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Publication Date
1983

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to Physical Review Letters

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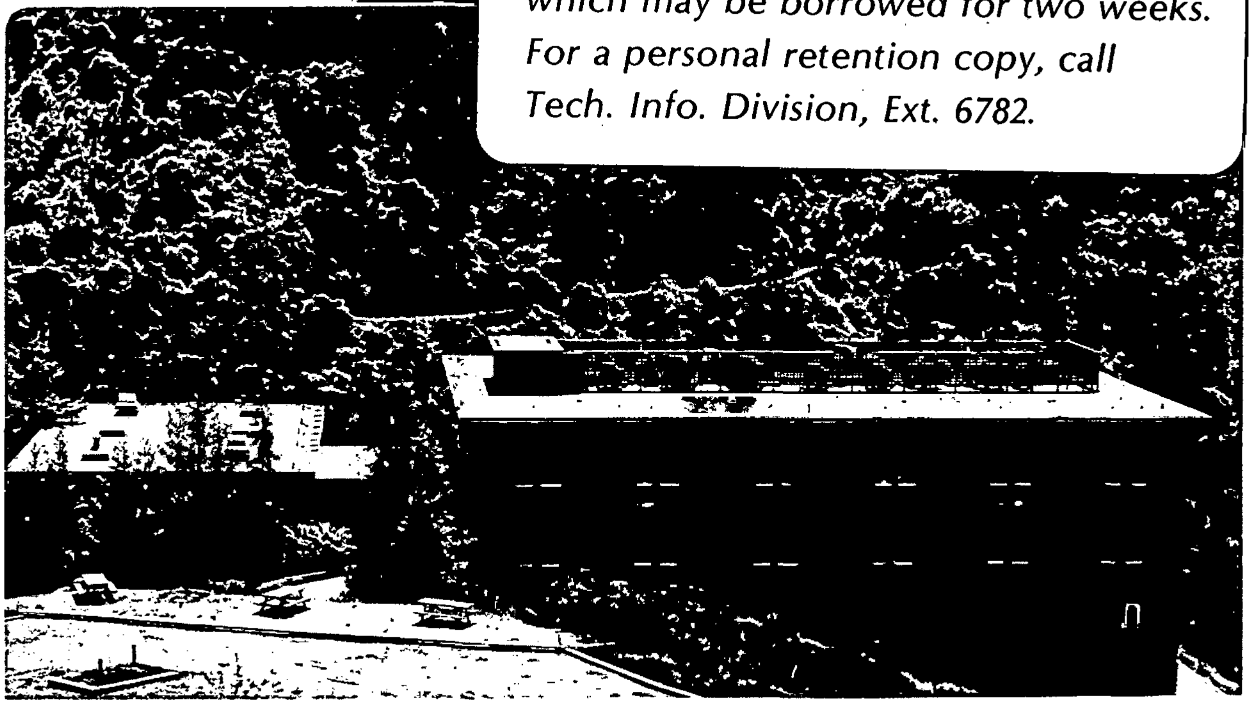
January 1983



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-12873

SHAPE RESONANCE PHENOMENA IN CO FOLLOWING K-SHELL PHOTOEXCITATION

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ABSTRACT

Electron cross sections and asymmetries following photoexcitation of the CO K-shells were measured directly. Energy analysis of ejected electrons yielded cross sections exhibiting σ shape resonances in the C(1s), C(KVV), and O(1s) channels, and a π resonance in the C(KVV) channel, confirming earlier indirect measurements. Asymmetry measurements showed a σ shape resonance in the C(1s) channel, in good agreement with the predictions of Dehmer and Dill. The C(KVV) π resonance showed nearly isotropic behavior.

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Dehmer and Dill[1] and Dill et al.[2] have predicted shape resonance phenomena in the vicinity of the carbon and oxygen K-edges of CO for the following parameters:

1. the photoelectron cross sections, $\sigma(C1s)$ and $\sigma(O1s)$,
2. the photoelectron asymmetry parameters, $\beta(C1s)$ and $\beta(O1s)$, and
3. the Auger orientation parameters, $\beta_m(CKVV)$ and $\beta_m(OKVV)$.

In this Letter, we report the first direct measurements of these parameters by photon excitation of a gaseous sample. Carbon monoxide was chosen so that our results could be compared to published theoretical predictions,[1-4] as well as to related experiments.[5-11] This prototype experiment also illustrates some of the issues which will arise as synchrotron radiation sources become more widely available for studying core-level shape-resonance phenomena.

Beam Line III-1 at the Stanford Synchrotron Radiation Laboratory (SSRL) provided a variable-energy photon source for the energy range ($275\ \mathrm{eV} \leq h\nu \leq 630\ \mathrm{eV}$) used in this work. A "grasshopper" monochromator with a 1200 line/mm grating and 20 micron entrance and exit slits yielded monochromatic radiation with an energy resolution of 0.5 eV FWHM at $h\nu = 300$ eV. A 1500Å thick aluminum window separated the sample chamber from the ultra-high vacuum of the monochromator. Two time-of-flight electron analyzers, coupled with the excellent time structure of the SPEAR storage ring, permitted simultaneous measurement of the entire electron spectrum. By placing the two detectors at angles of $\theta = 0^\circ$ and $\theta = 54.7^\circ$ relative to the photon polarization direction, we were able to determine both the total cross section $\sigma(\varepsilon)$ and the asymmetry parameter $\beta(\varepsilon)$, which are related to the differential cross section $d\sigma/d\Omega$ by

$$\frac{d\sigma(\varepsilon,\theta)}{d\Omega} = \frac{\sigma(\varepsilon)}{4\pi}\left[1 + \beta(\varepsilon)P_2(\cos\theta)\right],$$

where ε is the electron kinetic energy and $P_2(\cos\theta)$ is the second Legendre polynomial.

The primary goal of this initial experiment was a survey of shape-resonance phenomena near the carbon K-edge. Figure 1 shows the electron spectrum at $h\nu = 315$ eV, after conversion from time-of-flight (TOF) to kinetic energy. The presence of second-order light made it possible to report fragmentary data above the oxygen K-edge as well.

The carbon K-edge Auger results are shown in Figure 2. The KVV Auger spectrum is complicated,[12] and is, of course, different above and below the carbon 1s ionization threshold at 295.9 eV. Because the individual Auger lines are substantially unresolved in the TOF spectra, we report only spectrum-integrated parameters.

The Auger yield (Fig. 2a) shows a sharp π resonance of width 0.5 eV (FWHM) at $h\nu = 287.3$ eV,[6,8] in complete accord with electron-ion coincidence results,[6] shown by the dashed curve. The σ shape resonance, peaking at $h\nu = 305$ eV, shows similar agreement. This work also confirms the production of Auger electrons from excitation in the range 290 eV $\leq h\nu \leq$ 296 eV, below the carbon 1s ionization threshold.

The Auger asymmetry (Fig. 2b) should be interpreted with the Auger yield (Fig. 2a) in mind. There are four qualitatively different energy ranges. First, below 285 eV there is no Auger intensity. Second, in the π-resonance region around 287.3 eV, β is slightly positive, but very near zero. The resonantly-excited $CO^*(^1\Pi)$ state, which is the initial state for the KVV Auger transitions, must be aligned perpendicular to the photon polarization vector.[2] The near-zero average β may be attributable to near cancellation of the various unresolved Auger branches, a possibility which should be checked by high-resolution studies. Another possibility is that the excited electron is essentially a "spectator" in a weakly-coupled π^* orbital, and that both the intensities and the angular distribution asymmetry parameters of the Auger channels are dominated by the isotropy of the hole in the carbon 1s shell.

In the third region, above the π resonance and below the 1s ionization threshold at 295.9 eV, there are several discrete resonances. The small maximum in β of the carbon Auger in the range 292-295 eV indicates a net alignment in these resonances. Finally above 296 eV, the Auger process is "conventional", with the initial state being a carbon 1s hole. Dill et al.[2] have predicted an orientation parameter β_m that varies according to the curve in Fig. 2b, because of the σ shape resonance. The asymmetry parameter β_i for a given Auger channel should vary as the product $\beta_m A_i$, where A_i is independent of photon energy. The average asymmetry parameter of all the carbon KVV Auger $\overline{\beta(h\nu)}$, should vary as

$$\overline{\beta(h\nu)} = \beta_m(h\nu)\bar{A} = \beta_m(h\nu) \sum_i f_i A_i ,$$

where f_i is the fractional intensity in channel i. Thus, the observed β should show a variation with hν that is proportional to the β_m curve, with proportionality constant $\bar{A}$ (which could be zero). In fact, our data do not show this behavior: $\bar{\beta}$ is near zero, but is essentially flat and slightly positive, with most points falling in the range $0.0 \leq \beta \leq 0.2$. This disagreement is puzzling and inescapable, especially so because our $\bar{\beta}$ data give no indication of crossing zero near hν = 300 eV. Because $\bar{\beta}$ is so close to zero, we are reluctant to assert that $\bar{A}$ is not actually zero, which would reconcile theory and experiment. Clearly more work on this point is needed.

The carbon 1s results, in contrast, are readily interpreted. The cross section peaks near 305 eV, as shown by the filled circles in Fig. 3a. This result is in good agreement with the electron-ion coincidence results,[6] shown as open circles. There is good agreement with the Stieltjes-Tchebycheff Moment Theory (STMT), shown as the solid curve, and there is qualitative agreement with the multiple-scattering Xα results.[1]

Fig. 3b shows the carbon 1s asymmetry parameter β(hν) together with predictions based on multiple-scattering Xα theory by Dill et al.[2] and by Grimm.[3] The experimental β(hν) varies through only about two-thirds of the predicted ranges, and the minimum is slightly less pronounced. The overall agreement with theory is very good, however, providing the first confirmation of the predicted shape resonance interference phenomenon in β of molecular K-shells.

Fig. 4 shows incomplete results for the oxygen K-edge, based on both first-order and second-order light. The oxygen 1s cross section data, shown as filled circles in Fig. 4a, show generally good agreement with photoabsorption results[13], shown by the open circles [to which our data were scaled at 545 eV (2nd order) and 562 eV (1st order)], and a STMT calculation by Padial et al.,[4] shown as the solid curve. Our low-energy $\beta(h\nu)$ results (Fig. 4b) do not confirm the predicted decrease toward a minimum predicted by Dill et al.[1] at 552 eV or by Grimm[2] at 555 eV. Our data are sparse in this range, however. At higher energies, $\beta(h\nu)$ approaches a constant value of about 1.6, in agreement with theory.

In summary, this work has given the first direct measurements of molecular core-level photoelectron and Auger cross sections and asymmetry parameters. The cross sections exhibited shape resonances, in agreement with energy-loss results. The integrated carbon KVV Auger asymmetry was essentially zero for the π resonance and slightly positive but very small over the σ resonance. The carbon 1s photoelectron asymmetry showed a broad minimum, in good agreement with theoretical predictions, while the oxygen 1s asymmetry did not, based on incomplete data. This work combined with the available theoretical predictions provides early evidence that these asymmetry parameters will be readily measurable, theoretically tractable, and sensitive to subtle features of molecular potentials.

Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. It was performed at the Stanford Synchrotron Radiation Laboratory, which is supported by the NSF through the Division of Materials Research. One of us (H.G.K.) would like to acknowledge support by a Wigner fellowship.

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Figure Captions

FIG. 1. TOF photoelectron spectrum of CO^+ showing the C1s peak, the O1s peak from second-order light ($h\nu = 630$ eV), the CKVV Auger (B-1), valence photoelectrons (V), the C1s(2nd order), and the OKVV Auger (B-5). The notation of the CKVV Auger and OKVV Auger peaks is that of Moddeman et al. In this time-of-flight spectrum, the energy resolution is 3% of the kinetic energy ε, and the data density varies as $\varepsilon^{-3/2}$.

FIG. 2. (a) Measured C(KVV) cross section (open and filled circles), and the electon-ion coincidence measurements of Kay et al. (x16, dashed curve). (b) The measured C(KVV) asymmetry (filled circles) and the orientation parameter β_m calculated by Dill et al. (solid curve).

FIG. 3. (a) Measured C1s cross section (filled circles), the electron-ion coincidence measurements of Kay et al. (open circles), the STMT results of Padial (solid curve), and the multiple-scattering results by Dehmer and Dill (dashed curve). (b) Measured C1s asymmetry (filled circles), and the multiple-scattering results of Dill et al. (solid curve) and Grimm (dashed curve).

FIG. 4. (a) Measured O(1s) cross section (filled circles), the photoabsorption results of Barrus et al. (open circles), and the STMT results of Padial et al. (solid curve). (b) Measured O(1s) asymmetry (filled circles), and the multiple-scattering results of Dill et al. (dashed curve) and Grimm (solid curve).

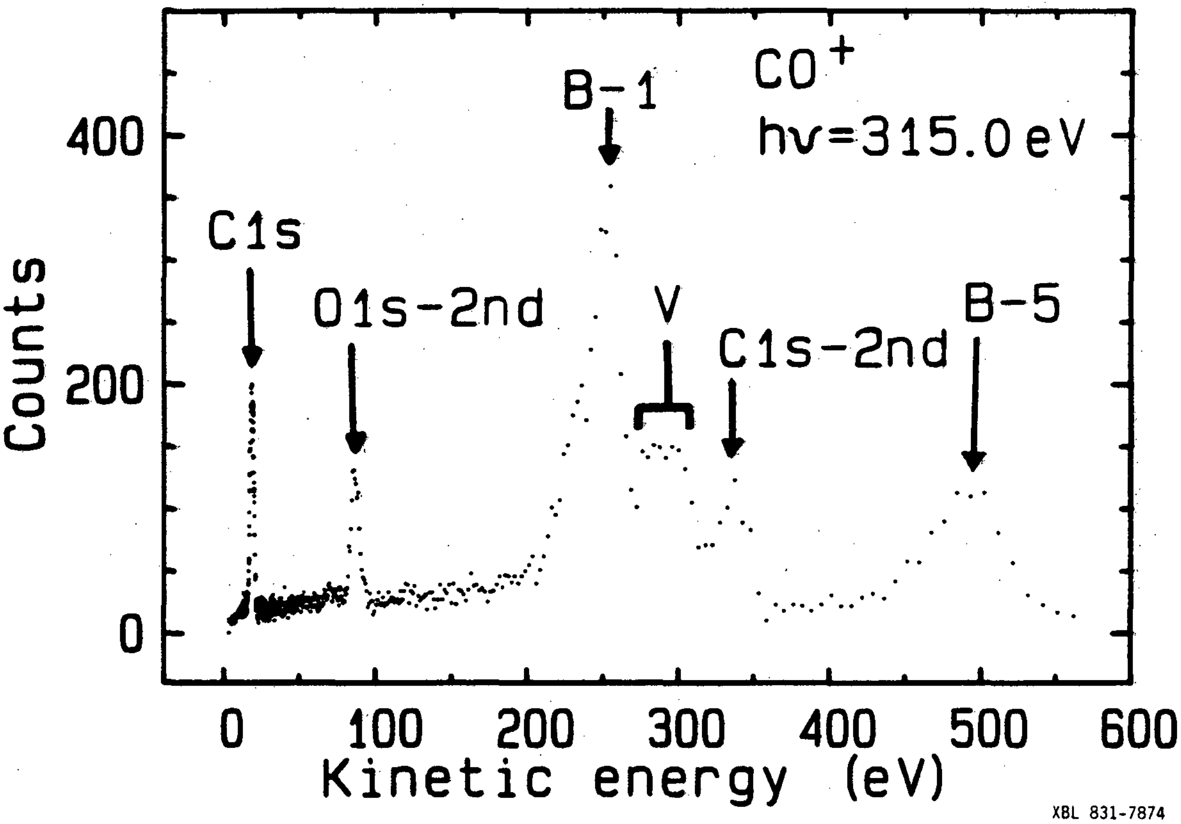

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Figure 1

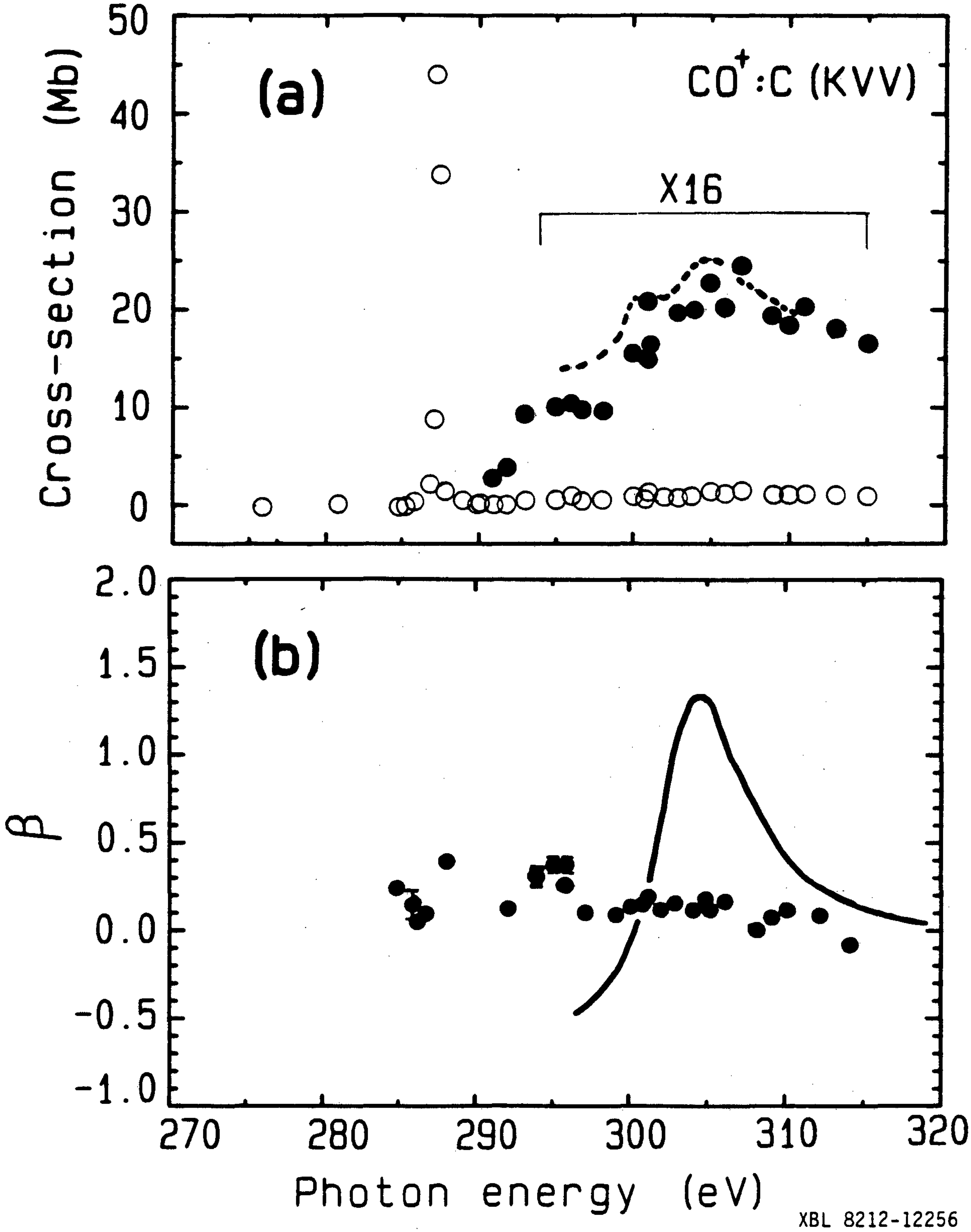

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Figure 2

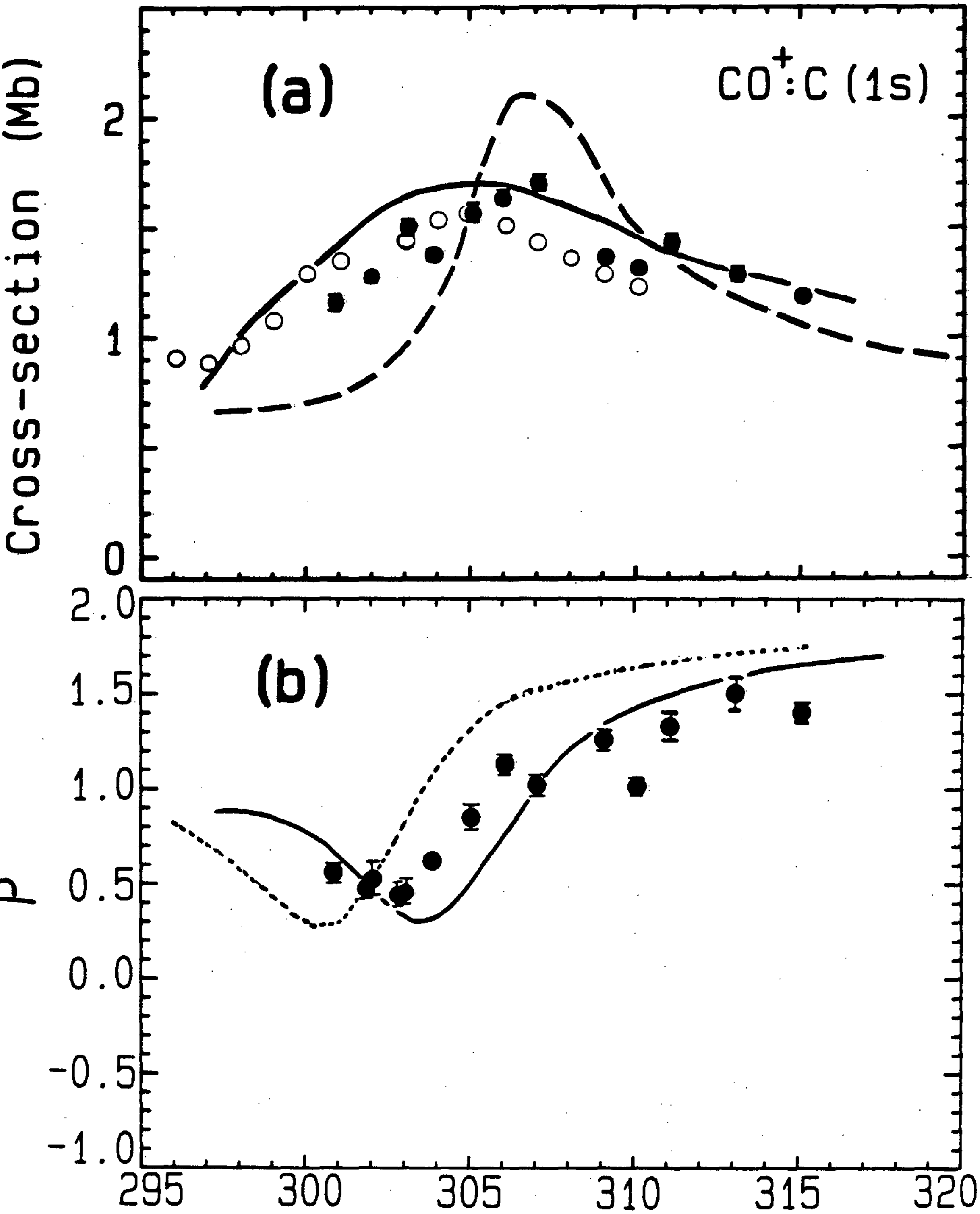

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Figure 3

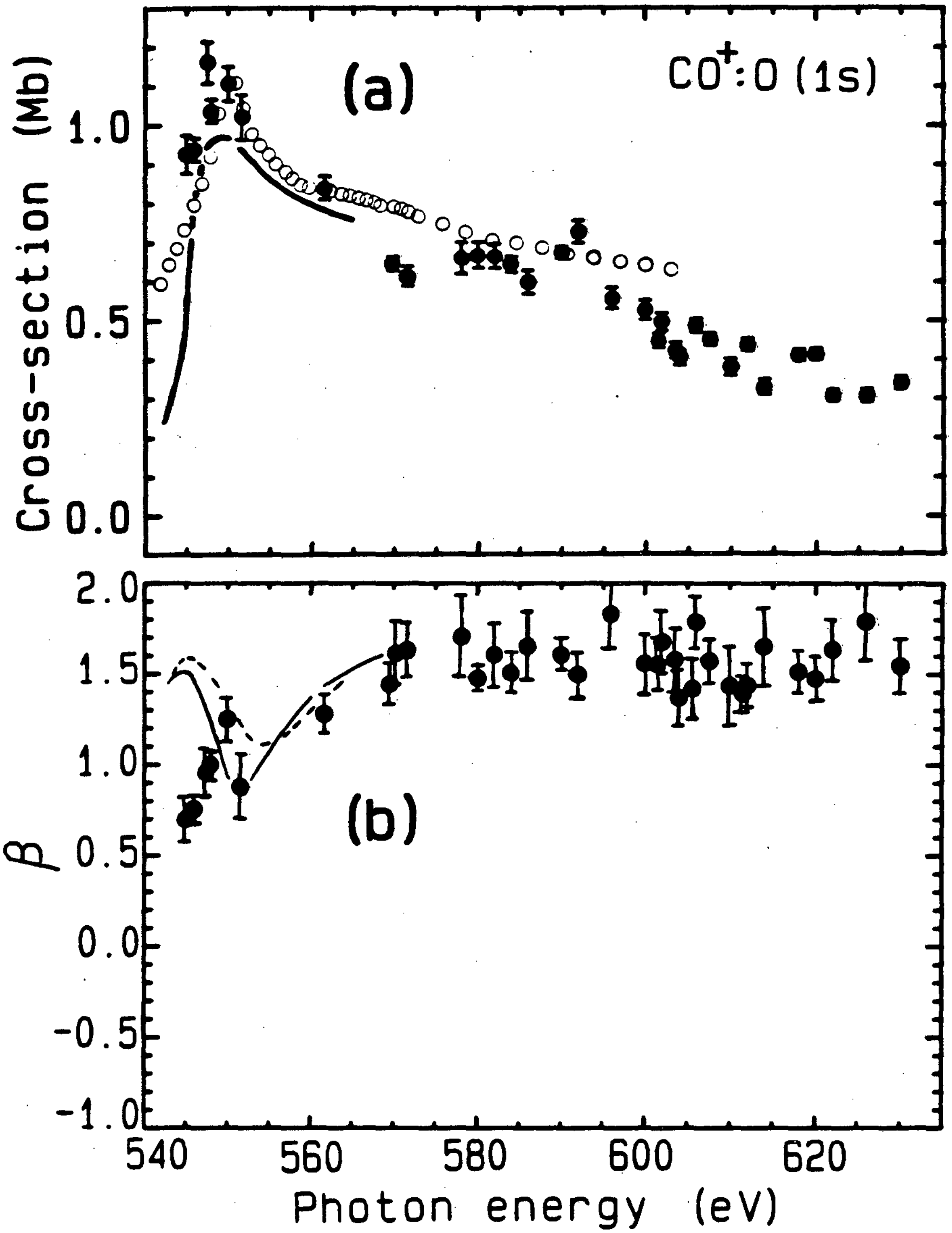

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Figure 4

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