Partial photoionization cross sections of CO_2 between 20 and 40 eV studied with synchrotron radiation

T. Gustafsson and E. W. Plummer
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

D. E. Eastman and W. Gudat*
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 23 June 1977)

The partial photoionization cross sections for the four lowest-lying states of CO_2^+ have been measured with synchrotron radiation between 20 and 40 eV. The results are compared to previous photoemission measurements at discrete photon energies as well as fluorescence measurements using continuous radiation. The interrelation between photoemission and fluorescence data is discussed. The existence of four weak states of CO_2^+ with binding energies between 22 and 37 eV is verified. The dominant part of the photo-current at 40 eV is found to be associated with low-lying ionic states.

I. INTRODUCTION

Photoemission has proven to be a very powerful tool for the study of the electronic structure of gases and solids and their interactions with each other. One of the most significant technical developments has been the increasing use of synchrotron radiation which is a polarized intense continuum light source.[1] Studies of gases and solids are closely related as an understanding of the photoelectric properties of chemisorbed molecules must be based on an understanding of the same properties of the free molecule.[2] The present paper, which deals with the CO_2 molecule, is one of a series devoted to the study of the photoemission spectra of simple gases using synchrotron radiation.[3-6] It is hoped that this work will provide some insight into the basic mechanisms for interaction of photons with molecules and in addition serve as reference data for surface studies.

The two quantities that are most easily accessible for study with photoemission are the ionization potentials (electron binding energies) and the strength of the transitions to various ionic states (the partial cross sections). In most cases ionization potentials[7,8] are determined using only a few photon energies, usually He I ($\hbar\omega = 21.2$ eV) or He II (40.8 eV) for valence orbitals[7] and Mg $K\alpha$ (1254 eV) or Al $K\alpha$ (1486 eV) for core levels.[8] Cross-section determinations should, on the other hand, ideally be performed continuously as a function of photon energy. Conventional continuum light sources (e.g., the Hopfield continuum) have only sufficient intensity to allow a determination of partial cross sections below approximately $\hbar\omega = 20$ eV. To measure partial cross sections one has to be able to discriminate between different states of the ion, e.g., by determining the energy of the outgoing electron. With conventionally designed electron energy analyzers this means that a high-intensity continuously variable stable light source is needed. Synchrotron radiation from electron storage rings fulfills all these requirements.[4]

Partial photoionization cross sections can of course also be studied with discrete line sources.[9] However, especially above 25 eV, such sources are often weak and widely separated in energy. An alternate method to determine partial photoionization cross sections is $(e, 2e)$ spectroscopy.[10] A third method that has been proposed is to study the fluorescent decay (when present) between different excited ionic states and the ground state of the ion.[11] There does not appear to exist a consensus in the literature as to the basic mechanisms involved in this process in CO_2.[11,12] This question will be discussed in relation to our results in Sec. IV.

The four lowest-lying states of CO_2^+ are the $X\ ^2\Pi_g$ state (adiabatic ionization potential 13.79 eV), $A^2\Pi_u$ (17.72 eV), $B^2\Sigma_u^+$ (18.08 eV), and $C^2\Sigma_g^+$ (19.40 eV).[7] In one-particle terms, these states correspond to the removal of an electron from the $1\pi_g$, $1\pi_u$, $3\sigma_u$, and $4\sigma_g$ orbitals. The vibrational progressions of the A and B states overlap and these states are not resolved separately in our spectra (see Fig. 1). There are also several higher-lying states. These are much weaker than the low-lying states in the $20 \leq \hbar\omega \leq 40$-eV range.

II. EXPERIMENTAL

A. Synchrotron radiation as a continuum light source

As discussed earlier,[4] synchrotron radiation has great advantages for studies of partial photoioniza-

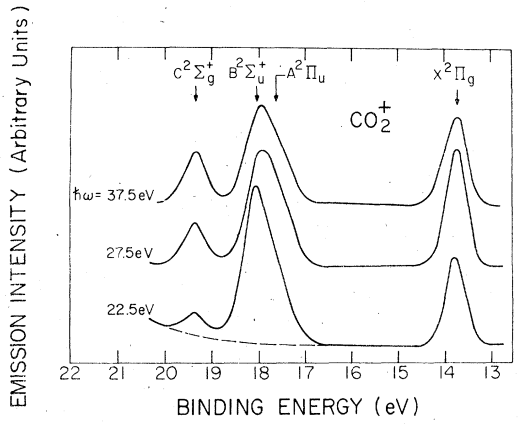

FIG. 1. Photoelectric energy-distribution curves for CO_2 for three difference photon energies. The adiabatic ionization potentials of the four lowest-lying states are indicated with arrows. The dashed line represents an estimated background. The three curves are not normalized in height relative to each other. Note the movement of the second peak towards lower binding energy as the photon energy is increased. This is due to an increase of the cross section of the A state relative to the B state.

tion cross sections. These advantages are of two kinds: First, due to its tunability, synchrotron radiation allows us to study branching ratios in a much more systematic fashion than with conventional light sources, i. e., at arbitrary photon energy. Second, with a continuous wavelength source (as opposed to a line source) it is possible to sacrifice resolution for intensity. The longest sweeping time used in the present work (for the data to be discussed in Sec. III C) was of the order of 30 min at a total experimental resolution of 0.6 eV. This is to be compared with sweeping times of 4 to 5 days with a total experimental resolution of 0.07 eV for a comparable study with a line source.[12]

B. Energy-distribution curves and constant-ionic-state measurements

The kinetic energy E_{ke} of a photoemitted electron is given by

$$E_{ke} = \hbar\omega + E_0 - E_{ion}^i \ , \qquad (1)$$

where $\hbar\omega$ is the photon energy, E_0 is the total energy of the neutral molecule in its ground state, and E_{ion}^i is the total energy of the ion in the ith excited state. In the most common type of photoemission experiment $\hbar\omega$ is kept fixed and E_{ke} is swept. One then obtains information about the quantity $E_0 - E_{ion}^i$ for the various ionic states, that is the ionization potentials, as well as the transition strengths for one photon energy at a time. This type of measurement is referred to as an energy-distribution curve (EDC). In another type of experiment[4, 13] the difference $\hbar\omega - E_{ke}$ is kept fixed, while $\hbar\omega$ is swept. $E_0 - E_{ion}^i$ then correponds to a fixed ionic state. This measurement then, in principle, allows us to measure directly the partial cross section as a function of photon energy. This type of measurement is referred to as a constant ionic state[4] or constant initial state[13] (CIS). This method is obviously very helpful in following the rapid changes in photoionization cross sections that occur, for example, at autoionization lines.[4]

The majority of the data presented in the present paper are based on EDC's. The cross-section information from the CIS's is at present qualitative and not quantitative in nature. This is due to the fact that our spectra (CIS's and EDC's) are distorted at low kinetic energies ($\lesssim 5$ eV) by a background of low-energy electrons photoemitted by light hitting the magnetic shield surrounding the energy analyzer. This background is easy to separate out from the EDC's but not from the CIS's. In addition, the CIS's are distorted by spectral variations of the photon flux from the monochromator with wavelength. This distortion is approximately compensated for by dividing the measured signal by the current from an Al photodiode which intercepts the light beam from the monochromator after the light has interacted with the gas. The quantum efficiency of the diode varies with photon energy.[4] Since the CIS data in this paper will only be used to identify strong absorption lines, we have not corrected them for either of these two distorting factors.

C. Apparatus

The experimental setup has been described in some detail elsewhere[4, 14] and will therefore only be discussed briefly here.

Light from the 240-MeV electron storage ring at the Synchrotron Radiation Center of the Physical Sciences Laboratory at the University of Wisconsin is dispersed with a 1-m horizontally mounted Seya-Namioka monochromator. The wavelength resolution of the monochromator is externally variable in steps between 1.6- and 16-Å full width at half-maximum (FWHM). The photoemitted electrons are energy anlayzed with a two-stage cylindrical mirror energy analyzer. The angle between the analyzer and the direction of the light beam is such that a systematic geometry-dependent error is introduced in the branching ratio measurement due to the angular dependence of the photoelectrons.[4] This is due to the fact that the analyzer does not integrate over all emission directions. The error is

fairly small, however, as the collected solid angle is large. If the true branching ratio is B_0 and the angular asymmetry parameter is β, the measured branching ratio B_m is[4]

$$B_m \approx B_0(1 - 0.16\beta) . \quad (2)$$

Earlier, we have estimated the magnitude of this error for CO and N_2 at $\hbar\omega = 21.2$ eV to be between 4% and 8%, depending on the ionic state. This is well within the spread in published branching ratios at this photon energy.[4] The β values for CO_2^+ have been measured by Carlson *et al.* at $\hbar\omega = 21.2$ eV to be -0.2 for the $X\,^2\Pi_g$ state, $+0.7$ for the $A\,^2\Pi_u$, -0.5 for the $B\,^2\Sigma_u^+$, and $+1.2$ for the $C\,^2\Sigma_g^+$ states.[15] As the A and B states are not resolved in our spectra, we expect the difference between B_0 and B_m to be significant at $\hbar\omega = 21.2$ eV only for the C state with our geometry.

The experimental chamber is pumped with a turbomolecular pump. This pump contributes a significantly smaller background of ions and electrons than did the ion pump used in previous work.[4] The gas is admitted to the chamber via a capillary tube of 1 mm diameter. The energy analyzer is carefully positioned at the intersection point of the light beam and the gas beam from the nozzle. The pressure at this point is estimated to be between 10^{-3} and 10^{-4} torr. The differential pumping over the slits in the monochromator isolates the experimental chamber from the storage ring without the use of windows.

The energy analyzer is run at a high pass energy ($E_p = 40$ eV) in order to avoid distortion of the spectra due to variations in collection efficiency with electron kinetic energy.[4,16] The energy resolution ΔE of this analyzer is roughly $\Delta E = 0.008E_p$. This means that we cannot clearly resolve the A and B states in CO_2^+ since their adiabatic ionization potentials only differ by 0.36 eV.[7] Some spectra were, however, obtained at a lower pass energy ($E_p = 12$ eV) to separate A and B. As the binding energies of these states differ by less than 1 eV, the transmission of the analyzer will not vary greatly over the width of this band. Reasonably accurate determinations of the ratio of the A and the B states are thus obtained.

The signal from the energy analyzer was directly plotted with an XY recorder using a simple ratemeter counting system. The data on the higher-lying states presented in Sec. III C was, however, obtained via signal averaging with a multichannel analyzer.

III. RESULTS

A. Low-lying states of CO_2^+

Some representative energy distributions (EDC's) are shown in Fig. 1. The data are plotted as a function of binding energy to facilitate comparison between data for different photon energies. As mentioned above, the A and B states overlap in the photoelectron spectrum and are not resolved separately here.

The area under the peaks in EDC's such as those in Fig. 1 were measured in order to calculate the branching ratios. The results for the photon energy range from 20 to 40 eV are shown in Fig. 2. Below 20 eV there are many rapid variations of the cross sections due to autoionization. Some examples of this will be discussed in Sec. III C.

The total photoabsorption cross section for CO_2 has been measured continuously between 180(~70 eV) and 700 Å(~18 eV) by Lee *et al.*[17] The photoionization efficiency (η) has been determined by Cairns and Samson at more than 20 lines between 300(~40 eV) and 630 Å(~20 eV).[18] Their measurements indicate a η value of 1 (within the experimental error). We therefore take the photoionization efficiency to be 100% between 20 and 40 eV. Thus, by multiplying the branching ratios in Fig. 2 with the photoabsorption data by Lee *et al.*,[17] we obtain the partial photoionization cross sections shown in Fig. 3.

The summed cross sections of the A and B states vary quite appreciably over the range investigated. The X state is roughly constant, showing some weak structure. The C state increases from threshold. Its cross sections at $\hbar\omega = 40$ eV is more than twice the cross section at $\hbar\omega = 20$ eV. It is obvious from Fig. 3 that the significant fall off of the total photoabsorption cross section between 20 and 40 eV (Ref. 17) cannot be attributed to the X or to the C state.

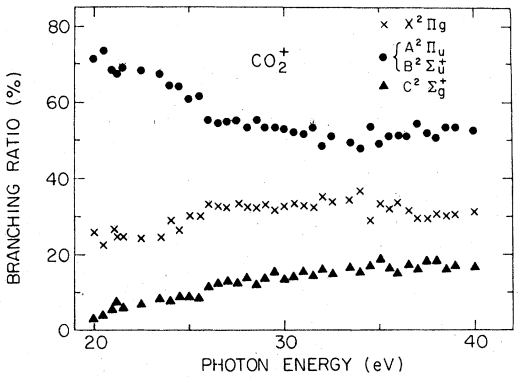

FIG. 2. Branching ratios for the three peaks in Fig. 1 as a function of photon energy. These branching ratios contain a β dependence described by Eq. (2). The influence on the branching ratios from higher-lying states, which is small, is not included in this plot (see Sec. III C). Hence, the branching ratios for the X, A, B, and C states will add up to 100% in this plot.

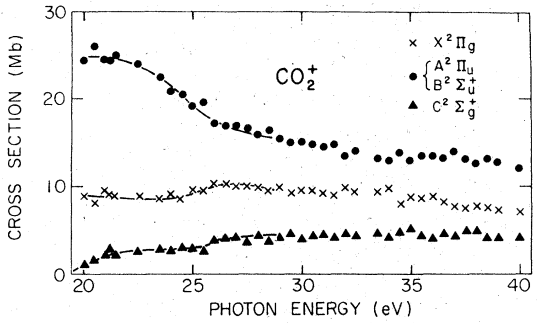

FIG. 3. Partial photoionization cross sections for CO_2. These data are not corrected for the variations of β between different photon energies and different ionic states. Neither is the (small) influence of higher-lying states taken into account (see Sec. III C). Hence, the cross sections for the X, A, B, and C states will add up to the total photoionization cross section in this plot.

B. Comparison with other branching-ratio data

1. Fluorescence

A proposed alternate way of determining partial photoionization cross sections is to measure the fluorescence when the excited ion decays to the ground state by emitting a photon. This method is obviously limited to excited states that decay by photon emission. It is, for example, well known that the $C\,^2\Sigma_g^+$ state of CO_2^+ decays by fragmentation.[9]

Lee *et al.* have measured the fluorescence yield for the $A\,^2\Pi_u - X\,^2\Pi_g$ transition in CO_2^+.[19] Carlsson *et al.* have measured the yield for the $B\,^2\Sigma_u^+ - X\,^2\Pi_g$ transition.[20] We have added their results and compare them in Fig. 4 to our branching ratio for the

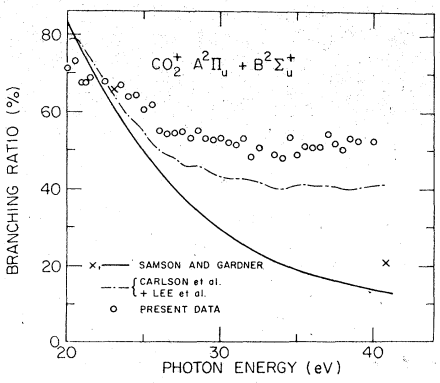

FIG. 4. Comparison of our data for the A and B states (○) from Fig. 2 with other measurements. The full curve is the fluorescence data by Samson and Gardner (Ref. 21) for the sum of the A and B states. The dash-dotted curve is the sum of the fluorescence data for the $A \rightarrow X$ transition by Lee *et al.* (Ref. 19) and the $B \rightarrow X$ transition by Carlson *et al.* (Ref. 20). The crosses denote the photoemission data by Samson and Gardner (Refs. 12 and 23).

$A+B$ states. The agreement is quite good, especially at lower photon energies. The agreement would be even better if we were to correct our data for the influence of the higher-lying ionic states. As we will show below, our data indicate that their contribution to the total photoionization cross section is less than 10% at 40 eV. Hence, some, but not all, of the difference between our data and the fluorescence data would be removed. Also included are the data for the total fluorescence yield ($A \rightarrow X$ plus $B \rightarrow X$) by Samson and Gardner.[21] There is little agreement with their data. The origin of this discrepancy is not understood. We note that the data of Samson and Gardner[21] also disagree with those of Refs. 19 and 20.

2. Photoemission

In Table I A we compare our data at $\hbar\omega = 21.2$ eV and $\hbar\omega = 21.0$ eV to those of Samson and Gardner[12] and Bahr *et al.*[22] at $\hbar\omega = 21.2$ eV. The agreement with Samson and Gardner[12] is good, whereas the agreement with Bahr *et al.*[22] is rather poor, especially for the X state. By decreasing the pass energy we could obtain an estimate for the ratio between the A and the B state at $\hbar\omega = 21.2$ eV. The result was $A/B = 0.7$ in good agreement with Samson and Gardner's result 0.65 ± 0.05.[12] In Table I B we also compare our data at $\hbar\omega = 22.5$ and 23.5 eV to Samson and Gardner's[12] data at 23.1 eV. The agreement is excellent.

In Fig. 4 we have also included the $A+B$ branching ratio measured by Samson and Gardner photoelectrically at $\hbar\omega = 40.8$ eV.[12,23,24] As was the case with the fluorescence data in this photon energy range, their photoelectron branching ratio differs very strongly from our data. We will show below that this is due to the fact that they give very large weight to the high lying ionic states. In order to obtain a meaningful comparison at high photon energies we have renormalized their data so that the sum of the X, A, B and C states is 100%. This agreement is then quite good (Table I C). Also shown are the (likewise-renormalized) data by Potts and Williams,[25] which show a quite different $X/(A+B)$ ratio.

C. High-lying states

Our data at $\hbar\omega = 40$ eV show, in addition to the four states discussed above, five higher-lying states. They correspond to electron binding energies of 22.8, 27.3, 31.3, 35.1, and approximately 38 eV. The last state corresponds to emission from O 2s derived orbital(s).[23,25,26] The binding-energy determination of the last state is somewhat uncertain due to the background problems discussed above. The four remaining peaks have to be

TABLE I. Branching ratios for CO_2^+.

	$X\,^2\Pi_g$	$A\,^2\Pi_u + B\,^2\Sigma_u^+$	$C\,^2\Sigma_g^+$
A. $\hbar\omega$ = 21.2 eV			
Bahr *et al.* (Ref. 22)	14.5	80.4	5.1
Samson and Gardner (Ref. 12)	22.6	73.9	4.3
This work	25.0	67.6	7.4
This work ($\hbar\omega$ = 21.0 eV)	26.5	67.7	5.8
B. $\hbar\omega$ = 23.1 eV			
Samson and Gardner (Ref. 12)	26.6	65.6	7.8
This work [a]	24.8	67.4	7.8
C. $\hbar\omega$ = 40.8 eV			
Samson and Gardner (Refs. 12 and 23) [b]	26.1	57.4	16.5
Potts and Williams (Ref. 25) [b,c]	46.7	41.1	12.1
This work ($\hbar\omega$ = 40.0 eV)	30.8	52.4	16.7

[a] Average of values obtained at $\hbar\omega$ = 22.5 and $\hbar\omega$ = 23.5 eV.
[b] Renormalized values (see text).
[c] "Band strengths."

classified as shake-up peaks.[25] The strongest one, with a branching ratio of ~2%, is the one at 27.3 eV. The 31.3- and 35.1-eV peaks are of roughly equal strength, ~1%. The 22.8-eV state is quite weak with a branching ratio of less that 0.5%.

In Table II we compare our data with those obtained at $\hbar\omega$ = 40.8 eV by Gardner and Samson[12,23] and by Potts and Williams.[25] The latter data are in very good agreement with ours, especially if one considers that the peaks under study are quite broad and weak and it is somewhat difficult to accurately determine their maxima. Also included in Table II are the electron-spectroscopy-for-chemical-analysis (ESCA) data by Allan *et al.*[26] The origin of the peak at 27.9 eV in the ESCA spectrum is of some interest. It was attributed to an X-ray satellite by Allan *et al.*[26] It may be that one cannot exclude the possibility of a weak state at ~27.2 eV hidden underneath this satellite.

Samson and Gardner have determined the branching ratios for the states with binding energies above 38 eV at $\hbar\omega$ = 40.8 eV to be 61.5%.[12,23,24] Our data are in serious disagreement with this value. We estimate the state at 38 eV to have a branching ratio of not more than 5% at $\hbar\omega$ = 40 eV.

Our intensity estimates for the high-lying states are in reasonable agreement with those of Potts and Williams[25] as far as the relative strength of these states are concerned. Our absolute estimates are, however, roughly a factor of 2 lower than theirs.

D. CIS spectra

The CIS spectra are extremely helpful in following rapid changes in partial photoionization cross-sections.[4] A particularly interesting region is the one in the $X\,^2\Pi_g$ state between $\hbar\omega$ = 15.5 and $\hbar\omega$ = 18 eV (Fig. 5). (These data were obtained with a wavelength resolution $\Delta\lambda$ = 1.6 Å.) The curve shown in Fig. 5 is the original data without smoothing. In this photon-energy range there are Rydberg states converging both to the A state and to the B state. Using available optical data, the structure in the *partial* photoionization cross section have been assigned (see Fig.5). Our data

TABLE II. Observed high-lying states of CO_2^+.

	$\hbar\omega$	Vertical ionization potential (eV)				
Gardner and Samson (Refs. 12 and 23)	40.8	•••	26.6	•••	•••	38.4	40.0
Potts and Williams (Ref. 25)	40.8	22.6	27.2	31.4	35.3	38.5	•••
Allan *et al.* (Ref. 26)	1253.6	•••	27.9(?)	32.5		37.6	•••
This work	40.0	22.8	27.3	31.3	35.1	~38	

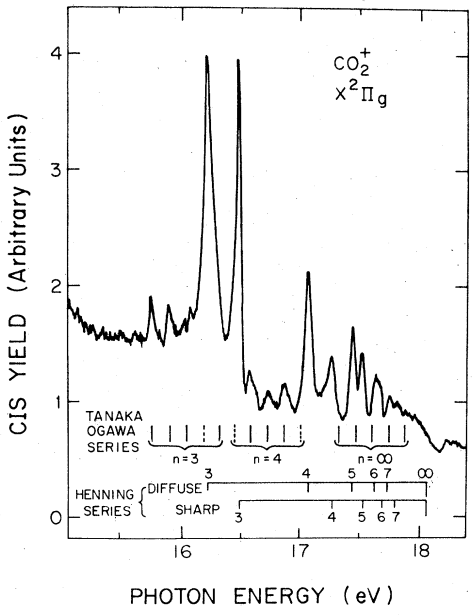

FIG. 5. CIS spectrum for the $X^2\Pi_g$ state of CO_2^+ between 15.5 and 18 eV. The pass energy of the energy analyzer was 40 eV and the wavelength resolution 1.6-Å FWHM. The identification of the structure follows Henning (Ref. 27) and Tanaka and Ogawa (Ref. 28). An alternate labeling has been suggested by Lindholm (Ref. 29).

are, after allowance is made for the difference in wavelength resolution, in good agreement with the high-resolution, *total* photoionization data by Cook *et al.*[30]

The CIS's have also been used to obtain confirmation of the finer details in the partial photoionization cross sections in the region below 30 eV. The full lines in Fig. 3 are interpolations based on CIS data.

IV. DISCUSSION

The ratio of the $A\,^2\Pi_u$ and $B^2\Sigma_u^+$ partial cross sections at $\hbar\omega = 21.2$ eV is of some interest. Using fluorescence measurements Wauchop and Broida determined an A/B ratio of 1.47,[31] whereas Lee and Judge obtained $A/B = 2.7$.[11] Gentieu and Mentall[32] obtained 2.2 and other measurements[33,34] also indicate an A/B ratio larger than 1 in fluorescence. These results are to be contrasted with the photoelectric value by Samson and Gardner of $A/B = 0.65 \pm 0.05$.[12] It was, therefore, somewhat surprising that the sum of the cross sections for the $A\,^2\Pi_u$ and $B\,^2\Sigma_u^+$ states was almost the same in fluorescence[11] and photoemission[12] (25.6 and 24.2 Mb, respectively).

To resolve this puzzling situation Samson and Gardner postulated that a perturbation existed between the A and B states.[12] The effect of this perturbation was suggested to be a crossover from the B to the A state, in such a manner that the total $A+B$ population remained constant, but the ratio A/B was changed. No specific mechanism was suggested for this crossover. This is potentially an important suggestion as it implies that photoelectron spectroscopy and fluorescence measure different quantities. As stated by Samson and Gardner,[12] if such a crossover occurs, it will most likely do so regardless of the mechanism for the initial population of the A and B states, i.e., independent of the photon energy. If one knows the crossover rate at one photon energy and the photoelectric A/B ratio at another, one should then be able to calculate the fluorescent A/B ratio at the second photon energy.

Samson and Gardner[12] suggested a crossover rate of 55% for the B state to the A state in order to reconcile their photoelectric A/B ratio with the data by Lee and Judge[11] at $\hbar\omega = 21.2$ eV. They then predicted an A/B ratio for fluorescence $(A/B)_f$ of 3.4 at 40.8 eV.[12] By using the data by Lee *et al.*[19] for the A state and by Carlson *et al.*[20] for the B state, we obtain the experimental value for $(A/B)_f$ which is 1.7. This disagrees with the prediction.

Samson and Gardner[12] saw additional support for the crossover mechanism from their measurements of the total $A+B$ fluorescence yield at $\hbar\omega = 40.8$ eV, which was in quite good agreement with the sum of their photoelectric branching ratios for the A and B states at this photon energy. However, as shown in Fig. 4, our photoelectric data do not agree with those of Samson and Gardner.[12]

We conclude that there is scant experimental evidence for a crossover mechanism as suggested by Samson and Gardner.[12] The fact remains, however, that the published A to B ratios for photoemission and fluorescence are quite different both for $\hbar\omega = 21.2$ and $\hbar\omega = 40.8$ eV. Also, there is at least an apparent agreement in Fig. 4 between our $A+B$ branching ratios and the sum of the fluorescent yield data for the two states. It seems that additional experimental data is needed to clarify the origin of these observations.

V. SUMMARY

We have presented systematic branching ratio and partial photoionization cross-section data for CO_2 between 20 and 40 eV photon energy. The cross-sections are fairly smooth in this energy range, showing few signs of the dramatic resonance effects we have observed in CO,[4] N_2,[4] and SF_6.[5] At photon energies overlapping those of conventional light sources, good agreement is obtain-

ed with some, but not all, earlier photoelectric data as far as the low-lying states are concerned. We have verified the existence of four weak states (shake-up satellites) with binding energies between 22 and 37 eV. In contrast to some earlier reports,[12,23] we have found that in the entire photon energy range under study, the main part of the photocurrent is associated with low-lying ionic states.

We have also discussed the relationship between fluorescence and photoemission branching ratio data. While the experimental situation is not quite clear, especially as far as the fluorescence data are concerned, it seems unlikely that the cross-over mechanism postulated by Samson and Gardner[12] can be successfully used.

ACKNOWLEDGMENTS

We wish to thank the staff of the Synchrotron Radiation Center, in particular E. M. Rowe and R. Otte, for their cooperation and assistance. The University of Wisconsin Physical Sciences Laboratory Synchrotron Radiation Center is supported by NSF Grant No. 74-15098. T. G. and E. W. P. were supported by the NSF, MRL Program, under Grant No. DMR 76-00678.

---

*Present address: Deutsches Electronen-Synchrotron DESY, D-2 Hamburg 52, Notkestieg 1, West Germany.

[1]See, e.g., The Extended Abstracts from the Proceedings of an International Symposium on Photoemission, Sept. 13–16, 1976, Noordwijk, The Netherlands, edited by R. F. Willis, B. Feuerbacher, B. Fitton, and C. Backx (unpublished), pp. 219–276; and notes from the Annual Synchrotron Radiation Users Group Conferences at Stoughton, Wisc. and Stanford, Calif.

[2]T. Gustafsson and E. W. Plummer, in *Photoemission from Surfaces*, edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, London, to be published).

[3]Other papers in this series include studies of CO (Ref. 4), N_2 (Ref. 4), SF_6 (Ref. 5) and Xe (Ref. 6).

[4]E. W. Plummer, T. Gustafsson, W. Gudat, and D. E. Eastman, Phys. Rev. A 15, 2339 (1977).

[5]T. Gustafsson *et al.* (unpublished).

[6]T. Gustafsson, Chem. Phys. Lett. (to be published).

[7]See, e.g., D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley, London, 1970).

[8]See, e.g., K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).

[9]See, e.g., J. A. R. Samson, Phys. Rep. 4, 303 (1976).

[10]See, e.g., C. E. Brion, Radiat. Res. 64, 37 (1975).

[11]L. C. Lee and D. L. Judge, J. Chem. Phys. 57, 4443 (1972).

[12]J. A. R. Samson and J. L. Gardner, J. Geophys. Res. 78, 3663 (1973).

[13]G. J. Lapeyre, J. Anderson, P. L. Gobby, and J. A. Knapp, Phys. Rev. Lett. 33, 1290 (1974).

[14]D. E. Eastman, D. W. Grobman, J. L. Freeouf, and M. Erbudak, Phys. Rev. B 9, 3472 (1974).

[15]T. A. Carlson, G. E. McGuire, A. E. Jonas, K. L. Cheng, C. P. Anderson, C. C. Lu, and B. P. Pullen, in *Electron Spectroscopy*, edited by D. Shirley (North-Holland, Amsterdam, 1972).

[16]The calibration in Ref. 4 was carried out at $\hbar\omega = 21.2$ eV. One would expect that the possible variations of the collection efficiency of the energy analyzer between different ionic states would become even less significant as the ratio of the difference in kinetic energy between ionic states to their average kinetic energy goes down, i.e., at higher photon energies. In fact, a recent calibration for N_2 at $\hbar\omega = 30$ eV [T. Gustafsson (unpublished)] of a system similar to this bears this expectation out.

[17]L. C. Lee, R. W. Carlson, D. L. Judge, and M. Ogawa, J. Quant. Spectrosc. Radiat. Transfer. 13, 1023 (1973).

[18]R. B. Cairns and J. A. R. Samson, J. Geophys. Res. 70, 99 (1965).

[19]L. C. Lee, R. W. Carlson, and D. L. Judge, J. Phys. B 9, 855 (1976).

[20]R. W. Carlson, D. L. Judge, and M. Ogawa, J. Geophys. Res. 78, 3194 (1973).

[21]J. A. R. Samson and J. L. Gardner, J. Chem. Phys. 58, 3771 (1973).

[22]J. L. Bahr, A. J. Blake, J. H. Carver, J. L. Gardner, and Vijay Kumar, J. Quant. Spectrosc. Radiat. Transfer 12, 59 (1972).

[23]J. L. Gardner and J. A. R. Samson, J. Electron Spectrosc. 2, 259 (1973).

[24]It is not quite clear if the data in Refs. 12 and 23 refer to different experiments or not. The branching ratios are (within 0.1%) identical. The data in Ref. 12 are estimated to be "accurate within 10%," whereas the data in Ref. 23 are stated to be "preliminary."

[25]A. W. Potts and T. A. Williams, J. Electron Spectrosc. 3, 3 (1974).

[26]C. J. Allan, U. Gelius, D. A. Allison, G. Johansson, H. Siegbahn, and K. Siegbahn, J. Electron Spectrosc. 1, 131 (1972/73).

[27]H. J. Henning, Ann. Phys. (Leipz.) 13, 599 (1932).

[28]Y. Tanaka and M. Ogawa, Can. J. Phys. 40, 879 (1962).

[29]E. Lindholm, Ark. Fys. 40, 125 (1969).

[30]G. R. Cook, P. H. Metzger, and M. Ogawa, J. Chem. Phys. 44, 2935 (1966).

[31]T. S. Wauchop and H. P. Broida, J. Geophys. Res. 76, 21 (1971).

[32]E. P. Gentieu and J. E. Mentall, J. Chem. Phys. 64, 1376 (1976).

[33]W. Sroka and R. Zeitz, Phys. Lett. 43A, 493 (1973).

[34]J. H. D. Eland, M. Devoret, and S. Leach, Chem. Phys. Lett. 43, 97 (1976).