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We have measured photoionization cross sections and photoelectron asymmetry parameters for each of the core levels of N$_2$O. We have also carried out frozen- and relaxed-core Hartree-Fock studies of these cross sections so as to better understand the underlying shape resonant structure and the role of electronic relaxation in these processes. A broad shape resonance is observed in each of the core-hole cross sections at 10-20 eV kinetic energy and there is some evidence of a second shape resonance near the thresholds, an energy region which is not accessible experimentally. The cross sections also exhibit site-specific behavior with maxima at widely separated photoelectron kinetic energies. These differences probably arise from the fact that photoelectron matrix elements for different core orbitals probe different regions of the shape resonant orbital which extends over the entire molecule. Although the higher energy shape resonances appear quite similar, Hartree-Fock studies show that the central nitrogen resonance is more sensitive to effects of electronic relaxation than the terminal nitrogen or oxygen resonances. Large differences are also seen between the photoelectron asymmetry parameters for the central and terminal atoms.

I. INTRODUCTION

The general properties of shape resonances in photoionization are fairly well understood from numerous studies on diatomics and other small molecules. However, one of the key questions for larger molecules, where several resonances can be present in the continuum, is to what extent a shape resonance can be viewed as spatially localized between particular nuclei (and thus attributed to specific bonds). Nitrous oxide, a linear molecule with the configuration N–N–O, is a prototypical example for the study of shape resonances since it bridges the gap between simple diatomics and polyatomic molecules. The question of localization of shape resonances in diatomics and polyatomic molecules has recently been addressed in combined experimental and theoretical, vibrationally resolved studies of 7σ photoionization leading to the A $^2Σ^+$ state of N$_2$O$^+$. Here, the presence of a σ shape resonance located 3–5 eV above the 7σ ionization threshold was seen to give rise to strong non-Franck-Condon behavior. The distinctly different behavior of the symmetric and antisymmetric stretch vibrational modes seen in the fluorescence and photoelectron experiments and in theoretical studies of these spectra, clearly show that this resonance spatially extends over the entire molecule and is not simply characteristic of the N–N or the N–O bond. In addition, a second, weaker shape resonance about 15–20 eV above the 7σ threshold is evident in the experimentally determined asymmetry parameter as well as in multiple scattering (MSXα) and in frozen-core Hartree-Fock (FCHF) calculations. The same is true for the isoelectronic molecule CO$_2$, where two shape resonances are also observed in photoionization studies. The observation of more than one shape resonance in a single partial channel may perhaps be quite normal in the photoelectron spectra of polyatomic molecules.

On going from valence to core excitation the continuum resonances usually shift a little (1–4 eV) towards lower kinetic energy due to differences in screening between localized and delocalized holes. There is, indeed, clear experimental evidence of shape resonances above the nitrogen and oxygen K edges of N$_2$O around 424 and 555 eV, respectively, in the total photoabsorption cross section curves. This would be consistent with a small shift to lower photoelectron energy of the weak shape resonance seen at higher energy in valence shell studies of N$_2$O. In contrast to the valence levels, vibrationally resolved photoelectron spectroscopy on the core levels of gas phase samples is not yet feasible since high-resolution monochromators with sufficient photon flux are not available. However, in the case of N$_2$O one can still probe the continuum resonances from all nuclear sites selectively and thus obtain valuable information: The anisotropic molecular potential gives rise to a large chemical shift of 4 eV between the ionization energies (IE) of the N 1s electrons. The values of the IEs are 408.5, 412.5, and 541.2 eV for the terminal nitrogen (N$_T$), the central nitrogen (N$_C$), and the oxygen atom, respectively. Site-specific studies of these N–core levels therefore require only moderate energy resolution and can be performed on existing monochromators. Recently, partial photoionization cross sections and their associated asymmetry parameters for the ionization of the different core electrons of N$_2$O have been measured and calculated by Grimm et al. using the continuum...
MSXα method. This study shows that a σ shape resonance, seen in ionization from the 7σ orbital, is also evident in 1s ionization. The shapes of the partial cross section and β parameter curves are found to depend on the specific atomic site from which the core electron is ionized. The agreement between theory and experiment in this study is generally good. However, large scatter in the data, due to low photon intensity, and a restricted energy range precluded a detailed comparison with theory. We have therefore measured the K-shell photoionization cross sections of N2O with much higher intensities and lower statistical errors and report here an angle-resolved photoelectron study down to a few eV above threshold. We also report calculations in both the frozen-core Hartree–Fock (FCHF) and relaxed-core Hartree–Fock (RCHF) approximations so as to more fully understand the origin of site-specific differences seen in these shape resonances.

In the next section we briefly describe the experiment and outline our data analysis procedure. In Sec. III we outline the procedures used in our Hartree–Fock level calculations of the photoionization cross sections and photoelectron angular distributions. In Sec. IV we present and discuss our experimental cross sections and asymmetry parameters and compare them with theoretical results obtained from MSXα, FCHF, and RCHF calculations.

II. EXPERIMENT

Angle-resolved photoelectron spectra were recorded using a cylindrical mirror analyzer (CMA) with its axis collinear with the synchrotron light beam. The electron collection angle is 54.7° relative to the axis, corresponding to the photoelectron “magic angle,” rather than to the more usual CMA value of 42.3°. Thus on integrating 2π around the axis, the measured intensities are directly proportional to the cross section and are independent of the degree of polarization of the light and of the angular distribution of the photoelectrons.15 In addition, point-to-ring focusing is used in the CMA. Hence by utilizing a multichannel-plate detector and an eightfold segmented anode, eight photoelectron spectra in different spatially symmetric directions can be recorded simultaneously, allowing the determination of the asymmetry parameter of each spectral line from the intensity variation between these segments. A more detailed description of the apparatus will be published elsewhere.16

All spectra have been recorded with a constant CMA pass energy (80 eV for the nitrogen, 100 eV for the oxygen spectra). The transmission of the instrument has been determined with the same monochromator from carbon 1s photoelectron spectra of CO and argon 2p spectra, whose cross sections and β parameters are fairly well known.17-20 However, at the lower kinetic energies there are certain discrepancies between the CO- and argon-derived transmission curves which limit the accuracy near threshold. The intensity and the degree of polarization of the monochromatic synchrotron light have been determined from neon 2s and 2p measurements using the cross sections and β parameters of Wuilleumier.21 The nitrous oxide was obtained commercially with a purity of 99.0%, the residual gases being mainly oxygen and carbon dioxide. Typical target pressures were of the order of 10^{-3} mbar in the interaction region, with the CMA and the detector at 10^{-6} mbar.

The measurements were performed at BESSY on the high energy TGM of the Fritz–Haber Institute22 during two different beamtimes. The photon flux at the sample was approximately 10^{11} photons per second, and the combined monochromator/CMA resolution was typically 2 eV for the nitrogen and 3 eV for the oxygen 1s lines. All spectra were recorded to give peak intensities, integrated over all eight segments, of about 10,000 counts for the nitrogen 1s lines and 3000 counts for the oxygen 1s line. Figure 1 shows two typical raw spectra of the nitrogen 1s levels of N2O, measured simultaneously on different anode segments at a photon energy of 436.3 eV. The collection time for such spectra was typically 15–30 min depending on ring current and monochromator throughput. The upper curve with higher 1s intensities was measured on a segment coincident with the polarization vector of the light, the other perpendicular to it. The different intensity ratios of the nitrogen lines directly reflect a difference in the β parameters. In this case, values of 0.77 and 1.64 are obtained for the β parameters of the NC and the NT lines, respectively. We note here that, in the particular case of near-threshold spectra, a scaled experimental secondary electron background has been subtracted. This background curve was obtained at one of the 1s-3π resonances where no photoelectrons are created and only the smooth secondary electron background produced by the fast auger electrons is present. Due to the high count rates the accuracy of the cross sections and β parameters is not limited by counting statistics but by uncertainties in the calibration data17-20 and by our method of background subtraction in this region. However, the statistical quality, as well as the stability of the operating conditions and of our methods of data analysis, can be estimated from the low scatter in the experimental partial cross section and β parameter curves shown in Figs. 2 and 4.
III. CALCULATIONS

The photoionization cross sections were calculated via the Schwinger variational method\textsuperscript{23,24} using two different approximations for the static-exchange potential: the frozen-core Hartree–Fock (FCHF) approximation and the relaxed-core Hartree–Fock (RCHF) approximation. These methods have been described in detail elsewhere.\textsuperscript{25,26} Briefly, the continuum photoelectron function is written as the partial-wave expansion,

\[
\psi_k^{-}\left(\mathbf{r}\right) = \left(\frac{2}{\pi}\right)^{1/2} \sum_{lm} \frac{i^l}{\varepsilon_{klm}} \psi_{klm}^{-}(\mathbf{r}) Y_{lm}^{*}(\hat{k}) ,
\]

where each partial wave \(\psi_{klm}^{-}\) satisfies its own Lippmann–Schwinger equation,

\[
\psi_{klm}^{-}(\mathbf{r}) = \phi_{klm}^{-} + G_{c}^{-}(\mathbf{r}) \psi_{klm}^{-} ,
\]

Here, \(G_{c}^{-}\) is the Coulomb–Green’s function with incoming wave boundary conditions, \(\mathbf{\hat{v}}\) is the static-exchange potential of the molecular ion, and \(\phi_{klm}^{-}\) is the partial-wave Coulomb function. In the FCHF approximation \(\mathbf{\hat{v}} = \mathbf{\hat{v}}^{\text{FC}}\) and the ion orbitals are taken to be the same as those of the neutral molecule. However, in the RCHF approximation \(\mathbf{\hat{v}} = \mathbf{\hat{v}}^{\text{RC}}\) and the ion orbitals are taken from an SCF calculation for the fully relaxed molecular ion. In this approximation, the nonorthogonality of the photoelectron wave function leads to complications in the evaluation of the photoionization transition moment and in the derivation of the ion potential.\textsuperscript{25} In K-shell ionization, however, these problems are not severe. The RCHF approximation has been shown to be superior to the FCHF approximation in that the former properly takes into account the screening of the nuclear charge brought about by electronic relaxation, an effect that can be profoundly important in regions of shape resonances.\textsuperscript{25,26}

We proceed by assuming a separable approximation to the potential

\[
\mathbf{\hat{v}} = \mathbf{\hat{v}} + 1/r ,
\]

of the form

\[
\mathbf{\hat{v}} \approx \mathbf{\hat{v}}^{*} = \sum_{i,j} \langle \mathbf{r} | \mathbf{\hat{v}} | \alpha_i \rangle (V^{-1})_{ij} \langle \alpha_j | \mathbf{\hat{v}} | \mathbf{r} \rangle ,
\]

where the set of functions \(|\alpha_i\rangle\) are discrete basis functions, such as Cartesian–Gaussian functions, which have been shown to be quite effective in describing the inner region of the molecular ion potential.\textsuperscript{23,24} The scattering basis sets used in the present calculations are specified in Table I. The solutions of the integral equations (2) can now be written as

<table>
<thead>
<tr>
<th>Photoionization symmetry</th>
<th>Type of Gaussian function\textsuperscript{a}</th>
<th>Exponents</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma)</td>
<td>Cartesian (s)</td>
<td>16.0,8.0,4.0,2.0,1.0,0.5</td>
</tr>
<tr>
<td></td>
<td>(x)</td>
<td>1.0,0.5</td>
</tr>
<tr>
<td></td>
<td>Spherical (l = 0)</td>
<td>2.0,1.0,0.5</td>
</tr>
<tr>
<td></td>
<td>(l = 1)</td>
<td>1.0,0.5</td>
</tr>
<tr>
<td>(\pi)</td>
<td>Cartesian (x)</td>
<td>8.0,4.0,2.0,1.0</td>
</tr>
<tr>
<td></td>
<td>(xz)</td>
<td>1.0,0.5</td>
</tr>
<tr>
<td></td>
<td>Spherical (l = 1)</td>
<td>2.0,1.0,0.5</td>
</tr>
<tr>
<td></td>
<td>(l = 2)</td>
<td>1.0,0.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Cartesian functions are centered at the nuclei and the spherical functions on the central nitrogen atom. For details of the forms of these functions and their use, see Refs. 23 and 24.

TABLE I. Basis sets used in separable potential of Eq. (4).

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FIG. 2. Partial 1s single-hole photoionization cross sections of the \(N_{\pi}\) (a), \(N_{\sigma}\) (b), and \(O_{1}\) (c) atoms of \(N_{2}O\). The experimental points are scaled as described in the text. The error bars contain both statistical and systematic errors. Full lines represent RCHF, dashed lines FCHF results. The MSX\(x\) results of Ref. 7 are shown as dotted lines. The 1s ionization thresholds are indicated by hatched bars.
\[ \psi_{kilm}^{-}(r) = \phi_{kilm}(r) + \sum_{l_j} \langle r | G_{c}^{-} | \alpha_{l_j} \rangle \times (D^{-1})_{ij} \langle \alpha_{l_j} | \hat{V} | \phi_{kilm}^{+} \rangle. \] (5)

Here \( V \) and \( D \) denote matrices with elements
\[ V_{ij} = \langle \alpha_{i} | \hat{V} | \alpha_{j} \rangle, \] (6)
and
\[ D_{ij} = \langle \alpha_{i} | \hat{V} - \hat{V} G_{c}^{-} \hat{V} | \alpha_{j} \rangle. \] (7)

The electronic wave functions used in these studies were obtained with the [5s3p] contracted Gaussian basis set of Dunning \(^{27}\) with additional 2\( d \) polarization functions. \(^{28}\)

This basis set gives an SCF energy of \(-183.729\) 404 a.u. at the equilibrium geometry, \( R_{e}(\text{NN}) = 2.1273 \) and \( R_{e}(\text{NO}) = 2.2418 \) a.u. for the ground electronic state, \( X^{1S^{+}} \). The energies of the relaxed \( \text{N}_{2}(1s) \), \( \text{N}_{2}(1s) \) hole, and \( O(1s) \) hole states are \(-168.670\) 876, \(-168.504\) 243, and \(-163.844\) 022 a.u., respectively, with this basis.

All matrix elements arising in the computation of the partial wave \( \psi_{kilm}^{-} \) are evaluated using single-center expansions about the central nitrogen atom. The details of these expansions are as follows:

(i) maximum angular momentum in the expansion of the occupied orbitals in the direct potential is 58.

(ii) maximum angular momentum in the expansion of the occupied orbitals in the exchange potential is 40 [10 \( \sigma \), \( 10 \] \( \pi \), \( 10 \] \( \rho \)], \( 20 \] \( 5\sigma \), \( 19 \] \( 6\sigma \), \( 19 \] \( 7\sigma \), \( 15 \] \( 1\pi \), and \( 15 \] \( 2\pi \).

(iii) maximum angular momentum in the expansion of \( 1/\alpha_{12} \) the direct and exchange terms is 116 and 58, respectively.

(iv) all other single-center expansions were truncated at \( l = 58 \).

The partial-wave expansion of the continuum orbital, Eq. (1), was truncated at \( l = 8 \) and the resulting radial integrals were obtained using a Simpson’s rule quadrature. The grid contained 750 points and extended to 90.5 a.u. with a step size of 0.01 near the nuclei and a maximum step size of 0.4 a.u.

As discussed previously, \(^{25}\) we write the spin-free transition amplitudes \( I_{lm\mu} \) for the partial waves \( \psi_{kilm}^{-} \)
\[ I_{lm\mu} = \frac{1}{\sqrt{2}} (A_{\lambda\alpha,klm\beta}^{(\mu)} + A_{\lambda\alpha,klm\alpha}^{(\mu)}) \]
\[ = \sqrt{2} \langle \Phi_{\alpha}^{N} | \Phi_{\beta}^{N} \rangle \langle \langle \psi_{kilm}^{-} | r_{\mu} | \phi_{\lambda} \rangle \]
\[ - \sum_{r' r} \langle \psi_{kilm}^{-} | \phi_{r'} \rangle (S^{-1})_{r r'} \langle \psi_{kilm}^{-} | r_{\mu} | \phi_{\lambda} \rangle. \] (8)

Here \( r_{\pm} \) corresponds to \( (x \pm iy)/\sqrt{2} \) and \( r_{0} \) to \( z \). The orbital \( \phi_{\lambda} \) refers to the particular core orbital which is being ionized and \( S \) represents the overlap matrix of spatially relaxed—frozen—core orbitals \( \langle \psi_{r} | \phi_{r} \rangle \). The \( N \)-electron relaxed—frozen overlap, \( \langle \Phi_{\alpha}^{N} | \Phi_{\beta}^{N} \rangle \), is given by the square of \( \text{det}(S) \). The decomposition of the full amplitude into direct \( I^{(1)} \) and conjugate \( I^{(1)} \) contributions,
\[ I_{lm\mu} = I_{lm\mu}^{(1)} + I_{lm\mu}^{(1)} \] (9)
shows that the maximum rise in these quantities, indicative of resonant behavior, occurs at nearly the same photoelectron energy for all of the core holes. This suggests that the resonant continuum wave functions associated with these holes have a similar character, but that the resonance profiles of the cross sections differ because the target K-shell orbital probes a different spatial part of the continuum orbital in the photoelectron matrix element. Vibrationally resolved calculations and studies which examine the electronic charge distribution of the continuum wave function near the ion core would be helpful in clarifying these ideas.

As is well known from many other examples, the cross sections calculated with the MSXα method \(^7\) are generally too narrow and overestimate the magnitude of shape resonance features. However, the peak positions agree very well with the experimental results, particularly for \(N_C\) and O 1s ionization. For \(N_T\), the calculated resonance position is shifted to lower energy by 2 to 3 eV. However, there still remains a 1.5 eV difference in photoelectron energy between the MSXα results for the \(N_T\) and the \(N_C\) shape resonance positions and the measured values which the authors attribute to relaxation effects. In their method relaxation is indirectly accounted for by adjusting the net charge on the individual atoms. In contrast, calculations based on HF methods can gauge the magnitude of relaxation by determining the continuum final state using relaxed core orbitals vs frozen core orbitals. In this regard, we note the different behavior of the shape resonance at each atomic site when relaxation is included within the HF model. For the central nitrogen atom, the FCHF resonance position is about 8 eV lower than the experimental value, and the RCHF result is 6 eV higher. A similar but smaller energy shift is observed for the \(\sigma\) shape resonance in CO. In contrast, for the terminal atoms, \(N_T\) and O, there is a very small energy shift between the FCHF and RCHF results for the shape resonance position and, in addition, the resonance positions are significantly higher in energy relative to the MSXα results. In this instance therefore the position of the shape resonance is much more sensitive to relaxation upon removal of a 1s electron from the central nitrogen atom than from the terminal atoms. Interestingly, all RCHF results are 6 to 7 eV higher than the experimental values, no matter which atom is ionized. Furthermore, a closer inspection of the cross section ratio \(\sigma(N_C)/\sigma(N_T)\) (Fig. 3) reveals that, except for an energy shift, the relative behavior of these cross sections is very well reproduced by the RCHF calculations, suggesting that the RCHF method includes relaxation effects correctly. The shift to higher energy is typical of this method and is attributed to the neglect of target polarization. \(^25\)

For both the terminal nitrogen and the oxygen atom the RCHF calculations predict a steep increase of the partial cross sections directly at threshold, in contrast to the experimentally determined values. Moreover, the RCHF \(k\sigma\) eigenphase sums (not shown) show two distinct rises indicative of resonant behavior, one near threshold and one 10–20 eV higher in energy. This behavior is reminiscent of the two shape resonances, but somewhat shifted in energy, as seen in valence shell ionization. \(^26\) Unfortunately, our experimental data do not extend down to threshold, and, in addition, the two points at lowest energies in all the experimental curves shown have larger error bars. Indeed, other experimental techniques such as electron-energy-loss spectroscopy (EELS) and zero-kinetic-energy (ZEKE) photoelectron spectroscopy are also limited in interpreting this low energy region. For example, the ZEKE measurements of Habenicht et al. \(^32\) show that the \(N_T\) 1s ionization cross section at threshold is about twice as large as for \(N_C\) ionization, in agreement with the trend observed in Fig. 3, but the results are not given on an absolute scale. As a first approximation, one can rescale these relative measurements to an absolute scale by combining them with the total photoabsorption cross section curve obtained from EELS \(^12\) and with our present data. However, one cannot justify extrapolating to threshold since an unknown fraction of transitions to other states, such as Rydberg orbitals belonging to the \(N_C\) atom, are superimposed on the \(N_T\) 1s continuum. The same holds, in principle, for O 1s ionization. In this case, however, the total photoabsorption cross section increases strongly at threshold. This could certainly be taken as a strong indication of the presence of another resonance very near the O 1s ionization threshold, corresponding to the one observed in the valence level photoionization studies. \(^4-6\) It is also instructive to compare with the core level ionization of the isoelectronic linear molecule CO\(_2\). \(^8\) Here, a resonance in the continuum, associated with the 4s(\(\sigma^*\)) molecular orbital, is present in the C 1s ionization cross section around 14 eV above the ionization threshold. In the O 1s cross section, this same resonance is apparent at a slightly higher electron energy (17 eV), and in addition there is clear evidence of a second resonance at threshold due to the 5s(\(\sigma^*\)) orbital. For symmetry reasons, this latter state is not accessible from the 2p\(_g\) C 1s orbital. The similarity with \(N_2O\) is remarkable, even though the inversion symmetry is broken in nitrous oxide.

Our measured values for the asymmetry parameter \(\beta\), along with those of theory, are shown in Figs. 4(a)–(c). Note the remarkably different behavior for the central nitrogen atom on the one hand, and the two terminal atoms, \(N_T\) and O on the other. For the \(N_C\) atom a broad oscillation is observed with a maximum at 423 eV and a mini-

![FIG. 3. Ratio of the \(N_C\) and the \(N_T\) partial cross sections, \(\sigma(N_C)/\sigma(N_T)\). Points: experiment; full line: RCHF theory.](image-url)
with a narrow minimum at 415 eV. Both the FCHF and RCHF calculations are in broad agreement but place the minimum at much higher energy. The overall appearance of the O 1s $\beta$ parameter is very similar, but in contrast to the N$_T$ case, no minimum near threshold is seen experimentally. In order to understand the striking difference between the terminal nitrogen and oxygen and the central nitrogen $\beta$ curves, we should consider the following factors: (i) the different environment of the excited atoms can introduce a change in the angular distribution, (ii) the influence of a shape resonance on the $\beta$ parameter extends over a much larger energy range than the separation of the two resonances, presumably present in this case and suggesting that interference effects could be possible and, (iii) the lower energy resonance at threshold could dominate the behavior of the terminal atoms and prevent another pronounced minimum in the vicinity of the upper resonance to form.

V. CONCLUSION

We have presented the results of experimental and theoretical studies of angle-resolved photoelectron spectra of the core levels of nitrous oxide. The measured and calculated cross sections and $\beta$ parameters show site-specific behavior in the sense that the central nitrogen atom behaves differently from the terminal atoms. In addition, it is quite interesting that the peak of the shape resonance occurs at different photoelectron energies for N$_T$ and N$_C$ ionization, whereas the transitions to the unoccupied 3$\pi$ orbital occur at the same energy. Examination of the RCHF eigenphase sums suggests that, in fact, the shape resonant photoelectron orbitals for the core holes are similar in character but that these (1s) target orbitals probe different spatial parts of the "resonance" wave function in the photoelectron matrix element. This is consistent with the interpretation of the vibrationally resolved studies of the near-threshold resonance in the 7$\sigma$ valence ionization where the resonant continuum state was seen to extend over the entire molecule and not to be localized between either the N–N or the N–O atoms.

The experimental data do not give a conclusive answer about the behavior within the region 5 eV above threshold where the RCHF method predicts a steep increase in the N$_T$ and O 1s ionization cross section. However, there are clear indications of the presence of an additional shape resonance based on the following considerations: (i) there is a strong enhancement in the O 1s total photoabsorption cross section at threshold, (ii) it is unlikely that the resonance would be shifted about 10 eV to higher energies in going from valence to core ionization. The energy position can be expected to shift a few eV in the opposite direction. This shift, in fact, identifies the near-threshold core ionization shape resonance with the strong shape resonance seen in 7$\sigma$ ionization 3–4 eV above threshold; and (iii), there are close similarities in core ionization of CO$_2$. In this respect it would certainly be interesting to carefully investigate the core levels of the series CO$_2$, OCS, and CS$_2$ and, of course, N$_2$O, directly at, and within the first few eV, above
threshold. Vibrationally resolved studies will be helpful in
examining the possible existence of a shape resonance near
threshold.

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1 See, for example, J. L. Dehmer, A. C. Parr, and S. H. Southworth, in
(North-Holland, Amsterdam, 1987).
2 T. A. Carlson, P. R. Keller, J. W. Taylor, T. Whitley, and F. A.
6 T. A. Ferrett, A. C. Parr, S. H. Southworth, J. E. Hardis, and J. L.
7 F. A. Grimm, T. A. Carlson, J. Jiménez-Mier, B. Yates, J. W. Taylor,
9 J. L. Dehmer, A. C. Parr, S. Wallace, and D. Dill, Phys. Rev. A 26,
3283 (1982).
10 J. L. Dehmer, A. C. Parr, S. Southworth, and D. M. P. Holland,
(1986).
12 G. R. Wight and C. E. Brion, J. Electron Spectrosc. Relat. Phenom. 3,
A 17, 1907 (1978).
14 K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K.
Baez, ESCA Applied to Free Molecules, (North-Holland, Amsterdam,
1969).
16 J. Feldhaus, A. L. D. Kilcoyne, K. J. Randall, M. Schindbauer, and W.
Erlebach (to be published).
17 C. M. Truesdale, D. W. Lindle, P. H. Kobrin, U. E. Becker, H. G.
18 R. B. Kay, P. E. Van der Leeuw, and M. J. Van der Wiel, J. Phys. B 10,
Piancastelli, S. H. Liu, D. A. Shirley, T. A. Carlson, P. C. Deshmukh,
20 U. Becker (private communication).
22 E. Dietz, W. Braun, A. M. Bradshaw, and R. L. Johnson, Nucl.
(1982).
(1986).
25 J. Schirmer, M. Braunstein, and V. McKoy, Phys. Rev. A 41, 283
28 J. Andzelm, M. Koblukowski, E. Radzio-Andzelm, Y. Sakai, and H.
Tatewaki, in Gaussian Basis Sets for Molecular Calculations, edited by S.
29 J. Schirmer (private communication).
ted).
31 D. M. Barrus, R. L. Blake, A. J. Burek, K. C. Chambers, and A. L.