Oxygen K-edge extended x-ray-absorption fine-structure studies of molecules containing oxygen and carbon atoms

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The absorption spectra of a group of selected molecules containing O—C bonds, carbon monoxide, carbon dioxide, carbonyl sulfide, acetone, ethanol, diethylether, tetrahydrofuran, and dioxane, have been recorded in a transmission mode in the energy region from 500 to 1000 eV. Earlier observation of extended x-ray-absorption fine structure (EXAFS) in some of these molecules is confirmed. A systematic analysis of the EXAFS spectra is performed. The results in both phase and amplitude show disagreement with the single-electron single-scattering theory with plane-wave approximation. The measured phase is systematically lower than the theory of Teo and Lee [J. Am. Chem. Soc. 101, 2815 (1979)] by about 0.7-1.5 rad, which may be significant in determining interatomic distances. The EXAFS amplitude function in the molecules containing oxygen-carbon single bonds also shows an appreciable deviation (decrease) in the first-neighbor backscattering at high-k values.

I. INTRODUCTION

Extended x-ray-absorption fine structure (EXAFS) refers to the small amplitude oscillations of the absorption coefficient starting from a few tens of eV above an absorption edge. It is due to the modification of the outgoing electron waves by the neighboring atoms in the photoionization process. The phenomenon is used extensively as a structural tool, and is particularly suitable for the study of the local atomic environment.^{1,2}

In the presence of EXAFS, the absorption cross section for the photoexcitation of an electron from the K shell of an atomic species in a material can be written as

$$\mu(E) = \mu_B + \mu_0(E) [1 + \chi(k)] , \qquad (1)$$

where μ_0 is the smooth atomiclike absorption coefficient for the particular core level of interest in the study, μ_B the background absorption coefficient which represents the contribution of electrons from other levels to the photoabsorption process, and $k = \sqrt{2m(E - E_0)}/\hbar$ the photoelectron momentum. The EXAFS function $\chi(k)$ is determined by the coordination number N of the neighboring atoms at distance R, their backscattering amplitude F(k), and the energy-dependent contribution to the phase shift $\phi(k)$ due to the atomic potentials of both excited and scattering atoms. In a randomly oriented local environment, the EXAFS at the oxygen K edge can be written as²

$$\chi(E) = \sum_{j} \frac{N_{j}}{kR_{j}^{2}} F_{j}(k) e^{-2k^{2}\sigma_{j}^{2} - 2R_{j}/\lambda} \sin[2kR_{j} + \phi_{j}(k)] , \qquad (2)$$

where the subscript j denotes various neighboring atomic shells in the material. The phase shift can be expressed in the form³

$$\phi(k) = a_0 + 2a_1k + \phi^{(R)}(k) , \qquad (3)$$

where $\phi^{(R)}(k)$ is a small nonlinear term in most cases.

In practice, different methods are used in the determination of the interatomic distances R. In a simple method the derivative of $\phi_j(k)/2$, a_1 , is subtracted from the *j*th peak position of the Fourier transform amplitude of $\chi(k)$ to obtain the distance R_j . In a widely used method,² the total phase function of the *j*th shell, $\Phi_j = 2kR_j + \phi_j$, is first derived from "filtering" and backtransforming the corresponding peak in the Fourier transformed $\chi(k)$. After subtracting the known phase shift $\phi_j(k)$ from it, the "corrected" phase $\Theta(k) = [\Phi(k) - \phi(k)]/2$ is fitted with a straight line. The slope of the resulting line is taken as the interatomic distance.

With both methods the accurate knowledge of the phase shift is crucial for the determination of the distance. In the second method, for example, the error in the phase shift, $\delta\phi(k)$, leads to an error in the derived distance

$$\delta R \simeq -\delta \phi(k_0)/2k_0 , \qquad (4)$$

where k_0 is approximately the centroid of the data section (Appendix A).

Numerous works, both theoretical³⁻¹⁰ and experimental¹¹⁻¹⁵ have addressed the phase problem. Early experimental work on empirical phase shifts of molecular systems¹¹ showed that the phase function is transferable to within 0.5 rad, which corresponds to $\Delta R \simeq 0.01$ Å. Cal-

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culations have also been made on the basis of different models. The most notable set of results is by Teo and Lee⁶ (henceforth denoted as TL). The authors used electron-atom scattering theory with a momentumdependent complex potential which adequately accounted for the exchange and correlation effects caused by the electrons in the atom. The data set has been tested in many experiments, generally with favorable results. An important assumption made in the calculation is the validity of the plane-wave approximation or equivalently the small-atom approximation. This has been questioned both from the theoretical $^{7-10}$ and the experimental 15 point of view. Pettifer showed⁹ that the data set should not be used for Z > 52 or for photoelectron energy less than 200 eV. From their detailed studies of Cu and Pt, Stern *et al.*¹⁵ concluded similarly that the data set is applicable only for k > 10 Å⁻¹. In systems involving small, low-Z central atoms, interatomic distances are particularly short and the curvature of the electron wave may once again modify the phase and amplitude significantly.

The early spherical-wave calculation proposed by Lee and Pendry⁷ was mathematically complex and computationally time-consuming. In recent years a more efficient algorithm has been developed.¹⁰ It is expected that a usable data base will be available in the near future.¹⁶ It will be of special interest to compare the results of these new calculations with the experimental data for low-Z atoms.

Chemical transferability of the phase and amplitude is also challenged in the case of low-Z scattering atoms. Here an often neglected phenomenon, the polarization of the electron distribution in the chemical environment, is particularly important. For the second-row elements, the majority of the electrons (2s and 2p) are involved in the chemical bonds or affected by it. For example, among six electrons of the carbon atom, four of them redistribute as the atom forms bond with other atoms. The distribution depends on the molecular orbitals (s, p, p)or hybridized orbitals sp^2 and sp^3). This change in charge distribution will certainly bring about a change in the molecular potential. And this in turn changes scattering phase and amplitude, particularly for lowenergy photoelectrons. In fact, the TL calculation already showed significant changes in these quantities with comparable potentials. An oxygen atom bonded to the carbon atom in a particular direction will see the asymmetry in the electron distribution in carbon. In oxygen K-edge EXAFS studies, this molecular effect manifests itself in the scattering phase and amplitude. A systematic study of the phase and amplitude in different chemical environments should shed light on this problem.

Adjusting the threshold energy E_0 to fit the phase function is common practice in EXAFS analysis. Following TL the experimental phase shift may be defined as

$$\phi(k) = \Phi(k) - 2kR \quad . \tag{5}$$

The longer the interatomic distance (R) the more sensi-

tive the phase shift to the change of E_0 , since E_0 affects the scale of k. In other words, molecules with shorter bonds give a more stringent test of the theoretical phase shifts since their EXAFS is less "adjustable".

Soft-x-ray EXAFS based on oxygen K-shell spectra has been useful for obtaining bond lengths in surface oxides.¹⁷ It has not been used to measure intramolecular bond lengths, partly because these parameters can be measured by other techniques, but also because EXAFS in these small molecules is very weak. There were speculations that the EXAFS might not exist. Advances in recent years in synchrotron radiation instrumentation and the detector technology provide us with the appropriate tools to study weak EXAFS in the soft-x-ray region. Our preliminary work¹⁸ revealed a discrepancy between the experimental phases and the TL data set in small oxygen-containing molecules. The objectives of this work are (1) to confirm the early observation of EX-AFS in small molecules at the oxygen K edge, and extend the detectable limit of EXAFS; (2) to study systematically molecules with an O-C bond, and test the validity of chemical phase transferability in these low-Z molecules; and (3) to determine the experimental phase shift and backscattering amplitude, and compare them with the TL data set.

II. EXPERIMENT

The EXAFS amplitude of small molecules at the oxygen K edge is very low due primarily to the weak backscattering of electrons by neighboring low-Z atoms. It is thus important to take special care to maintain a high signal-to-noise ratio and avoid artifacts which may result from flux normalization, i.e., due to the presence of higher-order radiation and stray light from the monochromator, or from pressure fluctuations in the sample chamber.

The schematics of our experimental setup is shown in Fig. 1. Slow flow of the sample gas is maintained during the experiment, i.e., the gas is leaked into the stainless-steel sample cell through a leak valve and pumped out through a metering valve. The flow rate is maintained at over two orders of magnitude higher than the outgas rate of the sample cell. Pressure in the cell is regulated manually and maintained within about 1% during data acquisition. It is monitored by an MKS Baratron absolute gauge (with an accuracy of < 0.4% full scale) and recorded during the experiment.

The cell is separated from the high vacuum of the beamline by a 1300-Å silicon nitride window. Flux monitors I_0 and I are P31 phosphor^{19,20} screens viewed by low-gain photomultipliers (PMT; Hamamasu R-431). The interaction region of the cell is also monitored by a high-gain PMT (Hamamasu R-269, photocathode sensitive range <700 nm) for simultaneous collection of visible photons generated by x-ray-excited gas molecules.

A modified Samson-type ion chamber^{21,22} is used to collect photoions. It is a cylindrical cavity with two small apertures on axis for passing the beam and a thin wire off axis for collecting positive ions. The cavity is positively biased to exclude the stray electrons and ions



FIG. 1. Experimental setup for the cross-section measurement. (A) I_0 monitor: phosphor P31 on a grid monitored by a PMT; (B) silicon nitride window (1300 Å); (C) ion chamber; (D) I (transmitted) flux monitor. L = 83.8 cm.

generated outside, especially from the front window. The background noise of the ion chamber is estimated to be three orders of magnitude lower than the true signal from scans without gas in the cell. The I-V characteristic curve of the ion chamber shows a sizable plateau extending down nearly to zero voltage.

We used phosphor detectors for monitoring the incoming (I_0) and transmitted (I) x-ray flux. Three kinds of detectors are commonly used in the soft-x-ray spectroscopy: photodiodes, gas counters, and phosphors. Photodiodes are not useful in a gaseous environment simply because of the interference of ions and electrons from the ionized gas molecules. Gas counters are hindered by the need for a number of additional thin windows which may in turn add artificial features in the EXAFS spectra (see Appendix A). Phosphor P31 turns out to be an excellent detector for spectroscopy near the oxygen K edge. A detailed discussion of its characteristics can be found in Refs. 19 and 20, and hence will not be repeated here.



FIG. 2. The output of U-15 monochromator measured in the gas cell. Solid curve, first-order flux (ring current 100 mA); dashed curve, relative flux of the second-order radiation.

The experiment was performed at the U-15 beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. The beamline is equipped with a toroidal grating monochromator (TGM) with a 600line/mm gold-coated grating. The TGM has a constant wavelength resolution [full width at half maximum (FWHM)] of about 0.06-0.2 Å across the whole spectrum, depending on the size of the aperture in front of the grating and the electron beam in the ring. During this experiment the resolution is set to about 0.12 Å. The first-order photon flux of the U-15 beamline monochromator output is shown in Fig. 2. The harmonics and stray light from the monochromator were estimated using the K edges of aluminum from a photodiode and Ledges of xenon gas in the cell. The relative intensity of the second order in the beam is also shown in Fig. 2. It was measured by a variable absorber technique;²² recording the transmitted flux as a function of the gas pressure (optical thickness) and fitting it with a sum of two exponential functions of pressure. The beamline has a 1500-Å aluminum window which separates the user area from the storage ring vacuum. While the window makes the beamline flexible for experiments, it also produces a flux jump of about 7% at the oxygen K edge due to the oxide layer on the window, clearly seen in Fig. 2.

The slight kink at about 850 eV is due to Wood's anomaly.^{23,24} At this angle, the first positive order emerges from the grating surface and shares intensity with the first negative order beam from which we make our measurement. Hence, the intensity curve drops beyond this angle. In the soft-x-ray region, anomalies are usually not as complicated as in the optical region²⁵ since the grating is highly absorbant for x-ray photons and the photon frequency is well above the frequency of surface plasmons. But the anomaly is still very sensitive to the grating profile and surface roughness; this makes it very hard to predict precisely the grating behavior around the anomaly from the theory. For most oxides the kink appears as a glitch in our EXAFS spectra around 9 Å⁻¹ in k space. At this time we do not have a

reliable way to remove the glitch and have to truncate the spectrum when the glitch becomes significant.

The gas samples are obtained from Matheson. The purities are (1) carbon monoxide (CO), 99.5% (commercial); (2) carbon dioxide (CO₂), 99.8% (bone dry); and (3) carbonyl sulfide (OCS), 97.5%. The purities of the liquid samples are (1) acetone [(CH₃)₂CO], 99 + % (analytical reagent); (2) ethanol (C₂H₅OH), 99 + % (analytical reagent); (3) diethylether [(C₂H₅)₂O], 99% (anhydrous); (4) tetrahydrofuran (THF, C₄H₈O), 99% (reagent); and (5) dioxane (C₄H₈O₂), 98% (reagent). All samples were used as received without further purification. The liquid samples were degassed a few times through a standard "freeze-and-thaw" procedure before their vapor was introduced into the sample chamber.

III. DATA ANALYSIS

The first part of the data treatment is to remove various instrumental factors from the raw data. The first step is to divide the experimental data I by I_0 to remove the temporal fluctuation of the x-ray-beam intensity. The ratio I/I_0 from runs with the gas sample in the cell is then divided by that from runs without it to remove the window transmission factor. The result still depends on the intensity of the second-order flux and the response function of the detector, namely,

$$\frac{(I/I_0)_P}{(I/I_0)_{\text{vac}}} = a_1 e^{-\mu_{P1}PL} + a_2 e^{-\mu_{P2}PL} , \qquad (6)$$

where P is the pressure in the gas cell, L = 83.8 cm the length of the cell, and μ_{P1} and μ_{P2} the absorption coefficients of the gas sample in $(torr cm)^{-1}$ for the firstand the second-order radiation. a_1 and a_2 are the relative intensities of the first- and the second-order radiation, respectively, measured by the P31 detector in the cell, i.e., it reflects the different response of P31 to firstand second-order radiation. These quantities are known from other measurements.²²

The next step is to subtract the second-order term by assuming that, far above the edge, the cross section of the gas molecule can be fairly well approximated by the sum of the cross sections of independent atoms. The atomic absorption data are taken from Henke *et al.*,²⁶ and normalized against the present data in the (700-800)-eV wavelength region where second-order flux is negligible. After the subtraction it is straightforward to calculate the absorption coefficient μ_{P1} and to convert it to absolute cross section. Since the gas pressure is measured simultaneously with the transmitted flux, small fluctuations of gas pressure are normalized out and do not affect the measured absorption spectra.

The small modulation of a_2 due to the EXAFS structure in the window absorption spectrum is also corrected. This correction is less than 0.1% of the absorption spectrum in all cases. The detailed discussion of this correction is presented in Appendix B.

A typical set of spectra is shown in Fig. 3. Before the correction for second-order flux, the apparent cross section is dependent on the sample thickness (pressure), known as the "thickness effect."²⁷ It can be seen from



FIG. 3. The oxygen K-edge x-ray-absorption cross section on carbon monoxide. Apparent cross sections show pressure dependence. From top to bottom: cross section corrected for the second-order radiation (0.1 torr), cross section corrected for the second-order radiation (0.3 torr), uncorrected cross section (0.1 torr), uncorrected cross section (0.3 torr).

Fig. 3 that above 540 eV the correction procedure results in nearly identical absorption spectra for data recorded with different sample pressures. The remaining discrepancies above 540 eV are likely due to instabilities, such as mechanical vibration of the device, or a slow drift of the electron beam in the storage ring, which may affect the alignment of the optics as well as the level of impurity radiation. Small discrepancies have been seen in the I/I_0 ratios from two vacuum scans under "identical" conditions, supporting this argument. Inspection of these curves shows that the most significant difference between scans is the change of normalization, probably due to small shifts in the alignment of the whole optical system. The change manifests itself in Fig. 3 as a vertical shift between curves. To scale the spectrum correctly, a series of pressure scans are performed;¹⁸ the monochromator is set at a fixed wavelength, and the pressure is gradually increased while I_0 and I are recorded along with the pressure. Fitting the I/I_0 data (about 300 points) to Eq. (6) gives more reliable cross-section values at a few discrete points. These data were used for normalization.

The remaining discrepancy of the absorption spectra obtained under different pressures gives us some indication on the systematic error of the measurement. It is less than 2% over most of the energy region, with two major exceptions. First, in the region beyond 1000 eV, where stray light dominates the impurity radiation, the error may be as high as 10%. Second, in the near-edge region, sharp structure is suppressed by the thickness effect resulting from the broad energy spread of the monochromator output. We made no correction for these effects which depend strongly on the monochromator resolution. After obtaining the absolute absorption spectrum, the background subtraction poses a special problem in soft-x-ray EXAFS data analysis. We used the following procedure to analyze our EXAFS spectra.²⁸

First the logarithm of the absorption spectrum is taken,

$$\ln\mu = \ln(\mu_0 + \mu_B) + \ln[1 + c\chi(k)]$$
,

where

$$c = \mu_0 / (\mu_0 + \mu_B)$$

A quadratic function of $\ln E$ is fitted with and subsequently subtracted from $\ln \mu$. The remainder, named "gross EXAFS," is again fitted with a spline function in k space. After subtracting the spline fit from the gross EXAFS, the final EXAFS function is obtained by scaling the difference with c.

This analysis algorithm was developed specially for extracting the normalized EXAFS function from a background with a steep slope and deriving the phase and amplitude function from data over a short interval. It was tested on calculated model spectra. The total error in the derived interatomic distance is roughly proportional to $M^{-2.5}$, where M is the total number of oscillations in the spectrum.

 $\Psi_j(k)$, the first approximation to the phase function $\Phi_j(k)$, is derived from $\chi(k)$ by the standard Fourier filter method.¹ It is then used to construct a reference function $\sin \Psi_j(k)$, which is made to go through the identical procedure as $\chi(k)$. The resulting amplitude function, no longer a constant, reflects the effect due to the application of the window functions. Dividing the first backtransformed amplitude function by the second one partly cancels this effect. The result, $G_j(k)$, is taken as the first approximation to the amplitude function. $G_j(k)$ and $\Psi_j(k)$ still depend on the windows used.

The corrected EXAFS function,

$$\chi(k) = \sum_{j} \frac{N_{j} H_{j}(k)}{k R_{j}^{2}} \sin \Phi_{j}(k) , \qquad (7)$$

where

$$H_j(k) = F_j(k)e^{-2\sigma_j^2 k^2 - 2R_j/\lambda}$$
(8)

may be written in terms of these approximate phase and amplitude functions in a factorized form,

$$\chi(k) = \sum_{j} \frac{N_{j}G_{j}}{kR_{j}^{2}} (P_{j}\sin\Psi_{j} + Q_{j}\cos\Psi_{j}) , \qquad (7')$$

i.e.,

$$H_{j} = G_{j} (P_{j}^{2} + Q_{j}^{2})^{1/2} ,$$

$$\Phi_{j} = \Psi_{j} + \arctan(Q_{j} / P_{j}) .$$
(8')

Further refinement of phase and amplitude functions is thus made by varying P(k) and Q(k) to minimize a sum of squares,

$$\sum_{k} \left[\chi(k) - \chi_{\text{expt}}(k) \right]^2 W(k) .$$
(9)

The weighting factor W(k) is chosen to be proportional to the signal-to-noise (S/N) ratio of the spectrum. The functional form of P(k) and Q(k), which is not crucial to the fit, is chosen as linear or quadratic polynomials. The fitting procedure is iterated until convergence. It usually takes two to four runs to reach convergence, depending on the complexity of the form of the final amplitude function.

In order to characterize the property of the experimental setup and the data analysis, a spectrum of argon, which does not have any significant features in this energy range, was taken and analyzed. The spectrum showed a low-frequency wiggle in k space, contributing a background of amplitude less than 0.03 to $k\chi(k)$. This is a few per cent of the EXAFS function of most molecules presented here.

IV. RESULTS AND DISCUSSION

The oxygen K-edge absorption spectra of the molecules after correction for second-order contribution are shown in Fig. 4. The spectra based on the sum of atomic cross-section data of Henke *et al.*²⁶ are also shown for comparison. The overall agreement of the two sets of data are quite good except near the absorption edge.

A sharp pre-edge peak can be seen in the spectra of the first four molecules, each of which contains a double or a triple bond. This is due to the transition of a 1s electron to a π^* -like antibonding molecular orbital. This feature is narrow and very sensitive to the sample pressure as can be seen from Fig. 3. In order to optimize the gas pressure for the best signal-to-noise ratio in the EX-AFS region, the pressure is usually chosen to make the cell equivalent to about one absorption length at the edge. This choice severely suppresses the π^* peaks due to the thickness effect discussed in Sec. III. Therefore, the amplitude shown is clearly an underestimate. Another feature, a broad resonance near the absorption edge, is present in all spectra. It is due to the transition of a 1s electron to a shape resonance of σ -like symmetry. Other spectral features near the edge, not clearly resolved by this monochromator, agree with previous work.^{$29-36^{\circ}$} These features will be discussed elsewhere.

The most interesting features of these data are the EXAFS shown in the spectra. They are shown in energy coordinates in Fig. 5 and in k space in Fig. 6. To convert these spectra into k space, we used the value of the binding energies measured by x-ray photoelectron spectroscopy (XPS, Table I) for E_0 . For THF and dioxane, where XPS measurements are not available, we used the value for diethylether, in which the bonding structure around the oxygen atom differs from the two molecules only in the third neighbor. Using XPS binding energy may slightly underestimate the k values, since the phenomenological parameter E_0 used in EXAFS analysis is usually below XPS ionization threshold. We nevertheless use these values for consistency in treating all molecules.

The EXAFS of the diatomic molecule carbon monoxide shows a single sine wave as expected, while others show more complicated structure indicating that more than one neighboring atom contribute to the EXAFS. The calculated EXAFS spectra based on the TL parameters, molecular constants, and the XPS E_0 are also shown in Figs. 5 and 6. In the calculation the central atomic phase shift is from the TL result obtained with Herman-Skillman wave functions, the backscattering phase, and amplitude are from the result with Clementi-Roetti wave functions. In general, the calculated spectra

differ from the experimental results. In particular, the maxima and minima of the calculated $\chi(k)$ are located at lower k than observed in the molecules with a double C = O bond.

The amplitudes of the Fourier transform of $k^2\chi(k)$ are shown in Fig. 7. These spectra show the basic features



FIG. 4. The oxygen K-edge-absorption cross section on carbon monoxide, carbon dioxide, carbonyl sulfide, acetone, ethanol, diethylether, tetrahydrofuran, and dioxane. Solid curve, experimental data; long-dash-short-dash curve, sums of the atomic cross sections taken from Henke *et al.* (Ref. 26).



FIG. 5. Gross EXAFS. Solid curves, experimental data; long-dash-short-dash lines, calculated spectra based on TL phase and amplitude.

of the molecular environment of the oxygen atom: The number of peaks corresponds to the number of distinct neighbors, but the peak positions only roughly correspond to the correct interatomic distances due to the phase shifts. A sum peak, located at the position equal to the sum of two peak coordinates on the left, also ap-



FIG. 6. k^2 weighted EXAFS function $k^2\chi(k)$. Solid curves, experimental data; long-dash-short-dash lines, calculated spectra based on TL; dashed lines, fitted by the analysis program.

pears in the case of dioxane and THF. The position and the shape of the peaks are somewhat dependent on the parameters of the window used in the Fourier transform. Hence, we shall make quantitative comparison only in phase and amplitude functions. These functions are extracted with the procedure described in Sec. III.

The experimental phase shifts are plotted in Fig. 8. Their error comes from four sources: (1) error in the known bond length, (2) error induced by the analysis program, (3) random noise in the spectrum, and (4) systematic error in the spectrum. The first is negligible in most cases (Table I). The second can be estimated from the model study of the analysis program;²⁸ it is usually small in the middle of the spectra and larger on both ends; its average can be roughly estimated as $M^{-1.5}$, where M is the number of the oscillations in the spectrum. Change of E_0 may alter the phase shifts by as much as 1 rad at the low-k end. The third may be estimated from the goodness of fit in the refinement procedure. In this study it usually results in an error less than 0.3 rad. The last source of error is very difficult to estimate. For the first three molecules, where the EX-AFS is strong, the systematic errors are not significant. But for the molecules with single O-C bonds, EXAFS is weak, the low-frequency background may interfere with the true signal and distort the nearest-neighbor peak. Hence we assigned larger error bars to the phase shifts derived from them.

In the case of dioxane we were not able to resolve the second shell, two carbon atoms, and the third, one oxygen atom. We had to combine them into a pseudosecond shell in the refinement. This resulted in a second-neighbor phase shift which is spurious and a first-neighbor phase shift which may contain significant error. In the case of ethanol, the signal is so noisy that no further analysis can be made.

F(k), the backscattering amplitude of carbon atoms, is shown in Fig. 9, together with that of Teo and Lee for comparison. The Debye-Waller factor in Eq. (8') is calculated with the parameter given in Table I. The factor $\exp(-2R/\lambda)$ is ignored for compatibility with the data of Teo and Lee (see the discussion below). It can be seen that experimental functions derived from neighbors in the double and triple bonds, carbon monoxide, carbon dioxide, carbonyl sulfide, and acetone, are comparable to the TL values. For the reasons discussed in the last paragraph, the amplitudes of the second shell of dioxane is not included in this figure. We now discuss the overall observation from the spectra shown in Figs. 5–9.

(1) The amplitude of EXAFS in these molecules does not show the general trend predicted by the "smallatom" approximation. In Eq. (2) the small-atom approximation predicts that the overall EXAFS amplitude equals $(N/R^2)F(k)e^{-2R/\lambda}e^{-2k^2\sigma^2}$, where N is the coordination number, F(k) the scattering amplitude of the carbon atom located at R, $e^{-2R/\lambda}$ the phenomenological inelastic term, and $e^{-2k^2\sigma^2}$ the Debye-Waller factor. Multielectron processes such as shakeup and shakeoff may reduce the observed amplitude by a constant fraction,¹ but their contribution should be nearly the same in all these molecules, especially for EXAFS due to different neighbors in the same molecule. Let us first consider the factor N/R^2 . This factor is 0.79 Å⁻² in carbon monoxide, 0.49 Å⁻² for the first scattering atom in ethanol, and 0.98 Å⁻² for the two nearest-neighbor atoms in diethylether, THF and dioxane.

We next consider the inelastic term. In the calculation of Teo and Lee a complex potential was used to account for the inelastic scattering process represented in Eq. (2) by $e^{-2R/\lambda}$, a factor characterized by a phenomenological mean free path. It is hence not necessary to include the factor for the first-neighbor calculation. For the second-nearest neighbors, the electron density in the interatomic region is low except in the linear molecules, since the electrons are fairly well localized in the bond region in free molecules. The factor $e^{-2R/\lambda}$ is again not important. can be estimated from molecular constants obtained by infrared spectroscopy or the mean-square amplitude deviation from electron diffraction data. The Debye-Waller factors of the nearest neighbors for alcohol and ethers (diethylether, THF, and dioxane) are comparable to that of carbon monoxide, while that of second-nearest neighbors for alcohol and ethers are slightly smaller than that of carbon monoxide (Table I). In both cases the Debye-Waller factors differ from each other by less than 20%.

Under the small-atom approximation, it appears from the above discussion that N/R^2 is the dominant factor and the EXAFS signal in diethylether, THF, and dioxane should be stronger than, or at least comparable to, that in carbon monoxide. From Figs. 5–9 one can see that it is clearly not the case.

Finally, the Debye-Waller factor of these molecules

One may also note that the backscattering from the

Molecule	<i>E</i> ₀ (eV)	R ^a (Å)	$\frac{v}{(\mathrm{cm}^{-1})}$	$\sigma^{2^{b}}$ (10 ⁻⁴ Å ²)	Ref. ^c
(1)		1.1282	2143	11.4	42,43,59
CO_2	540.8				38
(1)		1.1597		11.96	44,62
		1.162(1)			45
OCS	540.3			12.18	39,62
(1)		1.157(2)			46
		1.160(1)			47
$(CH_3)_2CO$	537.7				40
(1)		1.211(4)		12.86	48,62
		1.222(3)			49
(2) ^d		2.379(9)		37	48,61
		2.396(5), calculated			48,50
C ₂ H ₅ OH	538.6		1050		40
(1)		1.431(5)			55
(2)		2.38(1), calculated			55
$(C_2H_5)_2O$	537.9				40
(1)		1.43(1)	1090	15	56,61
		1.43(2)			57
(2)		2.38(1) calculated		33	56,61
C ₄ H ₈ O	537.9 ^e				,
(1)		1.4280(15)	1090	13	51,61
		1.43(3)			52
(2)		2.364(28)		34	51,61
		2.42(?)			52
$C_4H_8O_2$	537.9 ^e				
(1)		1.423(3)	1116	12	58,61
		1.42(2)			54
(2)		2.40(1), calculated		30	58,60
		2.42(4), calculated			53
(3)		chair configuration			53,54

TABLE I. Relevant parameters of the molecules. (1), (2), and (3) refer to different distances between the atoms of the molecule.

^aWhen more than one distance is listed for comparison, the first one is used for calculating the phase shift. The error in the last digit(s) are given in parentheses.

^bThe mean vibration displacement in C—O bond is calculated from $\sigma_1^2 = \hbar(4\pi\mu\nu)$, where ν is the stretching frequency of the C—O bond and μ the reduced mass. The displacement of the second neighbor is estimated by combining the vibration frequency of stretching C—O and C—C bonds. No attempt has been made to solve the normal mode coordinates. The combined error of the estimate of σ_2^2 is about 20%.

^cSee Refs. 37, 40, and 41.

^dThe distance to the second-nearest carbon atom(s).

^eValue for the diethylether, XPS binding energy is not available.

second neighbors in linear molecules, oxygen in CO_2 and sulfur in OCS, is enhanced as can be seen in the Fourier transform of χ (Fig. 7). These are examples of the focusing effect due to the presence of an intervening atom in the path of photoelectrons. It is very surprising, however, that the observed backscattering functions for firstneighbor carbon atoms in alcohol and ethers are much lower than that in carbon monoxide, while those for



FIG. 7. The amplitude of the Fourier transform (FT) of $k^2\chi(k)$.

second-neighbor carbon atoms are comparable to it. This again shows that the current theory is inadequate for describing the EXAFS of these low-Z molecules.

(2) The experimental phase shifts are systematically lower than the TL results. The difference between the experimental phase and that calculated by TL is clearly seen from the direct comparison of the EXAFS with the calculated spectra (Fig. 6). The difference cannot be reconciled by adjusting E_0 even by as much as 20 eV (Fig. 5). These observed phase shifts for the oxygencarbon pair, shown in Fig. 8, may be grouped in three classes: first carbon neighbor in linear molecules, first carbon neighbors in bent molecules, and second carbon neighbors.

The phases for the first neighbor in carbon dioxide and carbonyl sulfide, extracted from the spectra with the best S/N ratio, agree with each other within 0.2 rad., also within experimental error. It is not surprising since the molecular environment of oxygen in these two molecules is almost identical. The phase in carbon monoxide is also extracted from a spectrum with a good S/N ratio, but due to the lack of an adequate boundary condition at the high-k end of the spectrum, the error in the derived $\chi(k)$ is higher there. This is even more severe in the absence of another higher-frequency component.²⁸ Hence, the error in the phase derived from the spectrum is higher at the high-k end of the spectrum. Neverthe-



FIG. 8. The phase shifts for O-C pair. Curves are labeled with the molecules they represent, in particular, Et represents diethylether, Ac acetone, and Di dioxane, while T&L is the Teo and Lee theoretical prediction. Subscripts 1 and 2 refer to first- and second-neighbor carbon atoms. Estimated uncertainties of the curves are related to their respective signal strength. Solid curves, ± 0.5 rad at the low-k end and ± 0.2 rad at the high-k end; long-dash-short-dash curves, ± 1 rad (low k) and ± 0.4 rad (high k); and dashed curves, ± 1.7 rad (low k) and ± 0.7 rad (high k).

less, the phase generally agrees with that derived from carbon dioxide and carbonyl sulfide, within experimental error.

The single bond compounds, alcohol and ethers, are chosen to give the absorbing oxygen atom a similar local atomic environment, i.e., the first- and the secondneighbor distances are very similar in all four molecules. Hence their EXAFS spectra are expected to be similar. This is verified in the observed spectra, i.e., the main features of these spectra are indeed very similar, including the low-frequency bumps as well as the highfrequency wiggles. Even the peak positions are close to each other, as can be seen in Figs. 5 and 6. While the linear molecules (CO, CO₂, and OCS) show a good phase molecules transferability, the with nonlinear configurations show another interesting regularity. Above 4.5 \AA^{-1} the phase shift of acetone, THF, and dioxane are divided into two groups according to first and second neighbors. The difference reaches 1.5 rad in the high-k region, although the phase shift in each group, especially the second neighbor (longer R), may be made to coincide with those of linear molecules. It appears that the difference is not related directly to the number of bond electrons, but rather to the molecular configurations. For example, molecules with double C=O bonds such as O=C=O and O=C(CH₃)₂ do belong to two different groups. The common trend in the chemical effects most likely arises from the polarization of the distribution of all valence electrons (2s and 2p) with respect to the bonds, as well as multiplescattering pathways. A quantitative characterization of the effect would require better experimental data. In this experiment, the phase and amplitude data extracted from weak EXAFS signals may contain larger errors (dashed lines in Figs. 8 and 9) due to possible lowfrequency background in the system.

V. SUMMARY AND CONCLUSION

Recent observation of EXAFS in the absorption spectra at the oxygen K edge of the oxygen-containing mole-



FIG. 9. The backscattering amplitude F(k) of carbon atoms. Estimated uncertainties of the curves relate to their respective signal strength. Solid curves, $\pm 10\%$; longdash-short-dash curves, $\pm 20\%$; and dashed curves, $\pm 50\%$. The labels have the same meaning as in Fig. 8.

cules¹⁷ has been confirmed with an improved experimental setup. In addition, a systematic study of phase and amplitude of the O—C pair has been performed on carbon monoxide, carbon dioxide, carbonyl sulfide, acetone, ethanol, diethylether, tetrahydrofuran, and dioxane, with an improved analysis algorithm.

The results show that the observed amplitudes of the EXAFS in the molecules with a double or a triple O—C bond are comparable to the theoretical calculation, while those due to backscattering from first-neighbor carbon atoms in molecules with a single bond are considerably weaker than predicted by the theories using the smallatom approximation. The observed EXAFS amplitudes from the second neighbors in these molecules are enhanced compared to the first-neighbor atoms and are increasing with k, in disagreement with the theory.

The experimental phase shifts for the O-C pair are lower than the theoretical value by about 0.7-1.5 rad. This is probably due to the failure of the plane-wave approximation used in the calculation and the contribution of multiple scattering. Experimental phase shifts derived from most O-C pairs in the molecules agree with each other within experimental error. Phase transferability appears to be applicable to chemically similar compounds. We have also found some evidence for the effect of the polarization of the electron cloud on the phase and amplitude.

We showed that the commonly used EXAFS theory in the hard-x-ray region, i.e., single scattering from small atoms with the plane-wave approximation, is not adequate for describing the systems with O-C bonds. A more exact theory, which adequately treats the spherical waves, multiple scattering, and the molecular potential, is needed to provide a systematic understanding of EX-AFS in these systems.

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APPENDIX A: ERROR "PROPAGATION" FROM PHASE SHIFTS TO DERIVED DISTANCES

In a popular method,² the interatomic distance is obtained from the phase function derived from the $\chi(k)$. One first "filters" a peak from the Fourier-transformed spectrum and then backtransforms it into k space. This gives the total phase $\Phi(k)$ function. After subtracting the known phase shift $\phi(k)$ from it, the "corrected" phase,

$$\Theta(k) = [\Phi(k) - \phi(k)]/2 , \qquad (A1)$$

is fitted with a straight line by using a least-square method, i.e., the weighted sum,

$$\sum_{i} [\Theta_{i} - (h_{0} + h_{1}k_{i})]^{2} W_{i} , \qquad (A2)$$

is minimized. In addition, the threshold energy E_0 is adjusted to make the fitted line pass through the origin. The slope of the resulting line is taken as the interatomic distance.

The solution of (A2) can be expressed as

$$h_1[\Theta; E_0] = U/W, \quad h_0[\Theta; E_0] = V/W$$
, (A3)

where

$$U = \langle k^2 \rangle \langle \Theta \rangle - \langle k \rangle \langle k\Theta \rangle ,$$

$$V = \langle k\Theta \rangle - \langle k \rangle \langle \Theta \rangle ,$$

$$W = \langle k^2 \rangle - \langle k \rangle^2 ,$$

and $\langle \rangle$ is defined by

$$\langle f \rangle = \sum_{i} f(k_i, \Theta_i) W_i$$

The distance is hence determined by

$$R = h_1 \mid_{h_0 = 0} . \tag{A4}$$

If we introduce an error $\delta\phi(k) = A_0 + A_1k$ in the phase shift $[\delta\Theta(k) = -\delta\phi/2]$, the threshold energy E_0 will have to be adjusted to make a new fit. It is straightforward to work out the resulting error in the distance,

$$\delta R = -\frac{A_0 + A_1 k_0}{2k_0} = -\frac{\delta \Theta(k_0)}{2k_0} , \qquad (A5)$$

where k_0 is defined by

$$\frac{1}{k_0} = \frac{1}{\langle k \rangle} \left[1 - \frac{\langle k^{-1} \rangle \langle k^2 \rangle - \langle k \rangle^2}{\langle k^{-1} \rangle \langle k^2 \rangle - 2 \langle k \rangle + \langle k \rangle^2 \langle k^{-1} \Theta \rangle / \langle \Theta \rangle} \right], \tag{A6}$$

i.e., while the adjusted line pivots against the origin, it is the phase in the neighborhood of the weighted center of the data that determines the slope. This is understandable; the fitted line should always intercept the Θ curve on at least two points. While the point at low k may move around as E_0 is adjusted, the one at high k is not much affected.

APPENDIX B: EFFECT OF THE VACUUM WINDOW AND SECOND-ORDER RADIATION ON THE EXAFS SPECTRUM

In a spectroscopy experiment, the effect due to variation of the incident beam may not be completely cancelled by dividing the I flux monitor signal by I_0 . This problem of flux normalization can result from problems in the optical system: The I_0 monitor is not designed for the nonuniform beam, or it intercepts a larger area than the I monitor. While these problems can be fixed by an appropriate design, the problem associated with nonmonochromaticity of the beam requires much more effort. The impurity radiation in the beam may have different spectra and origins: smooth background from scattered light, peaks at multiples of the fundamental energy from monochromator higher order harmonics, and significant population around the nominal energy due to poor resolution of the monochromator. These impurity radiations lead to nonexponential behavior of the transmitted flux through a sample (thickness effect²⁷) and other artifacts in experimental spectra. Since the soft-x-ray EXAFS is very weak, a quantitative understanding of these artifacts is necessary in order to guide the experiment and data analysis.

Let us consider a simple case where an x-ray beam has only two components: fundamental and second-order harmonics, with intensities b_1 and b_2 , respectively:

$$b_1 + b_2 = 1$$
, (B1)

where b_1 and b_2 are smooth functions of the photon energy *E*. After passing through a window of thickness *y* the two components are attenuated to $b_1 e^{-v_1 y}$ and $b_2 e^{-v_2 y}$, respectively, where v_1 and v_2 are the attenuation coefficients of the window for the two components, respectively. The normalized relative intensity at the downstream side of the window is

 $a_1 = \frac{b_1 e^{-v_1 y}}{b_1 e^{-v_1 y} + b_2 e^{-v_2 y}} ,$

and

(B2)

$$a_2 = \frac{b_2 e^{-v_2 y}}{b_1 e^{-v_1 y} + b_2 e^{-v_2 y}}$$

These are the parameters used in Eq. (6) for data analysis. In our experiment, a_2 is not measured precisely point by point. Instead, it is measured in intervals of 1 Å in photon wavelength and smoothly interpolated over the whole spectrum. In order to calculate the effect of the small modulation in a_2 on the measurement of gas absorption coefficient μ_1 , we write ν_1 in two parts, a smooth part and the EXAFS oscillation term,

$$\mathbf{v}_1 = \mathbf{v}_{10} + \delta \mathbf{v} \ . \tag{B3}$$

Differentiating (B1), we obtain

$$\delta b_1 + \delta b_2 = 0 \ . \tag{B4}$$

If we differentiate the logarithm of (B2) and assume $|\delta v_1| >> |\delta v_2|$, i.e., take $\delta v_2 = 0$ we obtain

$$\frac{\delta a_1}{a_1} = -y \left[1 - \frac{b_1 e^{-\nu_1 y}}{b_1 e^{-\nu_1 y} + b_2 e^{-\nu_2 y}} \right] \delta \nu_1 = -a_2 y \, \delta \nu_1 \; .$$
(B5)

We let $\mu_{pi}PL = \mu_i x$, (i = 1, 2), in Eq. (6), differentiate it, and take $\delta \mu_2 = 0$ since μ_2 is taken from a known source to obtain

$$0 = (e^{-\mu_1 x} - e^{-\mu_2 x})\delta a_1 - a_1 e^{-\mu_1 x} x \,\delta \mu_1 \,. \tag{B6}$$

Combining the equations above, we obtain the following:

$$\frac{\delta\mu_1}{\mu_1} = a_2 (e^{(\mu_1 - \mu_2)x} - 1) \frac{\nu_1 y}{\mu_1 x} \frac{\delta\nu_1}{\nu_1} . \tag{B7}$$

The EXAFS feature of the window is thus "tagged on" to the gas spectrum according to this expression.

In our experiment the absorption feature of the sample always dominates for photon energy below 600 eV. Beyond 600 eV, the sample EXAFS amplitude decreases and the effect of window may become noticeable. In this

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region, a_2 is less than 0.05 (Fig. 2). We have chosen the parameters of the setup so that

$$(\mu_1 - \mu_2)x < 1, \quad \frac{\nu_1 y}{\mu_1 x} < 3$$
,

and the amplitude of window EXAFS is measured to be

$$\frac{\delta v_1}{v_1} < 0.01$$

This sets an upper limit 0.002 for the error in gross EX-AFS spectra, in which normal signals have amplitudes of 0.01-0.02. It decreases at higher energies as a_2 decreases. An even smaller error is expected when the error term (B7) is subtracted from the sample spectrum, based on vacuum scans.

Another implication of (B7) is that the amplitude of the transferred spectral feature is proportional to the ratio of the optical thickness of the window to the sample, i.e., the artifact decreases as the sample thickness increases. We also used this property to identify the true structural features.

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