



FIG. 2. Magnitude of the Fourier transform of the EXAFS data from Fig. 1 for Cu etioporphyrin I. Also shown in the figure is a comparison of the peak position with the intramolecular distances calculated from Refs. 3 and 4. α is defined as $r_j - r'_j$, where r_j is the calculated distance based on the known structure^{4,5} and r'_j are the measured distances as shown in the figure.

consistent with ~ 0.31 Å shift to within $\sim 10\%$. The peaks at 1.66, 2.71, and 3.18 Å agree quite well with the calculated, Cu-N, Cu-pyrrole carbon, Cu-methine carbon distances, respectively, but the peak at 3.95 Å probably contains contributions from both the 4.25 and 4.47 Å Cu-C distances. We have tentatively identified the peak at 3.50 Å with an intermolecular Cu-C distance at ~ 4 Å, which would require a value of 0.5 for α . This is not an unreasonable result, because the planar symmetry of the structure may require two values of α ; one for distances in the plane of the molecule and one for intermolecular distances out of the plane. The peak at 4.53 Å can not be readily identified with any of the expected crystalline distances.

In conclusion, we have applied the EXAFS technique

to Cu etioporphyrin I in order to demonstrate the capability of this technique to determine the location of neighboring atoms around a particular kind of atom (e.g., Cu in this case) in many metalloproteins. This simple measurement easily identified at least 5 distances within 5 Å of the average Cu atom which could be correlated with the distances determined from the crystal structure. These distances were accurate within 2–3%, which is sufficient to study such important problems as the change in Fe atom location as a function of oxygenation in hemoglobin. As experience in analyzing EXAFS data in other complex systems is applied to these metalloproteins, it should be possible not only to refine the accuracy of the distance measurements but to determine information on the numbers and kinds of atoms at these distances as well.

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Electron excitation cross sections for neutral beryllium atoms

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The Born approximation has been used to calculate electron excitation cross sections for beryllium. We have used simple HSHFS wavefunctions¹ to describe the target atom and have calculated the cross section up to one-hundred threshold units of energy. An asymptotic form of the cross section was used to estimate oscillator strengths for the corresponding transitions.²

The atomic wavefunctions used in the calculations

were generated from a modified HSHFS program.³ The final state wavefunctions were found by solving the HFS equation for the final state in the self-consistent potential of the inert core corresponding to the initial state configuration, i.e., the one electron common central potential unrelaxed core approximation. The single particle wavefunctions have the form,

$$\phi_{nlm}(r) = R_{nl}(r) Y_{lm}(\Omega) = P_{nl}(r)/r Y_{lm}(\Omega),$$

TABLE I. Excitation cross sections.

<i>n</i>	$2s^2 - 2s2p$ $\epsilon = 5.28$ eV			$2s^2 - 2s3s$ $\epsilon = 6.78$ eV			$2s^2 - 2s3p$ $\epsilon = 7.19$ eV			$2s2p - 2s3s$ $\epsilon = 3.73$ eV			$2s2p - 2s4s$ $\epsilon = 2.81$ eV			$2s2p - 2s5s$ $\epsilon = 3.32$ eV			$2s2p - 2s4d$ $\epsilon = 3.25$ eV		
	<i>E</i> (eV)	σ	σ	<i>E</i> (eV)	σ	σ	<i>E</i> (eV)	σ	σ	<i>E</i> (eV)	σ	σ	<i>E</i> (eV)	σ	σ	<i>E</i> (eV)	σ	σ	<i>E</i> (eV)	σ	σ
1.05	0.554(1)	0.749(1)	0.712(1)	0.712(1)	0.374	0.755(1)	0.336	0.392(1)	0.176	0.295(1)	0.202	0.348(1)	0.521(-1)	0.341(1)	0.140	0.348(1)	0.521(-1)	0.341(1)	0.341(1)	0.341(1)	0.140
1.10	0.581(1)	0.101(2)	0.746(1)	0.746(1)	0.496	0.791(1)	0.429	0.410(1)	0.329	0.309(1)	0.282	0.365(1)	0.733(-1)	0.357(1)	0.179	0.365(1)	0.733(-1)	0.357(1)	0.357(1)	0.357(1)	0.179
1.20	0.634(1)	0.130(2)	0.814(1)	0.814(1)	0.620	0.863(1)	0.500	0.447(1)	0.627	0.337(1)	0.383	0.398(1)	0.102	0.390(1)	0.211	0.398(1)	0.102	0.390(1)	0.390(1)	0.390(1)	0.211
1.80	0.950(1)	0.169(2)	0.122(1)	0.122(1)	0.702	0.129(2)	0.438	0.671(1)	0.175(1)	0.506(1)	0.572	0.597(1)	0.154	0.585(1)	0.186	0.597(1)	0.154	0.585(1)	0.585(1)	0.585(1)	0.186
2.50	0.132(2)	0.162(2)	0.170(2)	0.170(2)	0.601	0.180(2)	0.327	0.932(1)	0.218(1)	0.702(1)	0.565	0.829(1)	0.151	0.812(1)	0.138	0.829(1)	0.151	0.812(1)	0.812(1)	0.812(1)	0.138
5.00	0.264(2)	0.120(2)	0.339(2)	0.339(2)	0.357	0.360(2)	0.165	0.186(2)	0.218(1)	0.140(2)	0.418	0.166(2)	0.110	0.162(2)	0.099(-1)	0.166(2)	0.110	0.162(2)	0.162(2)	0.162(2)	0.099(-1)
10.0	0.528(2)	0.791(1)	0.678(2)	0.678(2)	0.192	0.719(2)	0.826(-1)	0.373(2)	0.167(1)	0.281(2)	0.270	0.332(2)	0.700(-1)	0.325(2)	0.350(-1)	0.332(2)	0.700(-1)	0.325(2)	0.325(2)	0.325(2)	0.350(-1)
15.0	0.792(2)	0.600(1)	0.102(3)	0.102(3)	0.131	0.108(3)	0.552(-1)	0.559(2)	0.135(1)	0.421(2)	0.202	0.497(2)	0.522(-1)	0.487(2)	0.233(-1)	0.497(2)	0.522(-1)	0.487(2)	0.487(2)	0.487(2)	0.233(-1)
20.0	0.106(3)	0.489(1)	0.136(3)	0.136(3)	0.992(-1)	0.144(3)	0.415(-1)	0.746(2)	0.114(1)	0.562(2)	0.164	0.663(2)	0.421(-1)	0.650(2)	0.175(-1)	0.663(2)	0.421(-1)	0.650(2)	0.650(2)	0.650(2)	0.175(-1)
30.0	0.158(3)	0.363(1)	0.203(3)	0.203(3)	0.669(-1)	0.216(3)	0.278(-1)	0.112(3)	0.878	0.843(2)	0.120	0.995(2)	0.307(-1)	0.974(2)	0.117(-1)	0.995(2)	0.307(-1)	0.974(2)	0.974(2)	0.974(2)	0.117(-1)
50.0	0.264(3)	0.244(1)	0.339(3)	0.339(3)	0.405(-1)	0.360(3)	0.168(-1)	0.186(3)	0.617	0.140(3)	0.802(-1)	0.166(3)	0.205(-1)	0.162(3)	0.731(-2)	0.166(3)	0.205(-1)	0.162(3)	0.162(3)	0.162(3)	0.731(-2)
80.0	0.422(3)	0.168(1)	0.542(3)	0.542(3)	0.254(-1)	0.575(3)	0.106(-1)	0.298(3)	0.438	0.225(3)	0.548(-1)	0.265(3)	0.139(-1)	0.260(3)	0.579(-2)	0.265(3)	0.139(-1)	0.260(3)	0.260(3)	0.260(3)	0.579(-2)
100.0	0.528(3)	0.141(1)	0.678(3)	0.678(3)	0.204(-1)	0.719(3)	0.85(-2)	0.373(3)	0.370	0.281(3)	0.456(-1)	0.332(3)	0.116(-1)	0.325(3)	0.555(-2)	0.332(3)	0.116(-1)	0.325(3)	0.325(3)	0.325(3)	0.555(-2)

where $P_{nl}(r)$ is the numerically generated radial wavefunction and $Y_{lm}(\Omega)$ is a spherical harmonic.

Most standard quantum mechanics textbooks give an analytical expression for the Born amplitude and the Born cross section.⁴ Using single particle HSHFS wavefunctions the amplitude may be written,

$$f(K) = -\frac{2}{K^2} \int_0^\infty dr r^2 R_{n_f l_f}(r) R_{n_i l_i}(r) \times \int d\Omega Y_{l_f m_f}^*(\Omega) e^{i\mathbf{K} \cdot \mathbf{r}} Y_{l_i m_i}(\Omega), \quad (1)$$

and the total cross section

$$\sigma = \frac{2}{n\epsilon} \int_{K_-}^{K_+} |f(K)|^2 K dK, \quad (2)$$

where

$$K_{\pm} = (n\epsilon)^{1/2} [1 \pm (1 - 1/n)^{1/2}]. \quad (3)$$

In the above $\mathbf{K} = \mathbf{k}_i - \mathbf{k}_f$, $R(r)$ is the radial wavefunction, and $E = n\epsilon$, where E is energy of the incident electron in Rydbergs and ϵ is the threshold energy of the excitation in question. The total cross section is in units of πa_0^2 .

The asymptotic form of the Born cross section for optically allowed transitions may be written,²

$$\sigma E(eV) / \pi a_0^2 = 1704 [f/\epsilon(eV)] \log_{10} E(eV) + o(1/E), \quad (4)$$

where f is the oscillator strength. We used this expression to estimate the oscillator strengths from the calculated cross sections.

The angular integrations in Eq. (1) are trivial and the radial integrations can be numerically integrated. The results of the calculation for the excitations considered are presented in Table I. The oscillator strengths given by Eq. (4), as well as the threshold energies used in the calculations are given in Table II.

The cross sections presented in Table I are given down to $n = 1.05$, however, little credence should be placed in values below $n \sim 20$ because the Born approximation is a high energy approximation. Even at higher energies the data should be regarded with some degree of caution since we have used relatively simple wavefunctions (HSHFS) which do not include configuration mixing.

A comparison of our estimated oscillator strengths with those calculated using configuration interaction wavefunctions (CIW) shows that in the $2s^2 - 2s2p$ and $2s2p - 2s3s$ excitations the agreement is poor.^{5,6} Our $2s2p - 2s4s$ and $2s2p - 2s5s$ oscillator strengths compare favorably with those of Wiese.⁵

Ideally one would prefer to calculate differential and total excitation cross sections using the Glauber or full eikonal approximation⁷ with CIW's. From a practical point of view the computational time could be formidable if a number of excitations are calculated at various energies. Alternatives to the eikonal or Glauber approximations are the use of elaborate CIW with the Born approximation such as recently done by Robb⁸ for calcium and magnesium, or using relatively simple wave-

TABLE II. Threshold energies and oscillator strengths.^a

	$2s^2 - 2sp$	$2s^2 - 2s3s$	$2s^2 - 2s3p$	$2s2p - 2s3s$	$2s2p - 2s4s$	$2s2p - 2s5s$	$2s2p - 2s4d$
ϵ (eV)	5.28	6.78	7.19	3.73	2.81	3.32	3.25
ϵ_w (eV)	5.28			3.73	2.81	3.32	3.25
f	1.03			0.16	0.87(-2)	0.29(-2)	
f_w	1.36			0.34(-1)	0.87(-2)	0.27(-2)	0.84(-1)
f_{Hl}	1.42			0.268			
f_{Hv}	1.39			0.91(-1)			

^a ϵ (eV) = threshold energy, this paper. ϵ_w (eV) = threshold energy, Wiese (Ref. 5). f = oscillator strength, this paper. f_w = oscillator strength, Wiese (Ref. 5). f_{Hl} = oscillator strength (length), Hibbert (Ref. 6). f_{Hv} = oscillator strength (velocity), Hibbert (Ref. 6).

functions and the Born approximation. Although we feel the former alternative (Robb's) gives much more reliable results than the latter we feel the simple approach serves a useful purpose.

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ERRATA

Erratum: Molecular photodissociation [J. Chem. Phys. 60, 4760 (1974)]

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We have handled¹ the problem of interfragment coupling in molecular photofragmentation in terms of our intercontinuum coupling model. For the case of a collinear triatomic system consisting of a diatomic fragment BC and an atom A we have used the Hamiltonian²

$$H_{BO}^f = -\frac{1}{2m} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} y^2 + V(x-y), \quad (1)$$

where x and y are the reduced coordinates¹ [Eq. (III. 2)] and the reduced mass parameter¹ [Eq. (III. 3)]. Defining a new coordinate system³ $z = x - y$ and $y' = y$, Eq. (1) takes the form

$$H_{BO}^f = -\frac{1}{2} \left(1 + \frac{1}{m} \right) \frac{\partial^2}{\partial z^2} - \frac{1}{2} \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial y' \partial z} + \frac{1}{2} y'^2 + V(z). \quad (2)$$

In Ref. 1 we have used the following incorrect Hamiltonian:

$$H_{BO}^f = \frac{1}{2m} \frac{\partial^2}{\partial z^2} - \frac{1}{2} \left(1 + \frac{1}{m} \right) \frac{\partial^2}{\partial y' \partial z} + \frac{1}{2} y'^2 + V(z). \quad (III. 5)$$

Equations (2) and (III. 5) differ only in the numerical coefficients of the kinetic energy terms. Thus the formal treatment of the problem presented in Ref. 1 is correct. However, the perturbation term for the intercontinuum coupling is

$$V_f = \partial^2 / \partial y' \partial z. \quad (3)$$

The coupling parameter [Eq. (III. 18)] is now $\alpha_{11'} = C_{11'}/\sqrt{2}$ while the reduced intercontinuum coupling [Eq. (V. 4)] takes the form $\beta = -i\pi C\rho_{11'}/2$.

The isotope effect for molecular photofragmentation does not result from a m^{-1} term in β , as previously implied by us¹ and the prediction for DCN given in Fig. 19 is wrong. The isotope effect will originate from the dependence of $C_{11'}$ on m and requires an explicit evaluation