Biochimica et Biophysica Acta, 722 (1983) 209–213
Elsevier Biomedical Press

BBA 41230

AB INITIO CALCULATIONS OF ELECTRON DISTRIBUTIONS IN HEME-CO MODELS

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(Received June 21st, 1982)

Key words: Heme; Carbon monoxide; Electron distribution; Redox potential; Heme protein

We have, by the use of ab initio calculations, found a back-bonding state of π symmetry close to the Fermi level for CO bound to FeN_5C_{14}. We thus find it likely that small shifts of the redox potential $|E_F - E_V|$ will cause relatively large changes of the CO vibrational frequency. The separation of Fe 3d orbitals in our heme model is found to agree with what is predicted by ligand field theory for O_h symmetry. This paper presents nonrelativistic Hartree-Fock-Slater calculations of the 5σ bonding and 2π back-bonding between CO and Fe. The effects of up to 19 additional atoms are discussed for models of heme (COFe to $COFeN_5C_{14}$). The filled back-bonding state is found to be strongly influenced by second nearest neighbor atoms. By use of symmetry orbitals we have resolved the Fe 3d orbitals into the T_{2g} and E_g representations of the O_h point group and find the former states to be occupied whereas the latter are unoccupied. The difference in occupancy is reduced when the CO ligand is removed which also causes an increased density of states at the Fermi level, i.e., the highest occupied and lowest unoccupied orbitals. Possible correlations between our data and experimental results are discussed for heme proteins as well as for metal surfaces.

Introduction

CO is extensively used as a probe of the reactivity of metal atoms in metalloproteins (see Ref. 1 and references therein) and on single crystal surfaces (see Ref. 2 and references therein). A common description of the interaction between the molecule and a metal atom with d electrons includes a bonding charge transfer from the primarily carbon 5σ orbital to the metal and a back-donation to the 2π orbital. More correctly, one should say that a new set of orbitals are formed, some of which are mixed with the unperturbed 2π wave functions. In surface studies, these new orbitals are denoted as a partly occupied resonance [3,4], since all sharp levels of the CO molecule are broadened by interaction with metal electron bands. The occupation of antibonding π orbitals will not only cause a reduction of the CO vibrational frequency but also an increased width at half height of the absorption band [5]. The latter effect, which is due to damped charge oscillations between a substrate and the adsorbed molecule, has been confirmed for CO adsorbed on a Cu single crystal surface [6]. Whether such an effect on the life-time of vibrations is present when the electron gas of a metal is replaced by delocalized states in large organic molecules is not known at present. However, a study of CO bound to heme in different proteins shows a strong correlation between redox potential ($E_{m,7}$), absorbtion band position (ν_{CO}) and half-band width ($\Delta\nu_{CO}$) [7]. Barlow et al. [7] found that an increased heme protein redox potential is correlated with an increased ν_{CO} and a decreased $\Delta\nu_{CO}$. We wish to study by means of quantum chemical calculations to what extent these data can be qualitatively understood as small changes of a back-bonding

0005-2728/83/0000–0000/$03.00

state close to the Fermi level (E_F). In solid-state terminology, the Fermi level is separated from the vacuum level by the work function, whereas in electrochemistry the redox potential, which is a macroscopic quantity referred to the hydrogen electrode, is given by the work function minus 4.48 eV. Effects of the surrounding protein and the solvent, which indeed do influence the redox potential, are neglected in these calculations.

Calculations

In the Hartree-Fock-Slater approximation the exchange terms of the Hartree-Fock equations are replaced by a local potential $V_X(r)$ [8]:

$$V_X(r) = -3\alpha\{(3/8)\pi(r)\}^{1/3}$$

where α, which represents the strength of this exchange potential, has been chosen equal to 0.70. The molecular wave functions are approximated by linear combinations of atomic orbitals and the integrals of the Hartree-Fock-Slater Hamiltonian are numerically evaluated by the discrete variational method [9]. Numerical atomic basis functions are generated in the Fe $3d^6 4s^2 4p^0$, O $2s^2 2p^4$, N $2s^2 2p^3$ and C $2s^2 2p^2$ configurations by an atomic Hartree-Fock-Slater program. The molecular potential is determined in the successive iterations from Mulliken gross orbital occupation numbers of these atomic basis functions [10,11]. Self-consistency is obtained when the input and output occupation numbers are equal, the self-consistent charge procedure [12]. We have applied this computational scheme (neglecting spin-orbit coupling) and our results are given as ground-state energies and partial densities of states for each symmetry and atomic orbital. It should be noted that these energies are not equivalent to other calculated or measured ionization potentials. Such energies, which have no ground-state properties, are calculated separately as transition-state energies in the Hartree-Fock-Slater scheme [8].

The geometry of the porphyrin skeleton was taken from Ref. 13 with the iron atom in the plane defined by the pyrrole nitrogens (Fig. 1). The CO molecule was fixed normal to the plane, since tilting or bending the CO has been stated not to affect the heme-CO energetics [14]. A Fe–C distance of 3.2 a.u. was taken from a total energy calculation of an Fe–C = O molecule [15]. Comparable structural parameters as determined by extended X-ray absorption fine structure measurements can be found in Ref, 16. previous calculations of porphyrin-like systems have also been performed by Goutermann [17], Loew and Kirchner [19], Johnson and Smith [20], Goddard and Olafson [21], and Case and Karplus [22]. The first two are done within the extended Hückel scheme whereas the latter three are ab initio calculations. Chemical analogies between enzymes and metal surfaces have been theoretically analyzed by Johnson [21].

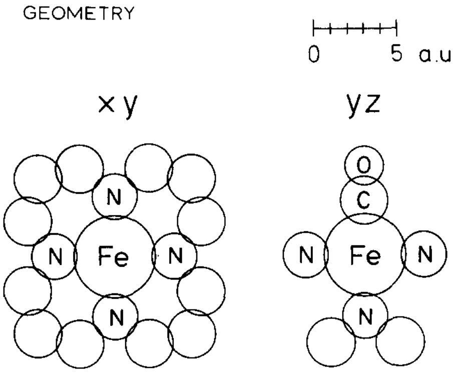

Fig. 1. Geometry of our calculated $COFeN_5C_{14}$ molecule for the *xy* amd *yz* planes. Blank circles indicate carbon atoms. The diameter of each circle is taken as the diameter of the neutral atoms. The D_{4h} symmetry of the naked porphyrin skeleton is reduced to C_{2v} when adding the NC_2 axial ligand.

Results and Discussion

Biochemistry has mapped the effects of equatorial substitutions in the heme group on specific biofunctions of heme proteins. It would be of interest to see to what extent such substitutions affect the electron distribution around the iron atom. For this purpose CO is a useful probe. The itinerant uncertainties with our present computational scheme are, however, too large to model small differences in the Fe-CO bond caused by these substitutions. For an analysis of the complete heme we have to replace the specially averaged potential by a multipolar one and preferably also design a scheme for the calculations of total energies.

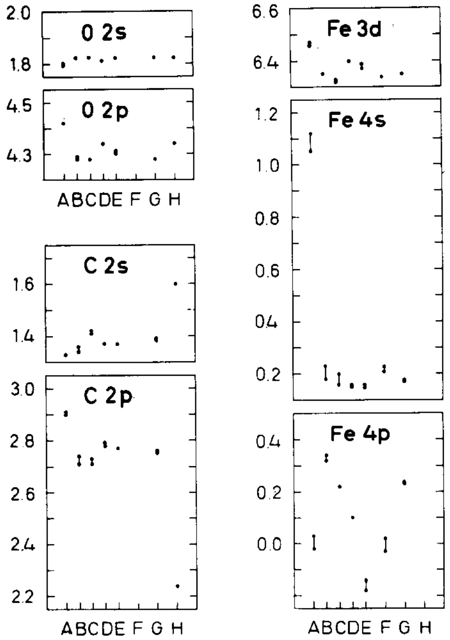

Fig. 2. Occupation numbers for Fe and the CO ligand as determined by Mulliken analysis for different computed molecules. The molecules are COFe (A), $COFeN_4$ (B), $COFeN_5$ (C), $COFeN_5C_{10}$ (D), $COFeN_5C_{14}$ (E), FeN_5C_{14} (F), $COFeN_4Cl$ (G) and free CO (H).

The present paper studies a sequence of models from Fe-CO to a chelate of Fe in an annular structure of 4 N and 12 C atoms with various additional ligands. Fig. 2 shows the converging occupation numbers of the atomic basis functions for different models from COFe to $COFeN_5C_{14}$. The latter includes a C_2N group as an approximate axial ligand. Error bars indicate incomplete convergence. The importance of the electronegativity of the nitrogen atoms and the oversimplification of the naked COFe model is clearly seen if we compare model A with B, C and G. In B we have added the four nitrogen atoms of the porphyrin, and in C and G the axial ligand is represented by a nitrogen or a chlorine atom. Two additional carbon atoms on each nitrogen (D) markedly changes the iron-carbon and carbon-oxygen bonding within each symmetry block provided there is no change of symmetry of highest occupied molecular orbital or lowest unoccupied molecular orbital. A decreased population of the carbon monoxide C 2s orbital and an increase in C 2p electron density are understood by the donation and back-donation of charge from the CO 5σ and 2π orbitals, respectively. If one assumes a linear relation between the CO force constants and the new electron population of C and O 2p orbitals, one could 'calculate' the CO vibrational frequency [24]. We find an energy of 2005 cm^{-1} for $COFeN_5C_{14}$ using the unperturbed value given by gas phase data as 2143 cm^{-1}. This compares well with 1986 cm^{-1} for CO one heme solvated in CCl_4 with an axial pyridine ligand [25]. It is fair to say that an increase in the total O 2p and C 2p occupation numbers is responsible for a decrease in ν_{CO}. Noteworthy is the strong coupling between the Fe 4p ($p\pi$) and the carbon (methyne) bridges between the pyrrole grous, i.e., the difference between $COFeN_5C_{10}$ (D) and $COFeN_5C_{14}$ (E). The possible effects exerted by the unpaired electrons of peripheral atoms are left as an itinerant uncertainty.

In Fig. 3 we compare the density of states for free CO, CO bound to FeN_5 and FeN_5C_{14}. The symmetry of each artificially broadened level is indicated. For free CO we have true σ and π symmetry ($C_{\infty v}$) whereas for $COFeN_5(C_{4v})$ 'σ' orbitals are represented by a_1(a) orbitals and 'π'

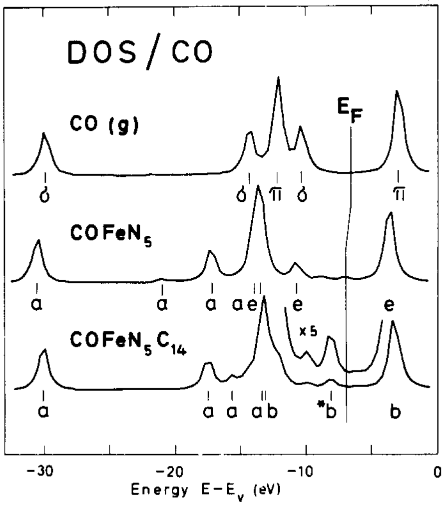

Fig. 3. Density of states (DOS) for CO in the gas phase, CO bound to FeN_5, and CO bound to FeN_5C_{14}. Each discrete level is replaced by a Lorentzian curve. The energy with respect to the vacuum level as well as the symmetry for each orbital is indicated in the figure. The σ orbitals of the free molecule are denoted as a (a_1) orbitals in the lower symmetries and the π orbitals as e or b (b_1/b_2). States with $E < E_F$ are occupied.

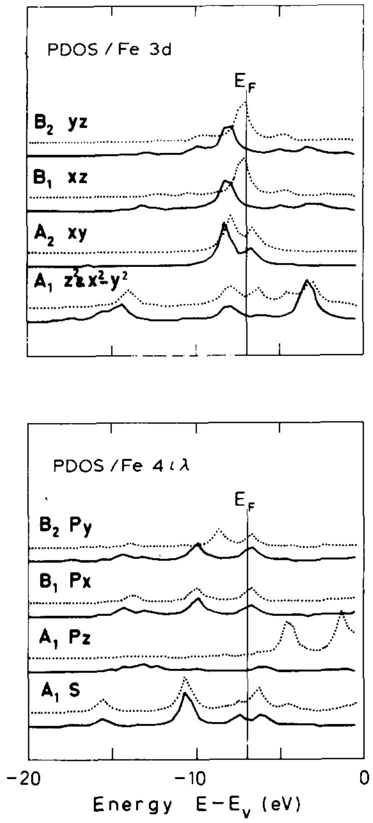

Fig. 4. Partial densities of states (PDOS) for different Fe 3d, 4s and 4p orbitals. The different symmetries and related orbitals are indicated for each curve. The dotted curve is for Fe in FeN_5C_{14} whereas the full line corresponds to $COFeN_5C_{14}$. The scale in the lower figure is enlarged by a factor of 5 compared to the upper one.

orbitals by two degenerate e orbitals. With the addition of the final 14 carbon atoms the symmetry is further reduced to C_{2v} (Fig. 1) and the e orbitals are split to b_1 and b_2 (together denoted as b). Note that the two 'pyridine' carbons reside in the plane defined by *yz* 'pyrrole' nitrogens.

The immediate results of a transition metal–CO bond is the energetic overlap of the 5σ and 1π orbitals and the existence of back-bonding states. We find such a π peak (b * in Fig. 3) between the main occupied peak and E_F (i.e., the mean energy of highest and lowest unoccupied molecular orbitals). If we integrate over b * we find that it consists of 0.35 O 2pπ electrons and 0.10 C 2pπ electrons. Since the total back-bonding charge transfer is 0.50 electrons, the b *, state is responsible for nearly all of the net π electron transfer. The dominant oxygen character implies a mixing with the CO 1π state, since 2/3 of the unperturbed CO 2π orbital stems from the carbon atom. The location of such an occupied state close to unoccupied ones indicates that small shifts of $|E_F - E_V|$, i.e., the redox potential, will cause relatively large differences in the back-bonding charge transfer thus directly affecting the CO vibrational frequency [7,26]. This could probably occur without much change of the total energy.

If we sum over the accupation numbers in Fig. 2 we find a net charge of + 1.4 for Fe in a singly ligated heme and + 1.6 when CO is present. These figures are compatible with the experimental observation that CO binds to Fe^{2+} and not to Fe^{3+}. To make a closer examination of the iron atom we have calculated the density of states for each orbital symmetry. These data are shown in Fig. 4 for FeN_5C_{14} (F in Fig. 2) and $COFeN_5C_{14}$ (E in Fig. 2). By the use of the orthogonality between different symmetries we have identified the b * peak in Fig. 3 as a mixed CO π–Fe 3dπ orbital. Another sensitive probe of the interaction between the Fe 3dπ and CO 2π orbitals is the absorption energy for the *z*-polarized Fe 3dπ $(b_1/b_2) \rightarrow$ CO 2π (b_1/b_2) excitation. Adar [18] reports that such excitations should give a strong band at 27000 cm^{-1} (3.3 eV) for FeCO whereas no such absorption is seen for carboxyhemoglobin for $h\nu < 40000$ cm^{-1} (5.0 eV). We calculate in the transition state approximation [8] the onset of these transitions to 3.5 eV for COFe versus 5.1 eV for $COFeN_5C_{14}$. This large difference is a result of interaction between the Fe 4pπ orbitals and the porphyrin model which changes the Fe-CO π-bond. Furthermore, we see that the Fe-CO σ-bond causes a complete redistribution of the $4p_z$ partial density of state (Fig. 4).

The Fe $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals transform according to the T_{2g} representation and $3d_z2$ and $3d_{x^2-y^2}$ according to E_g for the O_h point group. Even though we have spin-degenerate orbitals in this calculation our results are comparable to the ground-state $(t_{2g})^6$ configuration of Fe^{2+} in a strong ligand field [27]. When the CO molecule is removed, the iron density of states at the Fermi level is increased by a factor of 3. This increase in electron states generates the experimentally well known highly reactive singly ligated heme species; all reactive half-filled orbitals are located at E_F,

Acknowledgements

The calculations were performed at the Gothenburg University Computing Centre. The study was supported by the Swedish Natural Science Research Council (2560-106), the Swedish Medical Research Council (3X-6522) and Magn. Bergvalls stiftelse.

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