 | 359 | | | | |
| CuCl_2 | | | | | | | | |
| Small basis set (21 electrons correlated) | | | | | | | | |
| $^2\Sigma_g^+$ | | 366 | 365 | 360 | 516 | 512 | 503 | 101 (127 ^c) |
| $^2\Pi_g$ | | 355 | 350 | 354 | 504 | 511 | ... | |
| $^2\Delta_g$ | | 331 | 329 | 329 | 476 | 475 | 474 | |
| ANO basis set (25 electrons correlated) | | | | | | | | |
| $^2\Sigma_g^+$ | 364 | 365 | 364 | 357 (360 ^d) | | | 499 ^a (496 ^e) | |
| $^2\Pi_g$ | 354 | 335 | 366 | 358 | | | | |
| $^2\Delta_g$ | 340 | 356 | 355 | 352 | | | | |
| $^2\Pi_u$ | 219 | 244 | 266 | 265 | | | | |
| $^2\Sigma_u^+$ | 196 | 230 | 248 | 247 | | | | |

^a Obtained by scaling the symmetric stretch using the ratio of the symmetric to asymmetric stretch in the small basis.^b Reference 25.^c Reference 27.^d Reference 24.^e Reference 26.

state the fitting error in the CPF energies is very large. We therefore do not report the CPF results for this state. The fitting error is due to the fact that CPF is not invariant to orbital rotations, and for this state the difference in accuracy of the C_{2v} and D_{2h} geometries is sufficiently large that it is not possible to compute the asymmetric frequency. However, considering the small variation in the computed frequencies with level of treatment, we feel that the SDCI or SDCI + Q should be a good estimate for the $^2\Pi_g$ state. For the CT states, the loss of the inversion symmetry means that they are the second state of $^2\Pi$ or $^2\Sigma^+$ symmetry, and thus the CPF approach is not applicable. Further, the reduction in symmetry would lead to a very large calculation in the ANO basis set. However, the coupling between the Cu- X_a and Cu- X_b bond stretches is small, and therefore it is possible to obtain an estimate of the asymmetric frequency by either assuming that the coupling is zero, and using the symmetric stretch force constant to compute the asymmetric

stretch, or by scaling the symmetric stretch in the ANO basis set based on the asymmetric and symmetric stretch in the smaller basis set. For the $^2\Sigma_g^+$ state of $^{65}\text{CuF}_2$ scaling the ANO symmetry frequency based on the results in smaller basis yields a value of 740 cm^{-1} , while assuming no coupling of the stretches yields 784 cm^{-1} . Both values for the asymmetric stretch are in good agreement with the value of 765 cm^{-1} of Kasai, Whipple, and Weltner.²⁵ The symmetric stretching frequency for CuCl_2 of 358 cm^{-1} for the $^2\Pi_g$ state (or 357 for the $^2\Sigma_g^+$ state) is in excellent agreement with the experimental value reported by DeKock and Gruen.²³ Assuming no coupling of the stretches leads to estimates of asymmetric stretches of the CT states of about 450 and 360 cm^{-1} for CuF_2 and CuCl_2 , respectively.

Up to this point the effects of spin-orbit coupling have been neglected. However, especially for CuCl_2 , these effects can be substantial as the $^2\Sigma_g^+$ and $^2\Pi_g$ states are close in energy (calculated energy difference is 659 cm^{-1} at the CPF

TABLE III. Excitation energies and oscillator strengths for CuCl₂ including spin-orbit coupling.

| | <i>J</i> | SCF | SDCI | SDCI + <i>Q</i> | CPF | Expt ^a |
|--|----------|-------------------|-------------------|-------------------|-------------------|---------------------|
| The ligand field states ^b | | | | | | |
| " ² Π _g " | 1/2 | ... | ... | ... | ... | ... |
| ² Π _g | 3/2 | 2600 | 2279 | 2058 | 178 | |
| " ² Σ _g ⁺ " | 1/2 | 3447 | 3128 | 2921 | 1576 | |
| ² Δ _g | 5/2 | 4714 | 5243 | 5498 | 7514 | |
| ² Δ _g | 3/2 | 6948 | 7449 | 7692 | 9656 | 9000 ^c |
| CT states ^d | | | | | | |
| ² Π _u | 1/2, 3/2 | 33 551 (0.014) | 20 850 (0.005) | 17 974 (0.005) | 16 686 (0.012) | 19 000 ^e |
| ² Σ _u ⁺ | 1/2 | 35 517 (0.016) | 23 053 (0.010) | 20 294 (0.009) | 19 570 (0.005) | (0.014) |

^a Reference 22.^b The states are denoted from the CPF results. At other levels of theory the *J* = 1/2 states change character—see Table IV.^c The absorption band ranges from 6000 to 11 000 cm⁻¹ with a peak at 9000 cm⁻¹.^d Oscillator strengths for a transition from the computed ground state are given within parentheses. As discussed in the text, we feel that the observed absorption in the superposition of the ²Σ_u⁺ and ²Π_u states, and hence the sum of the values for the two upper states, should be compared to experiment.^e Broadband ranging from 14 000 cm⁻¹ to 22 000 cm⁻¹ with a peak at 19 000 cm⁻¹.

level). We use the same approximate treatment as in the earlier work on CuF₂,⁹ where the approximations are discussed in more detail and the relevant equations are given. The inclusion of the spin-orbit coupling leads to the state composition and energy separations given in Tables III and IV. Even after the inclusion of spin-orbit coupling we denote the states using *L-S* notation to simplify comparison with previous work. As noted above, we expect the CPF level of treatment to be the most reliable. However, due to the fact that the order of the two lowest states switches between the SDCI + *Q* and CPF treatments, we consider the effect of spin-orbit coupling on the wave functions at all levels of theory. Excluding the SCF, the resulting energies are in good agreement with the values observed in experiment.²²⁻²⁴ However, the composition of the wave functions are very different; at the CPF level the lowest state is dominated by the ²Π_g state, while at the other levels the lowest state is principally ²Σ_g⁺.

In order to further compare these values with experiment, the transition moments (TM) for the CT states were computed. The moments were obtained from SCF wave functions optimized for each state separately yielding the following results:

$$\langle {}^2\Pi_u | z | {}^2\Pi_g \rangle = 0.605,$$

$$\langle {}^2\Sigma_u^+ | \frac{x + iy}{\sqrt{2}} | {}^2\Pi_g \rangle = 0.181,$$

TABLE IV. Composition of the wave functions for the ligand field states including spin-orbit coupling.

| | |
|---------------------------|--|
| State 1 (<i>J</i> = 1/2) | |
| SCF | 0.96(² Σ _g ⁺) + 0.28(² Π _g) |
| SDCI | 0.95(² Σ _g ⁺) + 0.31(² Π _g) |
| SDCI + <i>Q</i> | 0.94(² Σ _g ⁺) + 0.33(² Π _g) |
| CPF | 0.65(² Σ _g ⁺) + 0.76(² Π _g) |
| State 2 (<i>J</i> = 3/2) | |
| SCF | 0.98(² Π _g) + 0.19(² Δ _g) |
| SDCI | 0.99(² Π _g) + 0.16(² Δ _g) |
| SDCI + <i>Q</i> | 0.99(² Π _g) + 0.15(² Δ _g) |
| CPF | 1.00(² Π _g) + 0.09(² Δ _g) |
| State 3 (<i>J</i> = 1/2) | |
| SCF | 0.28(² Σ _g ⁺) - 0.96(² Π _g) |
| SDCI | 0.31(² Σ _g ⁺) - 0.95(² Π _g) |
| SDCI + <i>Q</i> | 0.33(² Σ _g ⁺) - 0.94(² Π _g) |
| CPF | 0.76(² Σ _g ⁺) - 0.65(² Π _g) |
| State 4 (<i>J</i> = 5/2) | |
| All levels | ² Δ _g |
| State 5 (<i>J</i> = 3/2) | |
| SCF | 0.19(² Π _g) - 0.98(² Δ _g) |
| SDCI | 0.16(² Π _g) - 0.99(² Δ _g) |
| SDCI + <i>Q</i> | 0.15(² Π _g) - 0.99(² Δ _g) |
| CPF | 0.09(² Π _g) - 1.00(² Δ _g) |

$$\langle {}^2\Pi_u | \frac{x+iy}{\sqrt{2}} | {}^2\Sigma_g^+ \rangle = 0.203,$$

and

$$\langle {}^2\Sigma_u^+ | z | {}^2\Sigma_g^+ \rangle = 0.399.$$

The oscillator strength f is defined as

$$f = \frac{2}{g} \Delta E (\text{TM})^2,$$

where ΔE is the difference in energy between the two states and g is the statistical weight factor, which is one for all transitions except for $\Pi \leftarrow \Sigma$ where it is two. Using these SCF level transition moments and the CPF energy separations in Table I, the resulting f values are

$${}^2\Sigma_u^+ \leftarrow {}^2\Pi_g, \quad 0.0024;$$

$${}^2\Pi_u \leftarrow {}^2\Pi_g, \quad 0.0183;$$

$${}^2\Sigma_u^+ \leftarrow {}^2\Sigma_g^+, \quad 0.0090;$$

$${}^2\Pi_u \leftarrow {}^2\Sigma_g^+, \quad 0.0032.$$

These values are, however, modified by the spin-orbit coupling. For the wave functions and energy separations shown in Tables III and IV, we compute the oscillator strengths including spin-orbit coupling; these values are summarized in Table III. As discussed below, the two CT bands are overlapped and probably both contribute to the observed spectrum. If we sum over the two CT states, we find, excluding the SCF level, a total oscillator strength of from 0.015 to 0.017 for the CT band in CuCl_2 . This range of values is in good agreement with the experimental result of 0.014 reported by Hougen, Leroi, and James.²² Since the composition of the CPF and SDCI wave functions is very different, the value of the oscillator strength for the ${}^2\Pi_u$ and ${}^2\Sigma_u^+$ states is different. However, as the energy separations and total oscillator strength are similar for the CPF and SDCI wave functions, it is possible to use these calculations to interpret the available experimental data.

IV. DISCUSSION

The conclusion reached in the earlier study of CuF_2 (Ref. 9) was that the results for the $d-d$ transition energies were neither converged with respect to the AO basis set nor to the correlation contributions. The level of approximation used was comparable to the present small basis set SDCI + Q calculation. The conclusion is confirmed by the present result, especially the lower ${}^2\Pi_g \leftarrow {}^2\Sigma_g^+$ transition energy seems to be sensitive to the level of treatment where the large basis CPF result is 1400 cm^{-1} lower than the small basis set SDCI + Q value. It is unlikely that further extension of the basis set will lead to any large change of the present result. However, a refinement of the correlation treatment could result in modest changes in the computed separations.

One experimental study of the electronic spectrum of CuF_2 is known to us: Kasai, Whipple, and Weltner studied the gas-phase spectrum over a wide range of energies.²⁵ They found no bands in the region 11 000 to 30 000 cm^{-1} , and the infrared region between 5000 and 11 000 cm^{-1} was not

accessible. In the infrared region between 290 and 5000 cm^{-1} they found one strong doublet which they assigned to the asymmetric stretching mode of CuF_2 . The energy of 765 cm^{-1} for ${}^{65}\text{CuF}_2$ agrees very well with the present result of 740 cm^{-1} .

Kasai, Whipple, and Weltner concluded from their study that there are no electronic transitions between 290 and 30 000 cm^{-1} , except perhaps for the region between 5000 and 11 000 cm^{-1} . Since our T_e for the ${}^2\Delta_g$ states is slightly below 11 000 cm^{-1} , it is not surprising that it was not observed. However, our computed T_e for the ${}^2\Pi_g$ state, or the lowest $d-d$ transition in the present work, is found at 2500 cm^{-1} , which contradicts the conclusion of Kasai, Whipple, and Weltner. They estimated the energy to be 5200 cm^{-1} from their ESR results. This difference seems too large to be explained by the approximation inherent in the theoretical value, especially since an increasing level of accuracy leads to a lower excitation energy. The only possible explanation seems to be that this dipole-forbidden transition is too weak to be seen in an experiment of the type performed by Kasai, Whipple and Weltner. Clearly, a new experimental study in the region 2000–6000 cm^{-1} would be very desirable. The CT states are computed to lie above 30 000 cm^{-1} , which explains why they were not seen in the spectrum of Kasai, Whipple, and Weltner. We note, however, that they are around 10 000 cm^{-1} lower than the values obtained in the earlier, more approximate, study.⁹

The electronic spectrum of CuCl_2 has been studied in the gas phase by Hougen, Leroi, and James²² and also by DeKock and Gruen.²³ The latter authors also performed a matrix isolation study of CuCl_2 , which substantiated the earlier assignment of the CT band. The spectrum of DeKock and Gruen²³ contains two broad absorption bands with maxima at 9000 and 19 000 cm^{-1} , respectively. The intensity of the lower band is low with an f value of 1.8×10^{-3} , and it is assigned to a Laporte forbidden $d-d$ transition. It is clear from the present results that it corresponds to the transition to the ${}^2\Delta_g$ state. At the CPF level the calculated separations are 7500 cm^{-1} ($J = 5/2$) and 9700 cm^{-1} ($J = 3/2$) (cf. Table III). The experimental spectrum contains a vibronic structure with a separation of $360 \pm 15 \text{ cm}^{-1}$ which is assigned to the symmetric stretching mode of the ground state²³; this is in excellent agreement with the theoretical value of 357 cm^{-1} . In the upper part of the absorption band they find a progression with a spacing of 150–200 cm^{-1} which is assumed to be due to the difference between the antisymmetric stretching mode of the ground state and the symmetric stretch of the upper state. The present theoretical value for this difference is 147 cm^{-1} . Leroi *et al.*²⁶ have measured the IR spectrum of CuCl_2 and obtain a value of $496 \pm 20 \text{ cm}^{-1}$ for the asymmetric stretch in the ground state, again in excellent agreement with the predicted value of 499 cm^{-1} (cf. Table II). A Raman spectroscopic study of CuCl_2 has been performed by Dienstbach, Emmenegger, and Schl  pfer.²⁷ They arrived at a value of 373 cm^{-1} for the symmetric stretch mode, and 127 cm^{-1} for the bending frequency. The computed bending frequency of 101 cm^{-1} is in good agreement with the experimental value. The symmetric stretch frequency is also in good agreement with the comput-

ed value and, as noted above, that deduced from an analysis of the 9000 cm⁻¹ band.

DeKock and Gruen suggest that the lower *d-d* transition energy is to be found below the spectral range of their instrument, which is 4000 cm⁻¹. The present results are consistent with this suggestion, as the separation between the lowest three states is less than 3500 cm⁻¹ at all levels of theory. Thus, based on this and the agreement between theory and experiment for the band at about 9000 cm⁻¹, we conclude that the calculation of the *d-d* transition energies is in complete agreement with the available experimental data.

The absorption band with a peak at 19 000 cm⁻¹ (Ref. 23) is broad and asymmetric. Hougen, Leroi, and James²² give a slightly smaller value of 18 000 cm⁻¹ for the maximum. They assign this band to the *d-d* transition $^2\Delta_g \leftarrow ^2\Sigma_g^+$ (the lower energy band in their work is erroneously assigned as $^2\Pi_g \leftarrow ^2\Sigma_g^+$). The oscillator strength of the band at 19 000 cm⁻¹ is much larger [$f = 0.014$ (Ref. 22)] than the band at 9000 cm⁻¹, which is clearly a *d-d* transition. Therefore, DeKock and Gruen concluded that the assignment of the band at 19 000 cm⁻¹ to a *d-d* transition is doubtful, especially since they adopt the value of 0.8 for the oscillator strength (the present theoretical value is 0.017). The assignment suggested by them is instead the CT transition $^2\Pi_u \leftarrow ^2\Sigma_g^+$, while they assume that the $^2\Sigma_u^+ \leftarrow ^2\Sigma_g^+$ transition lies above 50 000 cm⁻¹.²⁴ The latter conclusion is inconsistent with the present calculations; both CT transitions occur in the same energy region (17 000 and 19 000 cm⁻¹) and probably both contribute to the asymmetric absorption band at 19 000 cm⁻¹.

V. CONCLUSIONS

The present investigation has used extended ANO-type basis sets in combination with size-consistent correlated wave functions to predict spectral properties of CuF₂ and CuCl₂. Both molecules are predicted to be linear in their ground state, and the calculated vibrational frequencies are in excellent agreement with the limited experimental information. Also, the calculated *d-d* and CT transition energies

are in accordance with measured absorption band maxima. It is desirable that the CuF₂ $^2\Pi_g \leftarrow ^2\Sigma_g^+$ excitation energy be determined directly by experiment as the computed value disagrees with that deduced from an ESR experiment.²⁵

The smaller basis set used here and in the earlier study of CuF₂ (Ref. 9) gives inferior results to the best results in the present study. While the results obtained in the best calculation agree very well with the available experimental results, the level of treatment required can hardly be used for larger transition-metal clusters. However, the situation may not be as discouraging as it initially appears. It is clear that a large basis set, including at least two *f*-type functions, has to be used for Cu in order to fully account for the important angular correlation effects in the 3*d*⁹ shell. It is also important to be able to treat the charge transfer of electrons to and from the ligands in a balanced way. This means that the basis set for the ligands must be chosen such that it reproduces properly the ionization potential and the electron affinity. To achieve this is probably less difficult in systems with more and larger ligands where a larger charge delocalization occurs. Therefore it might be feasible to devise calculations which would give equally accurate results as obtained here for larger transition-metal complexes. Further, if the basis sets are reduced in size, the vibrational frequencies and *d-d* transition energies are qualitatively correct, and therefore such calculations could be used to aid in the interpretation of experimental spectroscopic studies.

APPENDIX

The Cu basis sets are derived from the (20*s*12*p*9*d*) primitive set optimized by Partridge²⁸ for the $^2D(3d^9 4s^2)$ state of Cu. Three even tempered (α of 2.5 is used for all even-tempered functions in this work) *p* functions are added to describe the 4*p* orbital. An even tempered 3*d* function is added to describe the $^2S(3d^9 4s^1)$ state. A (6*f*4*g*) polarization set is also added: The most diffuse *f* and *g* exponents are 0.253 and 0.7589, respectively. The starting orbitals for the SDCI calculations are obtained from a state-averaged SCF

TABLE V. A comparison of the ANO sets with the uncontracted basis set; the ANO results are in parentheses (all values are in eV).

| | SCF | SDCI ^a | SDCI + <i>Q</i> | Expt |
|------------------------------|-----------------|-------------------|-----------------|--------------------|
| Cu ^b | | | | |
| Cu $^2S(3d^9 4s^1)$ | ... | ... | ... | |
| Cu $^2D(3d^9 4s^2)$ | 0.370 (0.369) | 1.620 (1.625) | 1.615 (1.614) | 1.49 ^c |
| Cu $^1S(3d^{10})$ | 6.408 (6.413) | 7.109 (7.086) | 7.271 (7.231) | 7.72 ^c |
| Cu $^3D(3d^9 4s^1)$ | 7.688 (7.693) | 9.954 (9.949) | 10.231 (10.214) | 10.53 ^c |
| Cu $^{2+2}D(3d^9)$ | 23.924 (23.930) | 26.924 (26.909) | 27.305 (27.274) | 28.01 ^c |
| F and Cl electron affinities | | | | |
| F | 1.357 (1.357) | 3.004 (2.960) | 3.191 (3.143) | 3.399 ^d |
| Cl | 2.581 (2.582) | 3.390 (3.308) | 3.498 (3.405) | 3.617 ^d |

^a For comparison the Cu separations in the big-segmented basis set are 1.607, 7.117, 9.970, and 26.996 eV, respectively. The F electron affinity is 2.938 eV.

^b In the basis set without the *g* functions.

^c C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circ. 467 (1949).

^d H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **14**, 731 (1985).

calculation involving the 2S and 2D states. The average natural orbitals for SDCI calculations for the 2S and 2D states are used for the $[6s5p4d2f1g]$ ANO contraction. The most diffuse s and p primitives are then uncontracted to improve the polarizability.²⁹ Note that because of the size of the basis set, the contraction is actually performed in two steps: the s - f functions are contracted first, then the g functions are contracted in a subsequent step. Table V compares the results in the uncontracted basis set with the ANO set. Clearly, the contraction has introduced virtually no error in the basis set.

The F primitive set is the $(13s8p)$ set of van Duijneveldt¹⁹ with a diffuse p function ($\alpha = 0.059\,326$) added to improve the description of F^- . A $(6d4f)$ polarization set is added; the exponents of the most diffuse functions are 0.16 and 0.49, respectively. For Cl we use the $(18s13p)$ set of Partridge³⁰ optimized for Cl. We add the diffuse s and p functions optimized by Partridge for Cl^- . A $(6d4f)$ polarization set is also added; the exponent of the most diffuse functions are 0.06 and 0.19, respectively. Separate SCF calculations are performed for F (Cl) and F^- (Cl^-). This is followed by SDCI for each state and the ANO contraction is based on the average natural orbitals of these SDCI calculations. The electron affinities of the contracted basis set is compared to the uncontracted results in Table V and the results are good. Thus, like Cu, the contraction is not introducing a large error in the one-particle basis set.

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