Table I. Determination of the Oxygen Proton Affinity of Phenol

Base	Proton affinity above that of ring protonated phenol (kcal/mol)[a]	Observation of BD^+?
HCO_2Et	3	Yes
HCO_2Me	7	Yes
MeCHO	9	Yes
CF_3CO_2Me	14	Yes
$CH_3CH{=}CH_2$	~15	Yes
HCN	20	No
CO	~56	No
CH_4	~73	No

[a] From ref 2, except: propene, unpublished; CO and CH_4, D. Holtz, J. L. Beauchamp, and S. S. Woodgate, *J. Am. Chem. Soc.*, **92**, 7484 (1970).

proximate enthalpy for protonation of phenol at oxygen. Our data are displayed in Table I. Reference bases methane, carbon monoxide, and hydrogen cyanide do not result in the formation of detectable amounts of BD^+. The proton affinity of HCN, the strongest of these bases, is some 20 kcal/mol below that of phenol (at carbon). On the other hand, deuterium incorporation into propene, methyl trifluoroacetate, acetaldehyde, and methyl- and ethylformates has been observed, implying that the base strengths of these compounds are greater than that of phenol at oxygen. The proton affinity of propene, the weakest of these bases, is about 15 kcal/mol below that of phenol. We conclude, therefore, that the oxygen proton affinity of phenol is some 13-20 kcal/mol less than the enthalpy for reaction on the ring, a value which is in good accord with our theoretical estimate (14.9 kcal/mol).

In aqueous solution protonation of phenol occurs predominantly on oxygen. In view of the present gas phase result regarding the sizable (~15 kcal/mol) preference for protonation on the aromatic ring, it is apparent that the solvent system is a major factor in determining the site of protonation.

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(11) This conclusion has also been reached by Beauchamp and co-workers[12] on the basis of deuterium exchange experiments and by Lau and Kebarle[9] by comparison of their experimental phenol proton affinity with a previously published theoretical value.[13] It is also consistent with the observation that the difference in proton affinities between anisole and phenol (4.8 ± 0.2 kcal/mol from our ICR measurements, see Scheme I, 4.5 kcal/mol from the high pressure mass spectrometry work of Lau and Kebarle[9]) is far smaller than that between typical aliphatic alcohols and the corresponding methyl ethers (7.9 kcal/mol for MeOH vs. $(Me)_2O$; 7.3 kcal/mol for EtOH vs. MeOEt[2]). It is, however, opposite to the conclusion reached by Martinsen and Butrill[14] as a result of their investigation of substituted benzene–water complexes in the gas phase.

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EXAFS: Approximation, Parameterization, and Chemical Transferability of Amplitude Functions

Sir:

Recently, extended x-ray absorption fine structure (EXAFS) spectroscopy using synchrotron radiation has gained wide recognition in providing valuable structural information for large and complex chemical or biological systems.[1-5] Major advances have been made in the understanding of the physics involved,[1,4a,6-10] which result in the improvement of the techniques of data analysis.[1,8-10] Until now, however, attention has been focused on the determination of interatomic distances via Fourier transform technique[1,8] or via curve fitting[9,10] based on the transferability of experimentally determined phase shifts. This article reports: (1) a simple analytical form for the amplitude function; (2) chemical transferability of amplitude functions; (3) the parameterization of theoretical[8b] amplitude curves; and (4) the utilization of these parameters in data analysis. The assumptions of both phase and amplitude function transferabilities in data analysis[1,8-10] greatly enhance the chemical content of EXAFS spectroscopy.

The normalized oscillatory part $\chi(k)$ of the absorption rate (μ) in EXAFS is given by[1,8]

$$\chi(k) = \frac{\mu - \mu_0}{\mu} = \frac{1}{k} \sum_i N_i F_i(k) e^{-2\sigma_i{}^2 k^2} \times \frac{\sin(2kr_i + \Phi_i(k))}{r_i{}^2} \qquad (1)$$

where $F_i(k)$ is the backscattering amplitude from each of the N_i neighboring atoms of the ith kind with a Debye–Waller factor σ_i (to account for thermal vibration and static disorder) and at a distance r_i away.[11] The phase shift $\Phi(k)$ has been parameterized with a quadratic function ($\Phi(k) = p_0 + p_1 k + p_2 k^2$) and shown to be chemically transferable for each pair of atoms by Citrin, Eisenberger, and Kincaid.[10] This allows accurate determination of interatomic distances for single-distance systems. For more complicated molecules with distances less than ca. 0.40 Å apart (which cannot be effectively separated by Fourier transform) more information on the amplitude function $F(k)$ is needed.

We find that, for all practical purposes, the amplitude function $F(k)$ for scatterers with atomic number $Z < 36$ can be approximated by a Lorentzian

$$F(k) = \frac{A}{1 + B^2(k - C)^2} \qquad (2)$$

where A is the peak height, $2/B$ is the width, and C is the peak position in k space. We note that a functional form of $F(k) = C/k^\beta$ ($\beta \approx 2$) has previously been utilized in fitting EXAFS spectra.[9] Our Lorentzian form, however, is preferred for

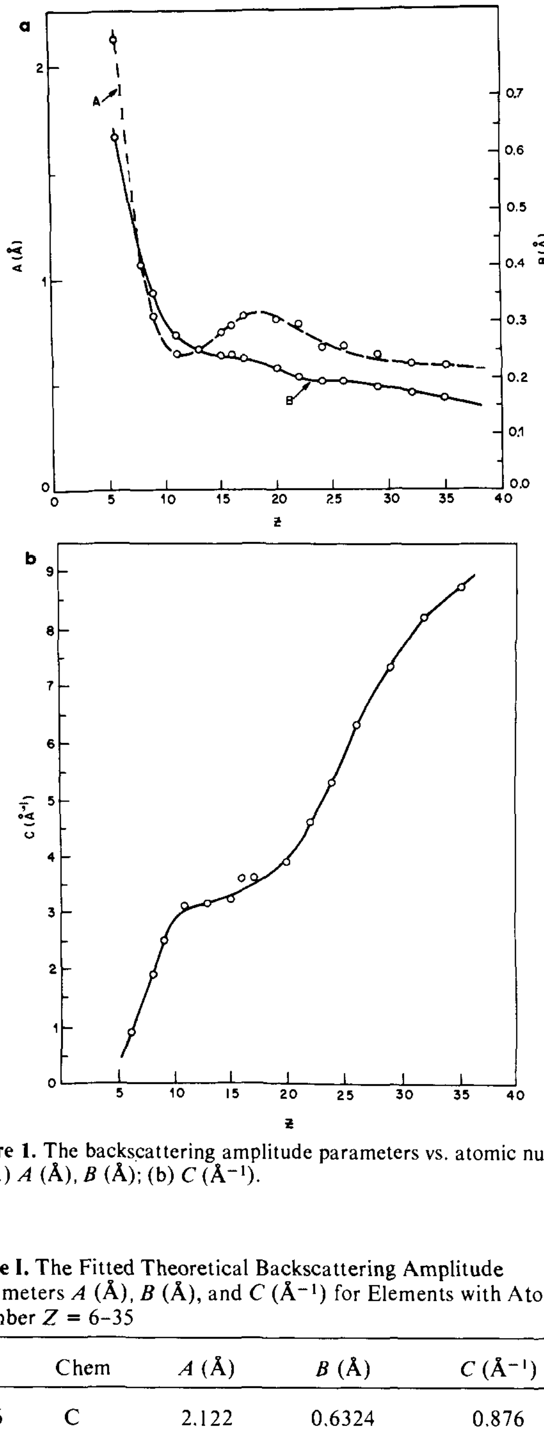

Figure 1. The backscattering amplitude parameters vs. atomic number Z: (a) A (Å), B (Å); (b) C (Å^{-1}).

Table I. The Fitted Theoretical Backscattering Amplitude Parameters A (Å), B (Å), and C (Å^{-1}) for Elements with Atomic Number Z = 6-35

Z	Chem	A (Å)	B (Å)	C (Å^{-1})
6	C	2.122	0.6324	0.876
8	O	1.079	0.4096	1.898
9	F	0.856	0.3533	2.499
11	Na	0.652	0.2788	3.150
13	Al	0.666	0.2505	3.194
15	P	0.747	0.2402	3.258
16	S	0.779	0.2439	3.644
17	Cl	0.822	0.2381	3.625
20	Ca	0.797	0.2158	3.943
22	Ti	0.783	0.2063	4.616
24	Cr	0.737	0.1952	5.320
26	Fe	0.679	0.1939	6.355
29	Cu	0.641	0.1842	7.382
32	Ge	0.601	0.1716	8.230
35	Br	0.590	0.1617	8.764

scatterers with $Z < 36$ in that it describes nicely the characteristic maxima of experimental amplitude curves.[1-10] At high enough energy ($k \gg C$), it reduces to the well-known Born approximation of scattering amplitude for fast electrons scattered elastically by a spherically symmetrical atom.

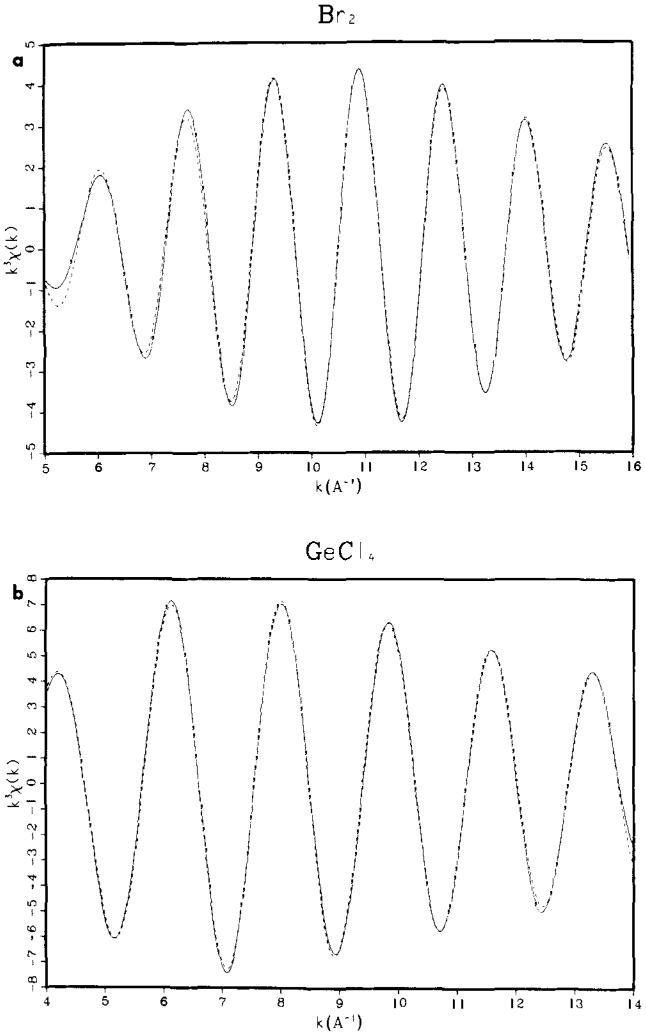

Figure 2. Comparison of theory (dashed curves) with experimental EXAFS spectra (solid curves) for: (a) Br_2 (ref 4a, 10); (b) $GeCl_4$ (ref 4a). Both theory (eq 1) and experiment have been multiplied by k^3 to compensate for amplitude reduction. Least-squares refined overall scale factors of 0.66 and 0.41 have been included in Figures 2a and 2b, respectively, to bring the theoretical A values into agreement with the experiment.[13b]

Experimentally these amplitude parameters can be extracted (via fitting) from EXAFS spectra of single-distance models with known Debye-Waller factors and then transferred to multiatom multidistance unknown systems. For example, by varying $F(k)$ and $\Phi(k)$ while holding σ and r fixed at their reported values of 0.045, 0.050 (2) Å and 2.283 (5), and 2.277 (3) Å for Br_2[4a] and $GeBr_2H_2$,[12,19a] respectively, the least-squares refined A (Å), B (Å), C (Å^{-1}) values for the scatterer Br are 0.36, 0.181, 8.57 in Br_2 and 0.45, 0.174, 8.25 in $GeBr_2H_2$.[13a] The parameters B and C are clearly transferable from Br_2 to $GeBr_2H_2$. They also agree well with the corresponding theoretical values of 0.162 Å and 8.76 Å^{-1} (cf. Table I, vide infra). If we use the experimental A, B, and C values extracted from Br_2 for $GeBr_2H_2$, we obtain a σ of 0.052 (8) Å which agrees with the known value of 0.050 (2) Å. In practice, however, Debye-Waller factors are often unknown and attempts to simultaneously obtain amplitude function and Debye-Waller factor from experiment have often been found to lead to unreasonable parameters.

Theoretically, the amplitude functions can be calculated from first principle. Using the theory recently developed by Lee and Beni,[8b] the amplitude functions for 15 elements with Z = 6-35 have been calculated and fitted with eq 2.[14] The resulting parameters are plotted vs. Z in Figure 1 and tabulated in Table I. It is obvious that these parameters vary smoothly as a function of Z, thereby allowing the intermediate elements to be interpolated. Two important chemical trends readily emerge: the inverse of the width (B) generally decreases whereas the peak position (C) generally increases with increasing atomic number Z. It is apparent that these two slowly varying parameters (as a function of Z) can be used for chemical identification in complex or unknown systems. Examples include the differentiation of metal-metal from metal-ligand (lighter atom) bonds in polymer,[15] biological,[16] or metal cluster[17] systems. Due to effects not accounted for in the theory,[8b] parameter A requires an additional scale factor in the fitting of the EXAFS spectra.[13b] However, in cases involving direct bonding it is possible to use the relative values of A to infer the relative number of neighboring atoms (coordination numbers, N_j) and hence to differentiate plausible structures.[15-17] Another important utility of these theoretical parameters is the estimation of Debye-Waller factors which is difficult, if not impossible, to extract from experimental EXAFS data alone (vide supra).[20]

Using these amplitude parameters, along with the parameterized theoretical phase shifts,[21] we have fitted a number of known systems. Figures 2a and b show the least-squares fit (dashed curves) to the EXAFS (full curves) spectra of Br_2 and $GeCl_4$, respectively.[4a,10] It is evident that the agreements between theoretical and experimental amplitudes (vide supra) are fairly good. Experimentally, the $\chi(k)k^3$ data peak at ca. 10.9 and 7.1 $Å^{-1}$ in Br_2 and $GeCl_4$, respectively. In the absence of Debye-Waller factor, our amplitude function multiplied by k^2 (viz., $F(k)k^2$) peaks at 13.1 and 8.5 $Å^{-1}$ for scatterer Br and Cl, respectively.[18] A Debye-Waller factor of 0.050 (6) Å in Br_2 and 0.043 (6) Å in $GeCl_4$ is found by least-squares refinement to lower the peak position to the observed values (cf. Figure 2). These are in good agreement with the reported value of 0.045 Å for both compounds.[4a,19b]

Finally, it should be emphasized that amplitude functions (and hence our parameters A, B, and C) depend upon the backscatterer only, unlike phase shifts which depend on both the absorber and the backscatterer. We believe the transferability of amplitude functions can be used to provide valuable chemical (coordination numbers and Debye-Waller factors) as well as structural (interatomic distances) information in EXAFS spectroscopy.[20]

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(13) (a) The EXAFS spectra were "approximately" normalized with Victoreen's true absorption coefficient $\mu_0/\rho = C\lambda^3 - D\lambda^4$ ("International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, pp 161, 171). This partly explains why A is not in as good agreement as B and C. (b) The theoretical A value, which includes inelastic processes in the scattering atom is found to be off by ~50%. Part of this discrepancy is due to core relaxation effects.[8b] Furthermore, the absolute value of A is expected to be somewhat sensitive to the chemical environment and will depend on the distance r_i (an exponential damping factor $e^{-2\gamma r_i}$ is usually added to eq 1). An overall scale factor (e.g., 0.66 in Br_2 and 0.41 in $GeCl_4$) is therefore included in the refinements.
(14) (a) To compensate for amplitude reduction, the actual theoretical amplitude functions were multiplied by k^2 and then fitted with $F(k)k^2 = Ak^2/(1 + B^2(k - C)^2)$. This procedure corresponds to fitting the experimental $\chi(k)k^3$ data with both sides of eq 1 multiplied by k^3. (b) We note that the theory is less reliable for energy below 60 eV ($k \lesssim 4$ $Å^{-1}$) due to the inadequate treatment of valence electrons. This problem is particularly serious for light atoms ($Z < 9$) where the peak at $k \lesssim 2$ $Å^{-1}$ should be treated with caution.
(15) J. Reed, P. Eisenberger, B. K. Teo, and B. M. Kincaid, submitted for publication.
(16) R. G. Shulman, B. K. Teo, P. Eisenberger, G. S. Brown and B. M. Kincaid, to be submitted for publication.
(17) B. K. Teo, P. Eisenberger, J. D. Sinclair, and B. M. Kincaid, to be submitted for publication.
(18) Note that $F(k) = A/(1 + B^2(k - C)^2)$ peaks at C whereas $F(k)k^2 = Ak^2/(1 + B^2(k - C)^2)$ peaks at $C + 1/(B^2C)$.
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(20) It should be cautioned that there are two sets of highly correlated variables in fitting EXAFS spectra: $\{\Phi(k), E_0, r\}$ and $\{F(k), \sigma, N\}$. For example, the amplitude parameters A and B correlate strongly with N and σ, respectively. Our theoretical functions eliminate the danger of false minima due to uncertainties in phase and amplitude.
(21) P. A. Lee, B. K. Teo, and A. L. Simons, *J. Am. Chem. Soc.*, following paper in this issue.

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EXAFS: a New Parameterization of Phase Shifts[1]

Sir:

Extended x-ray absorption fine structure (EXAFS) spectroscopy has become an important structural tool for complex systems in recent years.[2-10] There are two major approaches in data analysis: the Fourier transform[2,3,9] and the least-squares fitting[4-6] techniques. Both of these methods require a detailed knowledge of the phase function[2,5] $\phi(k)$ (cf. eq 1 of preceding article). If we have an absorbing atom A and a backscattering atom B, the phase function ϕ_{ab} is given by

$$\phi_{ab}(k) = \phi_a(k) + \phi_b(k) - \pi \qquad (1)$$

where $\phi_a = 2\delta_1'$ is the $l = 1$ (for K and L_I edges) phase shift of the central atom and ϕ_b is the phase of the backscattering amplitude.[9] The factor of π is required (as a matter of convention) to make the amplitude function $F(k)$ positive. Citrin, Eisenberger, and Kincaid[5] have parameterized experimental phase shifts by a quadratic function in k. They also demonstrated that phase shifts are transferable from one chemical system to another, thereby enabling accurate determination of interatomic distances in unknown systems based on known distances of model compounds.[5] Unlike the backscattering amplitude[1] which is a function of the scatterer[9] only, the phase shift depends upon both the absorber (central atom) and the backscatterer (neighboring atom).[9] Thus, while phase shifts can be deduced empirically from model compounds with known distances,[2,5] it is only possible to determine the combination $\phi_{ab}(k)$ for each atom-pair A-B and not the two contributions ϕ_a and ϕ_b separately. To avoid the trouble of searching for model compounds in each EXAFS problem, it