



ELSEVIER

Journal of Electron Spectroscopy and Related Phenomena 77 (1996) 143–148

JOURNAL OF
ELECTRON SPECTROSCOPY
and Related Phenomena

Hartree–Fock study on the lower excited states of a Cu^+ impurity in NaF using large embedded clusters

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Received 20 July 1995; accepted in revised form 26 September 1995

Abstract

We report spin-restricted and symmetry-restricted Hartree–Fock cluster calculations on the lower excited states of a Cu^+ impurity in NaF in order to investigate their dependence on cluster size. In contrast to previous work on smaller clusters, we found all states arising from the configurations $e_g^4 t_{2g}^5 a_{1g}^1$ and $e_g^3 t_{2g}^6 a_{1g}^1$ to be local. Delocalization can occur when an unbalanced choice of cluster and set of embedding point charges is made. These results confirm the local perspective from which previous spectroscopic assignments have been made. However, the inconsistency with the results from OD-EPR spectra remains.

Keywords: Cu^+ impurity; Delocalization; Embedded cluster; Hartree–Fock; NaF; OD-EPRS

1. Introduction

In the host crystal NaF, which has cubic NaCl crystal structure with O_h site symmetry, the impurity Cu^+ is thought to replace a Na^+ ion. From a local perspective, the lower excited states of the impurity can be thought of as being due to $\text{Cu}^+(3d^{10})$ to $\text{Cu}^+(3d^9 4s^1)$ transitions. In the clusters the 3d electrons of Cu occupy t_{2g} and e_g orbitals. Hence the possible excited states associated with these transitions are $^1,^3E_g$ and $^1,^3T_{2g}$.

Both experimental [1–6] and theoretical [7–10] studies have been performed on these excited states. Much of the experimental data was provided by McClure and co-workers [1,3–5], who studied these states using one- and two-photon

laser spectroscopy. They interpreted their results in terms of localized excitations. This contrasts with the experiments of van Tol et al. [6], who concluded from the width of their optically detected (OD)-EPR signals and from the absence of any appreciable hyperfine splitting that there is almost no Cu(4s) spin density in the luminescent state. Early theoretical work includes that of Winter et al. [10] and Meng et al. [9]. They used small embedded clusters, hence the states were restricted to be local. To study the possible delocalization, Broer et al. [7] performed restricted Hartree–Fock (RHF) calculations using the large $\text{CuF}_{14}\text{Na}_{18}$ embedded cluster. They found only the $^3T_{2g}$ state localized on Cu, whereas the $^1,^3E_g$ and $^1T_{2g}$ states were primarily centred around the outermost Na^+ ions.

In the present work we show that the choice to embed the $\text{CuF}_{14}\text{Na}_{18}$ cluster in point charges is

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not a balanced one. The six outermost Na^+ ions provide a means for the wave function to extend to the region occupied by the embedding point charges, resulting in a cluster artefact. When larger clusters are used the lower excited states are all localized on Cu.

2. Computational details

Spin-restricted and symmetry-restricted Hartree–Fock–Roothaan calculations were performed using the SYMOL package [11]. The geometries used are based on the experimental [12] nearest neighbour distances of 4.38 bohr for the pure NaF host. Four embedded clusters were used in the calculations. The largest cluster consists of a Cu^+ impurity in the centre surrounded by six shells of host ions, $\text{CuF}_{44}\text{Na}_{18}$. In Fig. 1 the $\text{CuF}_{44}\text{Na}_{18}$ cluster is shown. The other clusters are respectively one, two and three shells of host ions smaller: $\text{CuF}_{38}\text{Na}_{18}$, $\text{CuF}_{14}\text{Na}_{18}$ and $\text{CuF}_{14}\text{Na}_{12}$.

To include the effect of the crystalline environment a set of fitted point charges was used around the cluster. These point charges have been optimized [1] to reproduce the external Madelung

potential inside the $\text{CuF}_{14}\text{Na}_{18}$ cluster (the standard deviation is 1.14×10^{-3} and the maximum difference between the Madelung potential and the fitted potential is 8.97×10^{-3} a.u.). For the smallest cluster the six outermost Na^+ ions were replaced by +1 point charges. The point charges on the (0,1/2,1) lattice positions were replaced by F ions in the $\text{CuF}_{38}\text{Na}_{18}$ cluster. In the $\text{CuF}_{44}\text{Na}_{18}$ cluster the point charges on the (0,0,3/2) lattice positions were also replaced by F ions.

The primitive Gaussian basis set used for Cu was [15s,11p,6d], optimized by Wachters [13] for $\text{Cu}(^2\text{D})$. This basis was extended [7] with a diffuse d function, two diffuse p functions and an extra s function and subsequently reduced by general contraction to (6s,4p,3d). The basis set for F was [10s,7p], generally contracted to (3s,3p) for the first six F neighbours of Cu. This basis was optimized for F^- by Wachters and Nieuwpoort [14]. For the other F^- ions the basis was generally contracted to (1s,2p), yielding an effectively frozen description. The basis set for Na was [12s,6p] as optimized by Veillard [15]. This basis set was generally contracted to (4s,1p).

3. Results

Hartree–Fock–Roothaan calculations were performed on the lower excited states of Cu^+ -doped NaF using four large embedded clusters. If the smallest cluster $\text{CuF}_{14}\text{Na}_{12}$ already provides a reasonable description of the system, we expect the excitation energies and the character of the excited electron to change only slightly when the cluster size is enlarged. We shall see that this is indeed the case except for the singlet states in the $\text{CuF}_{14}\text{Na}_{18}$ cluster.

In Table 1 the calculated excitation energies (in cm^{-1}) are shown. The excitation energies change slightly, as expected, when different clusters are used. They become closer to the excitation energies deduced from optical spectra [2] when larger clusters are used, although they are still 20–25% smaller. This difference can be ascribed to differential electron correlation and relativistic effects. Comparable effects are also present in a free Cu^+ ion [16]: the difference in electron correlation

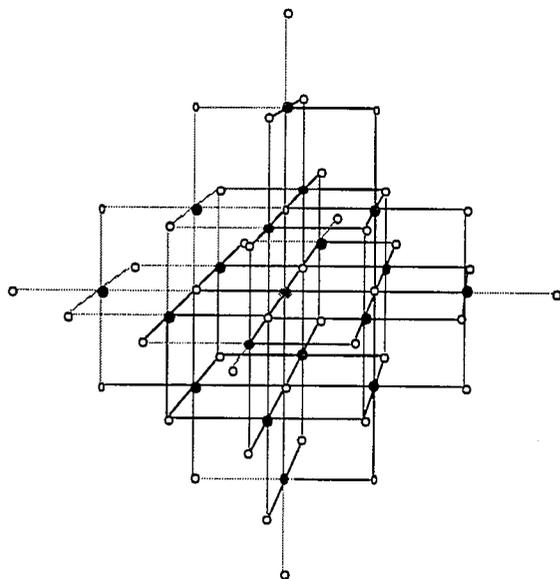


Fig. 1. Ball and stick representation of the $\text{CuF}_{44}\text{Na}_{18}$ cluster. Grey signifies Cu^+ , black Na^+ , and white F^- .

Table 1
Excitation energies in cm^{-1} relative to the 1A_g ground state

(a) First SCF solutions					
State	$\text{CuF}_{14}\text{Na}_{12}$	$\text{CuF}_{14}\text{Na}_{18}$	$\text{CuF}_{38}\text{Na}_{18}$	$\text{CuF}_{44}\text{Na}_{18}$	Berg and McClure ^a [1]
3E_g	22078	23228	23688	23670	30665
$^3T_{2g}$	24046	25241	25651	25636	33548
1E_g	24404	23625	26581	26521	32805
$^1T_{2g}$	26622	26013	28800	28742	36030
(b) Second SCF solutions					
State	$\text{CuF}_{14}\text{Na}_{12}$	$\text{CuF}_{14}\text{Na}_{18}$	$\text{CuF}_{38}\text{Na}_{18}$	$\text{CuF}_{44}\text{Na}_{18}$	
3E_g	33568	23311	31110	30585	
$^3T_{2g}$	35782	29527	33387	32850	
1E_g	34790	29128	32187	31750	
$^1T_{2g}$	37017	31361	34460	34016	
(c) Third SCF solutions					
State	$\text{CuF}_{14}\text{Na}_{12}$	$\text{CuF}_{14}\text{Na}_{18}$	$\text{CuF}_{38}\text{Na}_{18}$	$\text{CuF}_{44}\text{Na}_{18}$	
3E_g	74535	44599	50710	49756	
$^3T_{2g}$	76820	46992	53101	52153	
1E_g	75246	44742	50778	49828	
$^1T_{2g}$	77535	47137	53178	52227	

^a From one- and two-photon laser spectroscopy.

energy between the $3d^{10}$ ground state and the excited d^94s^1 states increases the excitation energy by ≈ 2 eV. This increase is partly counteracted by a smaller relativistic shift of about -0.5 eV. The trend that the calculated excitation energies get closer to values deduced from optical spectra when larger clusters are used is not followed by the singlet states in the $\text{CuF}_{14}\text{Na}_{18}$ cluster. These states lie lower in energy than in the smaller $\text{CuF}_{14}\text{Na}_{12}$ cluster. In the two largest clusters these excitations are raised in energy. On going from the small to the large clusters, better comparison with the values deduced from experiments is obtained. We shall see that the singlet states in the $\text{CuF}_{14}\text{Na}_{18}$ cluster are delocalized, in contrast to these states in the other clusters.

The ordering of the lower 1E_g and $^3T_{2g}$ states is dependent on the cluster size. In the $\text{CuF}_{14}\text{Na}_{18}$ clusters the 1E_g is lower in energy, in agreement with the ordering deduced by Berg and McClure [1]. In the other three clusters the $^3T_{2g}$ state is lower in energy, showing the same ordering of states as in previous theoretical work [9,10] on small clusters. The ordering of the states is influenced by the

crystal field splitting, which lowers the $^3T_{2g}$ and raises the 1E_g state in energy. In our clusters the crystal field splitting is such that minor changes of $\approx 170 \text{ cm}^{-1}$, which can arise when different clusters are chosen, lead to a change in ordering of the two states.

In contrast to the 3E_g state in the $\text{CuF}_{14}\text{Na}_{18}$ cluster previously reported by Broer et al. [7], we found a 3E_g state in this cluster that is 83 cm^{-1} lower in energy. As we shall see shortly this state is localized, whereas the state reached by Broer et al. is delocalized. As can be seen from Table 1, the second 3E_g SCF solution is lower in energy in the $\text{CuF}_{14}\text{Na}_{18}$ cluster than in the other clusters. All the second (third) SCF solutions in the other clusters are well separated from the first (first and second) SCF solutions. This again shows the $\text{CuF}_{14}\text{Na}_{18}$ cluster to be a special cluster.

To determine the character of each state we performed Mulliken population analyses. In Table 2 the gross population for the open a_{1g} orbital, which describes the excited electron, is shown. The third SCF solutions are all delocalized with most of the electron charge on the 12 Na^+

Table 2

Mulliken population analysis (MPA). The gross population of the open a_{1g} orbital is shown^a

(a) for the $\text{CuF}_{14}\text{Na}_{18}$ cluster												
Centre ^b	1st SCF solution				2nd SCF solution				3rd SCF solution			
	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$
Cu	1.09	1.10	0.91	0.92	0.43	0.41	0.56	0.55	0.08	0.08	0.05	0.05
$6F^c$	-0.21	-0.21	-0.19	-0.19	-0.01	-0.01	-0.04	-0.03	0.09	0.09	0.10	0.10
12Na	0.12	0.11	0.28	0.27	0.58	0.60	0.48	0.49	0.83	0.83	0.85	0.85
(b) for the $\text{CuF}_{14}\text{Na}_{18}$ cluster												
Centre ^b	1st SCF solution				2nd SCF solution				3rd SCF solution			
	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$
Cu	1.03	1.07	0.18	0.19	0.40	0.40	0.60	0.59	0.06	0.05	0.13	0.12
$6F^c$	-0.18	-0.18	-0.05	-0.05	-0.10	0.04	0.01	0.01	-0.04	-0.04	-0.05	-0.05
12Na	-0.04	-0.04	-0.12	-0.12	-0.13	0.15	0.21	0.20	1.37	1.39	1.25	1.26
6Na	0.19	0.15	0.99	0.99	0.83	0.41	0.19	0.19	-0.39	-0.4	-0.33	-0.33
(c) for the $\text{CuF}_{38}\text{Na}_{18}$ cluster												
Centre ^b	1st SCF solution				2nd SCF solution				3rd SCF solution			
	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$
Cu	1.15	1.16	1.08	1.08	0.26	0.24	0.42	0.40	0.00	0.00	0.04	0.03
$6F^c$	-0.18	-0.18	-0.19	-0.18	0.04	0.04	0.02	0.02	-0.03	-0.03	-0.04	-0.04
12Na	-0.02	-0.02	-0.02	-0.02	0.14	0.14	0.15	0.15	1.21	1.22	1.15	1.16
6Na	0.05	0.05	0.12	0.12	0.55	0.57	0.41	0.42	-0.18	-0.19	-0.15	-0.15
(d) for the $\text{CuF}_{44}\text{Na}_{18}$ cluster												
Centre ^b	1st SCF solution				2nd SCF solution				3rd SCF solution			
	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$
Cu	1.15	1.16	1.06	1.06	0.27	0.25	0.43	0.41	0.01	0.00	0.05	0.04
$6F^c$	-0.18	-0.18	-0.19	-0.18	0.04	0.04	0.02	0.02	-0.03	-0.03	-0.04	-0.04
12Na	-0.04	-0.04	-0.05	-0.05	0.10	0.09	0.13	0.13	1.34	1.35	1.27	1.28
6Na	0.06	0.06	0.17	0.17	0.59	0.61	0.42	0.43	-0.32	-0.32	-0.28	-0.29

^a The sum of the populations is 1.^b xA means centre A with x equivalent sites. The table shows the sum of the populations on these x sites.^c The populations on other F^- ions are negligibly small.

ions. The second SCF solutions are mixed in character, with most of the electron charge on Cu^+ and on the Na^+ ions. The first SCF solutions are localized on Cu except for the singlet states in the $\text{CuF}_{14}\text{Na}_{18}$ cluster. Note, however, that the second and third SCF solutions are not orthogonal to the lowest solutions, and that their character may change after orthogonalization.

To study further the effects arising in the $\text{CuF}_{14}\text{Na}_{18}$ cluster, we calculated the radial

distribution function for the excited electron in the 1E_g and 3E_g states. The radial distribution function can be calculated from the electron density function $\rho(r, \varphi, \phi)$ by integrating over the angular variables φ and ϕ . As can be seen from Fig. 2, the electron density in the clusters is more diffuse than that for the free Cu^+ ion. For the $\text{CuF}_{14}\text{Na}_{12}$ cluster the plot for the 1E_g state shows more delocalization than the plot for the 3E_g state. The same holds for the $\text{CuF}_{38}\text{Na}_{18}$ and

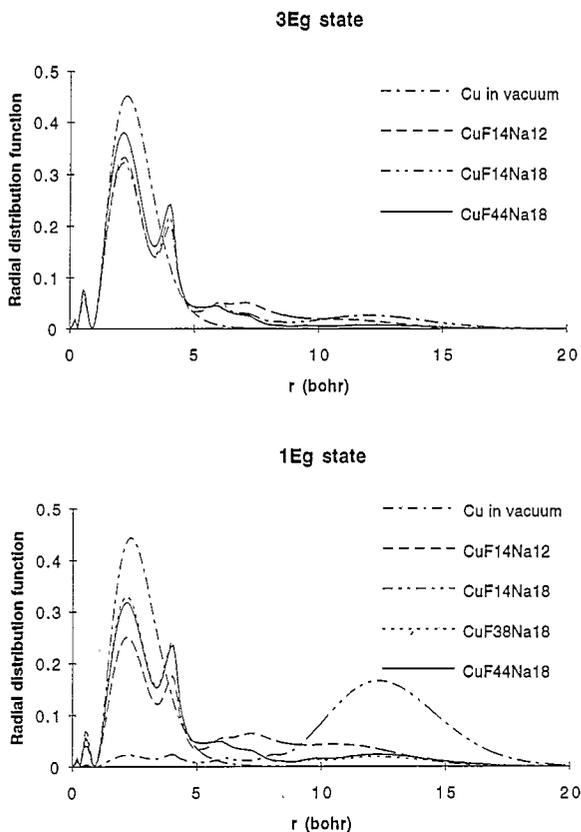


Fig. 2. Radial distribution function of the excited electron for the 1E_g and the 3E_g states. Note: the plots for the $\text{CuF}_{38}\text{Na}_{18}$ cluster and for the $\text{CuF}_{44}\text{Na}_{18}$ cluster coincide.

the $\text{CuF}_{44}\text{Na}_{18}$ cluster. Fig. 2 shows clearly that the 1E_g state is delocalized in the $\text{CuF}_{14}\text{Na}_{18}$ cluster, whereas the 3E_g state is localized. Similar results were obtained for the $^1T_{2g}$ and $^3T_{2g}$.

Because van Tol and Van der Waals [6] concluded that there is almost no spin density on Cu in the states on which they performed OD-EPR measurements, it is interesting to look at the spin densities on the Cu nucleus. Table 3 shows that the first SCF solutions, for all triplet states in all clusters, have a large spin density on Cu compared with the spin density on atomic Cu. The spin densities for the second and third SCF solutions are lower than those for the first SCF solution.

4. Discussion

At first sight it seems strange that artificial delocalization can occur in the $\text{CuF}_{14}\text{Na}_{18}$ cluster

Table 3

Density of the open a_{1g} orbital at the Cu nucleus

(a) 1st SCF solution				
Cluster	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$
Cu^+	6.50	6.50	5.82	5.82
$\text{CuF}_{14}\text{Na}_{12}$	5.10	5.20	3.51	3.56
$\text{CuF}_{14}\text{Na}_{18}$	5.03	5.32	0.30	0.33
$\text{CuF}_{38}\text{Na}_{18}$	6.01	6.06	4.77	4.77
$\text{CuF}_{44}\text{Na}_{18}$	5.97	6.02	4.59	4.60
(b) 2nd SCF solution				
Cluster	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$
$\text{CuF}_{14}\text{Na}_{12}$	2.06	1.98	2.34	2.30
$\text{CuF}_{14}\text{Na}_{18}$	1.27	2.84	3.57	3.52
$\text{CuF}_{38}\text{Na}_{18}$	1.69	1.58	2.27	2.20
$\text{CuF}_{44}\text{Na}_{18}$	1.84	1.73	2.44	2.37
(c) 3rd SCF solution				
Cluster	3E_g	$^3T_{2g}$	1E_g	$^1T_{2g}$
$\text{CuF}_{14}\text{Na}_{12}$	1.62	1.62	1.59	1.59
$\text{CuF}_{14}\text{Na}_{18}$	0.23	0.22	0.28	0.27
$\text{CuF}_{38}\text{Na}_{18}$	0.11	0.11	0.12	0.12
$\text{CuF}_{44}\text{Na}_{18}$	0.11	0.11	0.13	0.13

because the excited electron is repelled by the 24 embedding point charges, which are negative. To investigate this delocalization further, we calculated the radius of a sphere containing 90% of the excited electron in the 1E_g and 3E_g states for the three respective cluster sizes.

From Table 4 we see that in the clusters the excited electrons are more delocalized than in a free Cu^+ ion. In the $\text{CuF}_{14}\text{Na}_{12}$ cluster more than 10% of the electron is in the embedding region. When increasing this cluster to $\text{CuF}_{14}\text{Na}_{18}$ we replace six positive point charges by Na^+ ions with 3s basis functions, so that the wave function can now extend to this region. Fig. 2 and Table 4

Table 4

Radii (bohr) of spheres containing 90% of the excited electron

State	1E_g	3E_g
Cu^+	4.0	3.9
$\text{CuF}_{14}\text{Na}_{12}$	11.3	8.60
$\text{CuF}_{14}\text{Na}_{18}$	15.4	11.1
$\text{CuF}_{38}\text{Na}_{18}$	8.90	5.90
$\text{CuF}_{44}\text{Na}_{18}$	10.50	5.90

show that this indeed happens in the 1E_g state. When a more balanced cluster and set of embedding point charges is chosen by using larger clusters, the character of the states is local.

That the 1E_g state delocalizes in the $Cu_{14}Na_{18}$ cluster and that the 3E_g state does not is due to the difference in the way the exchange energy appears in the expression of the total energy. Minimizing the total energy favours a small open shell exchange interaction for the singlet state and a large open shell exchange interaction for the triplet state. Because the exchange interaction is smaller for delocalized states than for localized ones, the singlet state tends to delocalize more than the triplet state.

The results from the population analyses, the calculated radial distribution functions and the spin densities on Cu all show that the lowest lying states obtained are localized. When electron correlation and relativistic effects are included, the spectrum obtained by McClure and co-workers will be approached more closely. As the spin density on Cu in the luminescent 3E_g state should be easily detectable, it is unlikely that EPR occurs in this state. Instead, another metastable state may be involved that carries little or no spin density on Cu and undergoes radiationless decay into the 3E_g . The present results give us no clue as to the nature of this state, however.

5. Conclusions

The lowest excited states of a Cu^+ impurity in a NaF host are found to be localized within the RHF approximation. In the $CuF_{14}Na_{18}$ embedded cluster the singlet states are found to be delocalized, whereas the triplet states are localized. When a more balanced choice is made, by extending the cluster to $CuF_{38}Na_{18}$ or $CuF_{44}Na_{18}$, the four lower excited states are all localized on Cu.

Our findings are thus consistent with the assignments of the optical spectra given hitherto on the

basis of local “3d–4s” transitions. However, the discrepancy between this assignment and the OD-EPR results of van Tol et al. remains. This may indicate that another metastable state coupled to the luminescent state may be involved. The question of where the discrepancy originates cannot be answered from the outcome of the present study. To answer this question further work is necessary.

Acknowledgements

We thank Professors J.H. Van der Waals, Z. Barandiaran and L. Seijo for stimulating discussions.

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