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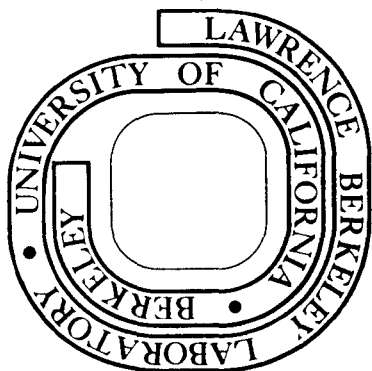
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## K-SHELL CORRELATION-STATE SPECTRA IN FORMAMIDE

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## ABSTRACT

Carbon, nitrogen, and oxygen K-shell correlation-state spectra give detailed qualitative confirmations of predictions by Basch. This prototypical study, with 1s holes on three different elements, shows that  $\pi-\pi^*$  excitations are differentially stabilized according to the location of the 1s hole.

Basch has recently performed multi-configuration self consistent field calculations with configuration interaction on the ground state and certain hole states of formamide [1]. From these he predicted the relative positions and intensities of the correlation-state or "shake-up" peaks accompanying photoionization of K electrons from carbon, nitrogen, and oxygen. The outermost three filled orbitals of planar formamide are described as  $\pi_1^2 n^2 \pi_2^2$ , while the lowest unoccupied orbital is  $\pi_3$ . Basch compared trends in shakeup states corresponding to the excitations  $\pi_2 \rightarrow \pi_3^*$ ,  $\pi_1 \rightarrow \pi_3^*$ , and  $n \rightarrow \sigma^*$  for K shell photoionization from C, N, and O, making qualitative arguments for the calculated variations. The intuitive appeal of these arguments makes an experimental test of the predicted trends very desirable. Their confirmation would provide evidence that correlation-state spectra are well enough understood to be used diagnostically. If this should prove to be the case, it may prove possible to use K-shell holes as "test charges" at different points in the molecule. The response of the outer molecular orbitals to these test changes, as clearly manifest in correlation state peak energies and intensities, could provide insight into the dynamics of electronic distributions during chemical reactions.

In order to compare Basch's calculations with experiment we have taken the XPS spectra of the carbon, nitrogen, and oxygen cores in formamide. The liquid was transferred to a glass bulb in a nitrogen atmosphere, then distilled under vacuum into the sample chamber to remove any trace of water. Mg K $\alpha$  x-rays (1253.6 eV) were used to irradiate the vapor (at  $3 \times 10^{-2}$  torr) above the room temperature liquid. The electron spectra (shown in Fig. 1) were measured on the Berkeley 50 cm radius

magnetic spectrometer with data points  $\sim 0.1$  eV apart. To determine whether any of the peaks arise from electron energy loss due to inelastic scattering, a gold foil was placed in the x-ray beam with formamide vapor between the gold and the entrance slit to the analyzer. Comparison of a gold 4f spectrum taken in this manner to a spectrum of gold with no formamide present shows a small extra peak at 7.6 eV lower kinetic energy, with 2% the relative intensity of each Au(4f) peak. An electron loss peak would be expected at about this energy because the lowest  $\pi \rightarrow \pi^*$  transition in the vacuum ultraviolet spectrum of formamide falls in a series of bands centered at 7.5 eV with a width of about 1 eV [2]. Presumably this is the  $\pi_2 \rightarrow \pi_3^*$  transition. In interpreting our K-level satellite spectra we allowed for this loss peak. It can account for the first weak satellite in the N(1s) spectrum but only for a small fraction of the 7.4-eV oxygen satellite. In the carbon spectrum it appears as a slight shoulder on the 9.5-eV peak.

Basch noted that the  $\pi_1, \pi_2,$  and  $\pi_3$  molecular orbitals (MOs) differ significantly in their distribution of atomic p $\pi$  character. The  $\pi_1$  orbital is roughly equally distributed over C, N, and O 2p atomic orbitals. In the  $\pi_2$  MO the carbon atomic character is very small, but the  $\pi_3$  MO is more concentrated on the carbon atom, with smaller and nearly equal admixtures of nitrogen and oxygen functions. A K hole on a given atom will stabilize orbitals that are concentrated on that atom. Thus Basch predicted that the  $\pi_2 \rightarrow \pi_3^*$  energy difference would be lower in the C(1s) satellite spectrum than in normal formamide, while in the N(1s) and O(1s) spectra the energy of the transition would be increased. Basch's calculations bore this

prediction out theoretically, as indicated in Table I.

The experimental spectra provide strong support for these predictions. Although all three spectra show satellites between 7 and 10 eV, the satellite so dominates the spectrum in the C(1s) case that we feel it should be assigned to the  $\pi_1 \rightarrow \pi_3^*$  transition, which is predicted to lie at 10.1 eV with 8.3% intensity. There is no spectral feature that can be positively identified as a peak in the C(1s) spectrum between the main peak and this intense  $\pi_1 \rightarrow \pi_3^*$  satellite, which lies at 9.6 eV relative energy and has an intensity of 7.2%. The small excursion at 5 eV is too narrow to be a true peak. It is not reproducible as such a well-defined peak, but there appears to be some spectral area at this energy. This would be consistent with the predicted  $\pi_2 \rightarrow \pi_3^*$  peaks of 0.36% and 0.45% intensities, at 3.26 eV and 6.45 eV, respectively. The limited statistical accuracy of this experiment and the possibility of interference by Mg  $K\alpha_{3,4}$  satellites of the peak at 13.8 eV combine to preclude a definite assignment, however.

The 9.9 eV peak of 3.5% intensity in the N(1s) spectrum fits well with the predicted values of 10.32 eV and 4.57% for the  $\pi_2 \rightarrow \pi_3^*$  transition. In the O(1s) case the 7.4 eV, 7.3% peak falls at a lower energy and shows less intensity than the prediction (9.13 eV, 16.81%), but the predicted trend in intensity is qualitatively borne out.

For the C(1s) and O(1s) spectra the next correlation states are expected to arise through the  $\pi_1 \rightarrow \pi_3^*$  excitation. K holes on C, N, or O would stabilize the  $\pi_1$  orbital by similar amounts because this orbital is distributed rather equally on the three atoms. The concentration of the  $\pi_3$  orbital on carbon implies that a K hole on carbon

will stabilize this orbital more than would a nitrogen or oxygen K hole. Thus the  $\pi_1 \rightarrow \pi_3^*$  transition energy should be lower in the C(1s) spectrum than in that of N(1s) or O(1s). The experimental spectra are consistent with this picture. The  $\pi_1 \rightarrow \pi_3^*$  peak is predicted to lie at 10.1 eV in the C(1s) spectrum, with 8.3% intensity. We interpret the observed peak at 9.6 eV, with 7.2% intensity, as the  $\pi_1 \rightarrow \pi_3^*$  peak. In the O(1s) spectrum the second large satellite, at 13.9 eV with 8.5% intensity, fits the predicted parameters (15.4 eV, 8.1% intensity) very well: We assign this peak to the  $\pi_1 \rightarrow \pi_3^*$  transition.

The  $\pi_1 \rightarrow \pi_3^*$  state in the N1s spectrum was predicted to lie at a higher energy than the  $n \rightarrow \sigma^*$  peak, and no intensity was predicted. One of the most intense peaks in the N(1s) spectrum (5% intensity) is the most likely candidate for the  $\pi_1 \rightarrow \pi_3^*$  transition.

Finally, some predictions were made for the  $n \rightarrow \sigma^*$  state. A peak from this state was predicted to lie at 12.4 eV in the N(1s) spectrum with an intensity of 1.76%. There is a shoulder at  $\sim 12.8$  eV in the spectrum, with  $\sim 1.7\%$  intensity. The C(1s) spectrum shows a well-resolved peak at 13.8 eV with 1.8% intensity, while the theoretical predictions are 13.8 eV and 0.5% intensity. In the O(1s) case there is a small peak at 20.6 eV with 1% intensity. This may be the  $n \rightarrow \sigma^*$  state, which was predicted at 19.2 eV (no intensity was predicted). All three of these  $n \rightarrow \sigma^*$  assignments are really only suggestions, both because the theoretical work is incomplete and because the spectra all show very broad features peaking near 20 eV.

These broad features are of some interest. Integration over their total areas would yield the total correlation-state (or "shake-up")



intensities, if it were feasible to ascertain reliably what fractions of their areas arise from intrinsic effects, as distinguished from inelastic energy loss. Unfortunately the intensities available with our spectrometer precluded the pressure-dependence studies that would yield this information. Indirect evidence, the return of the intensity to the baseline at 40-50 eV, analysis of the Au(4f) photoelectron loss spectrum in formamide, and comparison with correlation-state studies in other molecules--indicates that most of the spectral area does, in fact, arise from intrinsic effects. The total integrated area up to 50 eV is 40% of the main peak area in carbon, 41% in nitrogen, and 50% in oxygen. This corresponds to total probabilities for multiple excitation ( $P_M$ ) of 0.29 (C 1s), 0.29 (N 1s), and 0.33 (O 1s).<sup>†</sup> Basch did not calculate  $P_M$  in these three cases, but we may infer from his results that it is large. By comparison, Bagus, et al. [3] calculated  $P_M = 0.42$  for an oxygen 1s hole in  $O_2$ , and  $P_M(N\ 1s) = 0.25$ ,  $P_M(O\ 1s) = 0.28$  in NO.

A graphical summary of the principal results of this work is given in Fig. 2. Only the  $\pi \rightarrow \pi^*$  excitations are included. Basch's calculation provided the incentive for these measurements and were used extensively in their interpretation. Further calculations and experiments, when they become feasible, are clearly desirable. Nevertheless the detailed agreement of experiment with theory is very encouraging at this stage. This agreement indicates that correlation-state spectra can be used to determine the responses of individual molecular orbitals to "test charges"--1s holes--on individual atoms.

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<sup>†</sup>We emphasize that these values are really upper limits, for reasons given above.

- [1] Harold Basch, Satellite Bands and the Ion States of Formamide  
(to be published).
- [2] H. D. Hunt and W. T. Simpson, J. Am. Chem. Soc. 75 (1953) 4540.
- [3] P. S. Bagus, M. Schrenk, D. W. Davis, and D. A. Shirley, Phys.  
Rev. 9A (1974) 1090.

#### Acknowledgement

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Table I. Comparison of theoretical and experimental K-shell correlation-state spectra in formamide.

	Carbon				Nitrogen				Oxygen			
	Theory		Expt.		Theory		Expt.		Theory		Expt.	
	$\Delta E^a$	I <sup>b</sup>	$\Delta E$	I	$\Delta E$	I	$\Delta E$	I	$\Delta E$	I	$\Delta E$	I
(Main Peak)	0	100	0	100	0	100	0	100	0	100	0	100
$\pi_2 \rightarrow \pi_3^*$	3.26	0.36	5?	<0.5	5.52	0.01	9.9(2)	3.5(7)	5.87	0.01	7.4(1)	7.3(4) <sup>c</sup>
	6.45	0.45			10.32	4.57			9.13	16.81		
$\pi_1 \rightarrow \pi_3^*$	8.98	0.09	9.6(2) <sup>e</sup>	7.2(4) <sup>c</sup>	15.66	d	15.0(2)	5.0(8)	13.72	0.79	13.9(3)	8.5(5)
	10.10	8.33			17.06	d			15.37	8.11		
	12.53	0.10			11.70	0.90			19.21	d		
$n \rightarrow \sigma^*$	13.81	0.50	13.8(2) <sup>e</sup>	1.8(3) <sup>e</sup>	12.38	1.76	12.8(4) <sup>e</sup>	1.7(7) <sup>e</sup>				

a Energies in eV.

b Intensities are given as percentage of main peak intensities. The error arises partly from the uncertainty in the base line which was drawn with consideration for the broad band centered at about 22 eV.

c After correction for 2% of main peak intensity arising from 7.5 eV inelastic energy loss peak (see text).

d Not calculated.

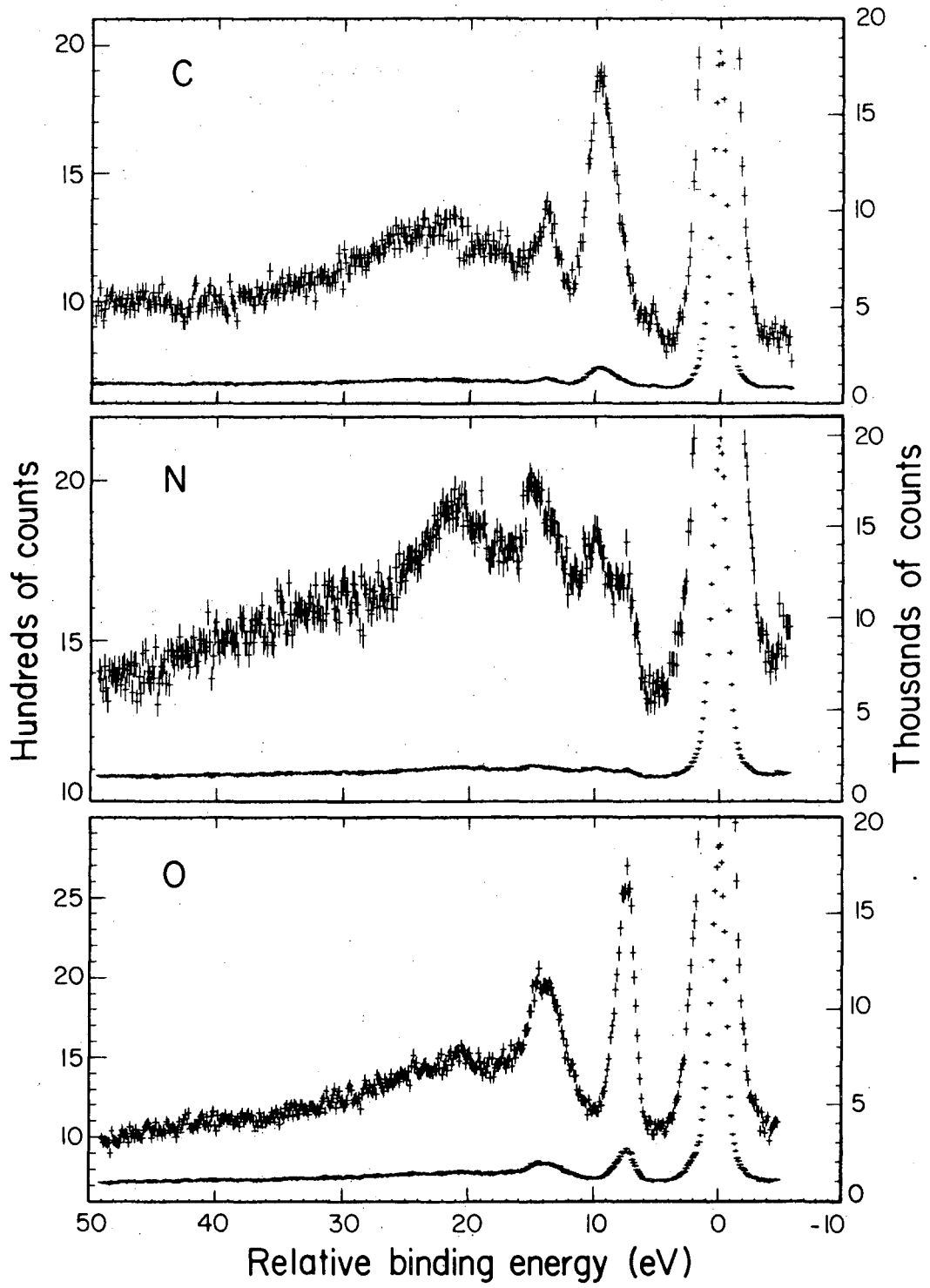
e The interpretation of  $n \rightarrow \sigma^*$  features is highly tentative. See text.

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Figure Captions

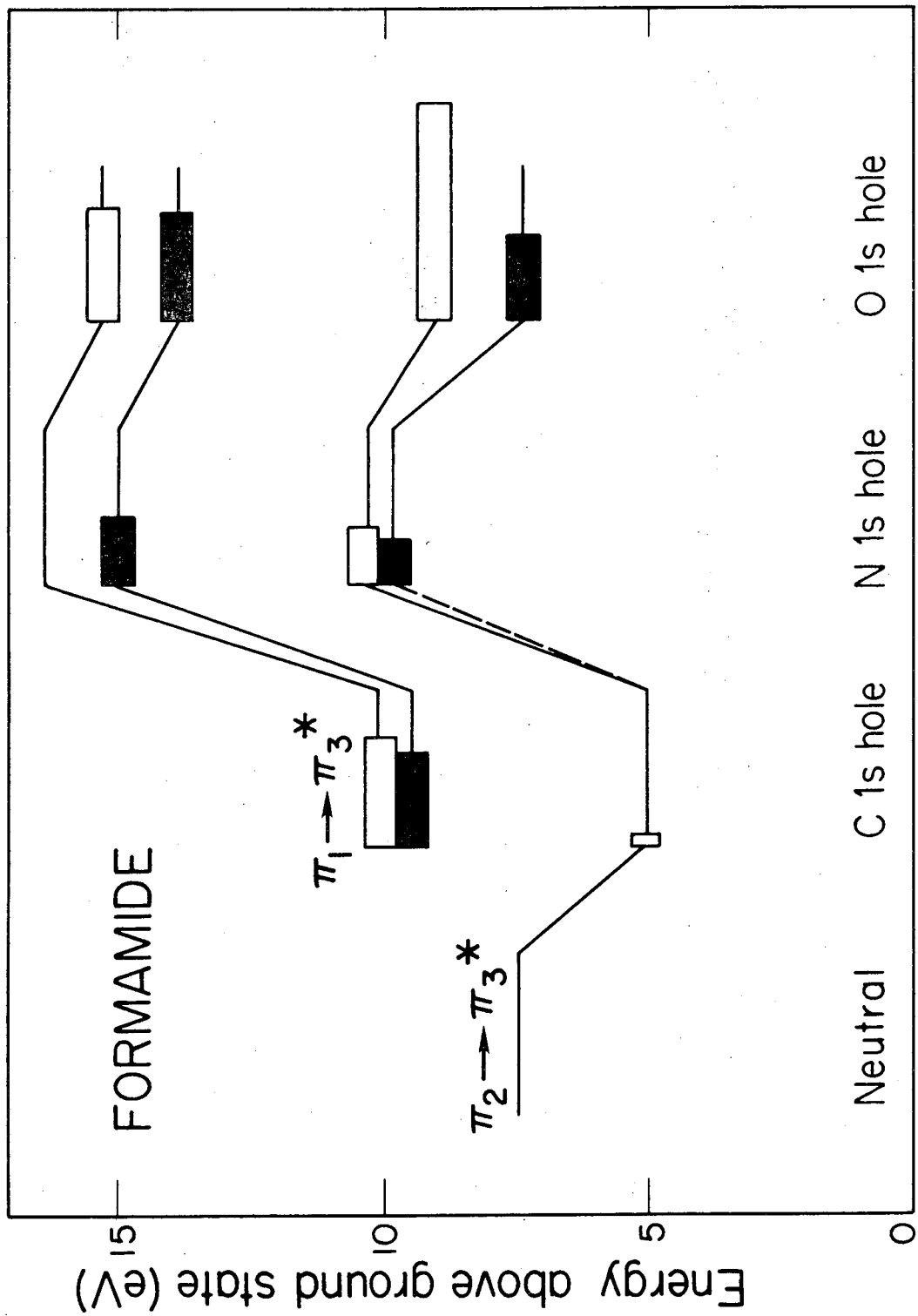
Fig. 1. Correlation-state spectra of the C(1s), N(1s), and O(1s) hole states in gaseous formamide at room temperature and  $3 \times 10^{-2}$  torr pressure, excited by Mg K $\alpha$  radiation. The right scale refers to the complete spectrum; the left, to the expanded spectrum.

Fig. 2. Systematic variations of  $\pi_2 \rightarrow \pi_3^*$  and  $\pi_1 \rightarrow \pi_3^*$  excitation energies and intensities in gaseous formamide. Where available, intensities are denoted by (horizontal) lengths of wide bars: open figures denote calculated values, filled figures, experimental results. The low excitation energies accompanying C(1s) ionization are attributed to stabilization of the  $\pi_3$  orbital, which is largely C(2p) in character, by the (positive) hole.



XBL 7511-9555

Fig. 1



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Fig. 2

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