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(3+1) resonance enhanced multiphoton ionization photoelectron spectroscopy on nf Rydberg states of carbon dioxide

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The (3+1) resonance enhanced multiphoton ionization spectrum of carbon dioxide has been investigated for the (${}^2\Pi_{g3/2,1/2}$) nf Rydberg states. The excitation spectrum has been obtained for the $n=4-13$ members, while photoelectron spectra with a resolution of 15 meV have been measured for the $n=4-7$ members. The photoelectron spectra demonstrate that a delicate balance exists between direct and indirect ionization processes as evidenced by the large differences in vibrational activity observed in the spectra obtained *via* various members of the (${}^2\Pi_{g3/2,1/2}$) nf Rydberg series. Strong vibrational activity, which would be forbidden by simple selection rules, is found and interpreted to arise in part from vibronic coupling between various ionic states. Long vibrational progressions, mainly involving the symmetric stretch vibration of the $X\ {}^2\Pi_g$ state of the ion, indicate further severe deviations from Franck-Condon behavior. Two-color excitation of the (${}^2\Pi_{g3/2,1/2}$) nf Rydberg states provides strong evidence that the superexcited states accessible at the four-photon level have a profound influence on the vibrational progressions and distributions in the photoelectron spectra. Finally, resonances associated with multiphoton excitation of atomic carbon and oxygen have been observed. The processes which might be responsible for the occurrence of these atoms are discussed. © 1994 American Institute of Physics.

I. INTRODUCTION

The spectroscopy and dynamical behavior of the excited states of the carbon dioxide molecule and its cation have since long attracted the attention of experimentalists and theoreticians alike. A plethora of studies have revealed the complexity of processes occurring at almost every level in the molecule and in the ion; and although these investigations have often provided detailed insight in these processes, several unresolved questions persist.

The ground state of CO_2 has a linear geometry (symmetry point group $D_{\infty h}$) with an electronic configuration given by $\dots(3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4\ 1\Sigma_g^+$. The molecule has three vibrational modes: the σ_g^+ symmetric C-O stretch ω_1 (1388.17 cm^{-1}), the π_u degenerate bending ω_2 (667.40 cm^{-1}), and the σ_u^+ asymmetric stretch ω_3 (2349.16 cm^{-1}).¹ The lower excited valence states are expected to arise from the $1\pi_g \rightarrow 2\pi_u$ excitation (${}^{1,3}\Sigma_u^-, {}^{1,3}\Sigma_u^+, {}^{1,3}\Delta_u$), and the $1\pi_g \rightarrow 5\sigma_g$ excitation, which gives rise to the ${}^{1,3}\Pi_g$ semivalence states. Several experimental²⁻⁶ and theoretical studies⁷⁻¹¹ have investigated the ordering and behavior of these states, in particular with respect to the bent geometry of the molecule expected in some cases.

The study of higher-lying excited states of CO_2 is considerably hindered by (pre)dissociative processes. Only recently Cossart-Magos *et al.* succeeded in performing a comprehensive study of excited states in the energy region from 87 600 cm^{-1} up to the lowest ionic state $X\ {}^2\Pi_g$ around 111 201 cm^{-1} , resulting in the assignments of np and nf Rydberg series.¹² From this study and accompanying theoretical work it could be concluded that the np Rydberg states are heavily predissociated by dissociative valence states,

whereas the nf Rydberg series seem virtually unperturbed in comparison.

The four lowest ionic states of CO_2 , viz., $X\ {}^2\Pi_g$, $A\ {}^2\Pi_u$, $B\ {}^2\Sigma_u^+$, and $C\ {}^2\Sigma_g^+$, result from the removal of an electron out of the $1\pi_g$, $1\pi_u$, $3\sigma_u$, and $4\sigma_g$ orbital, respectively, and are all located within an energy range of 6 eV. As a result of spin-orbit interaction (160 cm^{-1}) the $X\ {}^2\Pi_g$ ionic state is split up into two components, the $X\ {}^2\Pi_{g3/2}$ and $X\ {}^2\Pi_{g1/2}$ states, the former being the lowest in energy. For the present high-resolution photoelectron spectroscopy study the energies of the vibrational levels of the ion in the $X\ {}^2\Pi_g$ state are of utmost importance. In the following these levels will be denoted as ${}^2\Pi_g(v_1, v_2, v_3)$, i.e., the vibrational level with v_1 , v_2 , and v_3 vibrational quanta in the symmetric stretch, degenerate bend and asymmetric stretch vibrations with frequencies of 1244.27, 511.35, and 1423.08 cm^{-1} , respectively.^{13,14} The vibrational spectroscopy of the ${}^2\Pi_g$ state is complicated by a number of factors. First, the energy of the ${}^2\Pi_g(0,0,1)$ level mentioned above has been adopted from the diode laser spectroscopy studies of Kawaguchi *et al.*¹³ This value differs considerably from earlier values from HeI photoelectron spectroscopy.¹⁵⁻¹⁸ Kawaguchi *et al.* have shown that the ${}^2\Pi_g(0,0,1)$ and ${}^2\Pi_g(0,0,2)$ vibrational levels exhibit a strong negative anharmonicity as a result of vibronic coupling of the $X\ {}^2\Pi_g$ and $A\ {}^2\Pi_u$ ionic states *via* the asymmetric stretch vibration. An assignment of the ω_3 vibrational levels on the basis of the harmonic approximation should consequently be viewed with caution. Secondly, in the lowest ionic state Renner-Teller coupling is active and splits every degenerate ${}^2\Pi_g(v_1, v_2, v_3)$ level into $2(v_2+1)$ separate energy levels.¹ Fluorescence studies of the Renner-Teller effect in the ${}^2\Pi_{g3/2,1/2}$ states have led to an accurate description as well as to precise energy values for the various $2(v_2+1)$ levels for $v_2=1$ and 2.^{19,20} Finally, it has been

shown that Fermi resonances between, e.g., the ${}^2\Pi_g(1,0,0)$ and components of the ${}^2\Pi_g(0,2,0)$ levels are important.¹⁴

The excited ionic states mentioned earlier have been well characterized by fluorescence spectroscopy on the ion^{19,20} and by photoelectron spectroscopy.^{15-18,21,22} Ionization of the molecule by removal of an electron from the bonding $1\pi_u$ orbital is accompanied by a large geometrical change. As a result, the C–O internuclear distance in the $A\ {}^2\Pi_u$ ionic state (1.2274 Å) is considerably different from that in the $X\ {}^2\Pi_g$ state (1.1769 Å).²⁰ In the $A\ {}^2\Pi_u \rightarrow X\ {}^2\Pi_g$ fluorescence spectrum strong activity of the symmetric stretching mode is therefore observed.²³ The $B\ {}^2\Sigma_u^+$ and $C\ {}^2\Sigma_g^+$ ionic states, on the other hand, have internuclear distances which are comparable to the distance in the $X\ {}^2\Pi_g$ state. Accordingly, the $B\ {}^2\Sigma_u^+ \rightarrow X\ {}^2\Pi_g$ fluorescence spectrum shows a strong 0-0 transition with limited vibrational activity.¹⁹ HeI and NeI photoelectron studies of the ionic states by ionization from the neutral ground state exhibit similar behavior, i.e., long progressions in ω_1 on ionization to the $A\ {}^2\Pi_u$ ionic state and dominant 0-0 transitions on ionization to the $B\ {}^2\Sigma_u^+$ and $C\ {}^2\Sigma_g^+$ states.^{15-18,21,22}

The Rydberg series of neutral superexcited states converging to the $A\ {}^2\Pi_u$, $B\ {}^2\Sigma_u^+$, and $C\ {}^2\Sigma_g^+$ excited ionic limits are denoted by R_A , R_B , and R_C , respectively. In the R_A series an electron is excited from the $1\pi_u$ bonding orbital. As a consequence of the change in the C–O bonding distance various Rydberg series have been observed which converge to the $A\ {}^2\Pi_u(v_1^+ = 0-7)$ ionic limits.²⁴ These series, known in literature as the Tanaka–Ogawa (TO) (n, v_1) series, probably arise from the excitation of a $1\pi_u$ electron to an $ns\sigma_g$ orbital.^{25,26} Excitation of a $3\sigma_u$ electron gives rise to the R_B Rydberg series. Two Rydberg series, the Henning sharp ($3\sigma_u \rightarrow nd\pi_g$) and the Henning diffuse ($3\sigma_u \rightarrow ns\sigma_g$) series, have been observed for $v_1 = 0$ and 1.^{24,27} The assignments of these series have been taken from Fridh *et al.*,²⁶ but fluorescence polarization studies indicate that the assignment of the Henning sharp series might be incorrect, as the Rydberg levels were shown to be of ${}^1\Sigma_u^+$ symmetry.²⁸ Furthermore, it is noticed that the original n principal quantum number assignments have been revised by McCulloh.²⁹ Finally, excitation of a $4\sigma_g$ electron results in the R_C Rydberg states. For these states three series, known as the Tanaka–Jursa–LeBlanc absorption, weak absorption, and emission series have been assigned.³⁰ Dynamic processes occurring in the R_A , R_B , and R_C states have been studied extensively using mainly one-photon excitation in combination with various detection techniques.^{28,29,31-44} One of the important conclusions drawn from these studies is that these superexcited states are very strongly subject to competing electronic autoionization and neutral dissociation processes.

In studies of the $X\ {}^2\Pi_g$ ionic state by conventional HeI and NeI photoelectron spectroscopy,^{15-18,21} as well as in studies by threshold photoelectron spectroscopy,^{41,45-47} the observed vibrational activity is mainly concentrated near the vibrationless origin. Ionization pathways from the vibrationless ground state of CO_2 in which the ion is left in the $X\ {}^2\Pi_g$ ionic state with an odd number of vibrational quanta in the degenerate bending vibration ω_2 or in the asymmetric stretch vibration ω_3 are strictly forbidden within the Born–

Oppenheimer approximation.¹ Nevertheless, Renner–Teller components of the ${}^2\Pi_g(0,1,0)$ level have been observed with variable intensity.^{15-18,21,41,45-47} Such transitions have been explained either in terms of a vibronic coupling of the $X\ {}^2\Pi_g$ and $B\ {}^2\Sigma_u^+$ states via the ω_2 vibration,^{16,21,46,47} or through coupling with bent superexcited valence states.^{29,41,46,47} On the other hand, in studies with tunable one-photon excitation and low-resolution (~ 100 meV) photoelectron spectroscopy long vibrational progressions have been observed, which have been assigned to a single harmonic ${}^2\Pi_g(v_1, 0, 0)$ progression, possibly in combination with a weak ${}^2\Pi_g(v_1, 1, 0)$ progression.^{33,39,43} These progressions are generally believed to result from electronic autoionization to the $X\ {}^2\Pi_g$ ionic state of neutral superexcited Rydberg states converging to the $A\ {}^2\Pi_u$, $B\ {}^2\Sigma_u^+$, and $C\ {}^2\Sigma_g^+$ ionic limits.

The studies discussed until now are all concerned with excitation of the relevant excited states with one photon. It is well known that the selection rules for multiphoton excitation differ considerably from the ones for one-photon excitation, enabling the study of excited states which are not accessible with one-photon spectroscopy. Resonance enhanced multiphoton ionization in combination with photoelectron spectroscopy (REMPI-PES) offers the additional advantage that one can determine in which electronic, vibrational and, under favorable circumstances, even rotational levels the ion is left upon ionization. Such information is of fundamental importance for the spectroscopy of the excited resonant state as well as for the study of dynamical processes occurring in these states. Photoelectron spectroscopy allows for detailed investigations of processes such as autoionization and (pre)dissociation occurring in the ionization step of a REMPI experiment, since these processes have a profound influence on the electronic, vibrational and rotational branching ratios in the photoelectron spectrum.

Despite the obvious advantages of REMPI-PES CO_2 has for a long time resisted studies by this kind of spectroscopy. Only recently a (3+1) REMPI experiment has been reported in which the states arising from the $1\pi_g \rightarrow 3p\sigma_u$ and $1\pi_g \rightarrow nf$ ($n=4,5$) excitations were investigated.⁴⁸⁻⁵² The photoelectron-energy-dependent low-resolution photoelectron spectra obtained for ionization via these states showed unexpectedly long vibrational progressions, which were assigned to dominantly the ω_1 symmetric stretch vibration in the case of the $3p$ resonances, and the ω_3 asymmetric stretch vibration for the $4f$ resonances. The process responsible for these progressions was suggested to arise from autoionization during molecular dissociation of neutral superexcited states at the four-photon level. In the excitation spectra strong sharp resonances could be observed which were attributed to resonance enhancement by neutral superexcited Rydberg states at the four-photon level. The photoelectron spectra obtained via these resonances seemed to suggest a termination of the ionization process on the $C\ {}^2\Sigma_g^+$ ionic state after a five-photon absorption from the neutral ground state.

In the present study we investigate the $({}^2\Pi_{g3/2,1/2})nf$, $n=4-13$ Rydberg states of CO_2 by one- and two-color three-photon resonance enhanced multiphoton ionization combined with photoelectron-energy-independent high-

resolution (15 meV) photoelectron spectroscopy and mass-resolved ion detection. As a result of the high resolution in the present photoelectron spectra it will become clear that assignments and conclusions obtained in previous (3+1) REMPI-PES studies should be revised. It will be shown that the vibrational activity observed in the photoelectron spectra varies considerably with the excitation wavelength and may involve long vibrational progressions in the symmetric stretch vibration up to $v_1^+ = 16$, as well as strong activity of odd levels of the degenerate bending vibration ω_2 and the asymmetric stretch vibration ω_3 . Two-color excitation REMPI-PES spectra, in which the four-photon level is probed while the three-photon energy is kept constant, demonstrate independently that the appearance of the photoelectron spectra is to a major extent determined by autoionization processes occurring at the four-photon level. In our study REMPI processes, which will be shown to derive from atomic fragments, have also been observed. Most notably these processes concern the oxygen atom in its $2s^2 2p^4 \ ^1D_2^o$ state, which is identified as a photodissociation product by hitherto unobserved (3+1) REMPI *via* excited states above the lowest ionization energy.

II. EXPERIMENTAL DETAILS

In the present study two different spectrometers have been used: a "magnetic bottle" electron spectrometer with an effusive sample inlet system, and a mass-resolved ion spectrometer fitted with a molecular beam expansion.

The "magnetic bottle" electron spectrometer has been described previously.⁵³ Briefly, laser light from a nanosecond laser system is focused into the electron spectrometer by means of a 25 mm focal length quartz lens. A similar lens on the other side of the spectrometer provides the possibility to perform two-color experiments by focusing a second laser beam, counterpropagating to the first one, into the ionization region. Half of the electrons produced in a laser shot are parallelized in a strongly diverging magnetic field and analyzed with respect to their kinetic energies in a 50 cm long flight tube. The signal from a pair of microchannel plates is further amplified by a home-built preamplifier and connected to a transient digitizer, which can be read out by a microcomputer for further analysis. A 15 meV energy resolution full width at half maximum (FWHM) at all electron kinetic energies can be obtained by applying a retarding voltage on a grid in the flight tube. In the present study accurate absolute electron energy positions have been obtained by calibrating the system regularly using the well-known lower spin-orbit ionic states of atomic krypton. Application of appropriate voltages to two grids surrounding the ionization region of the spectrometer allows for mass-resolved ion detection, albeit with a lower detection efficiency than in the case of electron detection.⁵⁴

CO₂ gas (99.996%, Matheson, used without purification) was introduced into the spectrometer with typical pressures of 10^{-3} mbar in the ionization region and 8×10^{-6} mbar in the flight tube. The background pressure of the system is 2×10^{-7} mbar.

The experimental setup of the ion spectrometer has also been described before.⁵⁵ In this spectrometer the sample is

introduced into the ionization region by a supersonic jet expansion, resulting in a significant rotational cooling of the molecules. Ions produced at the intersection of the expansion and the focused laser beam are extracted by home-built ion optics and mass-analyzed by a quadrupole system. Optimal cooling is generally achieved by expanding a mixture of a few percent of the sample in helium or argon. Under these conditions the CO₂⁺ signal was, however, not large enough to perform experiments with a reasonable signal-to-noise ratio. We have therefore chosen to expand pure CO₂, resulting in rotational temperatures of about 40 K, which is still considerably lower than the temperature achieved in the effusive beam setup of the "magnetic bottle" spectrometer described earlier. As a result, the peak positions of the resonant molecular features could be determined more accurately. To produce sufficient CO₂ signal it proved necessary to position the laser focus as close as possible to the nozzle orifice, which resulted in reduced mass selectivity because of charge transfer processes occurring in this high pressure region of the expansion.

The nanosecond laser system starts from a XeCl excimer laser (Lumonics HyperEx-460) operating at a 30 Hz repetition rate, providing typically 170 mJ in a 10 ns pulse. The excimer laser pumps a dye laser (Lumonics HyperDye-500) operating on Coumarin 540A. Subsequent frequency doubling is achieved by an angle-tuned BBO crystal in a frequency doubler (Lumonics HyperTrak-1000). The energy per UV pulse (energy width ≈ 0.14 cm⁻¹) used in the present study on CO₂ was nearly always close to the maximum value of about 1.5 mJ per pulse. The power is adjusted carefully to avoid space charge effects in the laser focus.

In the present study we have also performed two-color excitation experiments. In these experiments the excimer laser beam is split by a 0.6/0.4 beamsplitter. One of the beams pumps the Lumonics HyperDye-500 dye laser as described before, the remaining beam now pumps a second dye laser (Lumonics HyperDye-300) operating on Rhodamine 6G. This dye laser is frequency doubled in an autotracker system (INRAD II) using an angle tuned KDP crystal. The timing of the two UV dye laser pulses is checked using a fast photodiode. In some experiments a picosecond laser system has been used. This system has been described in detail previously⁵⁴ and will not be discussed here.

III. RESULTS

A. Molecular excitation spectra

The (3+1) REMPI excitation spectrum of CO₂ in the one-photon range 34 500–37 000 cm⁻¹ has been investigated. This range, corresponding at the three-photon level to 103 500–111 000 cm⁻¹, has been examined previously in a one-photon absorption study¹² and partly by (3+1) REMPI.^{48–52} In one-photon absorption the *nf* Rydberg series have been observed up to high values of the principal quantum number *n* ($n \leq 32$), but the previous (3+1) REMPI studies have only reported the excitation spectra of the 4*f* and 5*f* members. From these studies the resonance energies of the *nf* Rydberg series are well known and the dominant reso-

FIG. 1. Three-photon excitation spectrum of the $(^2\Pi_{g3/2,1/2})4f$ vibrationless origins using electron detection (upper trace) and ion detection (lower trace). The sharp peaks on the high-energy side derive from (2+1) REMPI of atomic carbon.

nances in our excitation spectra can consequently be easily assigned to the $(^2\Pi_{g3/2})nf$ and $(^2\Pi_{g1/2})nf$ Rydberg series of CO_2 with $n=4-13$.

Selected parts of the excitation spectrum are shown in Figs. 1–4 which correspond to the excitation spectra of the $4f$ to $7f$ members, respectively. These spectra have not been corrected for changes in the dye gain, but since the parts shown in the figures cover relatively small wavelength regions, and since they have not been recorded at the edge of the dye gain curve, the excitation power within the four individual spectra can be assumed to be constant. Figures 1–4 consist of two parts: The upper traces have been recorded in the electron spectrometer collecting all generated electrons, while the lower traces have been obtained using the quadrupole mass spectrometer in combination with the molecular beam apparatus. The lower traces show considerable rotational cooling, resulting in narrower molecular CO_2 features when compared to the upper traces, thus allowing for a more accurate determination of the peak positions. Partially resolved rotational structures can be observed in the $4f$ and $5f$ excitation spectra. These structures disappear in the $6f$ spec-

FIG. 2. Three-photon excitation spectrum of the $(^2\Pi_{g3/2,1/2})5f$ vibrationless origins using electron detection (upper trace) and ion detection (lower trace). The eight sharp peaks in the right half of the spectrum derive from (2+1) REMPI of atomic carbon.

FIG. 3. Three-photon excitation spectrum of the $(^2\Pi_{g3/2,1/2})6f$ vibrationless origins and the $(^2\Pi_{g3/2,1/2})5f10$ levels using electron detection (upper trace) and ion detection (lower trace). The sharp peak at $36\,029.5\text{ cm}^{-1}$ derives from (2+1) REMPI of atomic carbon, while the peaks on the high-energy side of the spectrum result from (3+1) REMPI of atomic oxygen.

trum, in which only the rotational envelope is seen. The $7f$ excitation spectrum, on the other hand, shows once again resolved rotational structure. The positions of the resonant nf features as obtained with the quadrupole mass spectrometer are given in Table I. These positions are in good agreement with previous results. Several weak resonances, which can be assigned to $\omega_1=1$ vibrational levels of the $4f$, $5f$, and $6f$ states, have also been observed. The positions of these resonances are listed as well in Table I and are in good agree-

FIG. 4. Three-photon excitation spectrum of the $(^2\Pi_{g3/2,1/2})7f$ vibrationless origins using electron detection (upper trace 4a) and ion detection (lower trace 4a and 4b). The $(^2\Pi_{g3/2})7f$ origin state shows partially resolved rotational structures, which are enlarged in 4b.

TABLE I. Observed molecular CO₂ three-photon resonances to the (²Π_{g3/2,1/2})*nf* (*n*=4–13) Rydberg states with the quadrupole mass spectrometer. Frequencies are given in cm⁻¹.

Photon energy	Assignment	Photon energy	Assignment
34 661.0		36 036.1	(² Π _{g1/2})5 <i>f</i> 1 ₀
34 677.2		36 061.6	(² Π _{g1/2})6 <i>f</i>
34 707.1	(² Π _{g3/2})4 <i>f</i>	36 066.9	(² Π _{g1/2})6 <i>f</i>
34 712.6	(² Π _{g3/2})4 <i>f</i>	36 280.4	(² Π _{g3/2})7 <i>f</i>
34 724.0	(² Π _{g3/2})4 <i>f</i>	36 281.4	(² Π _{g3/2})7 <i>f</i>
34 729.2	(² Π _{g3/2})4 <i>f</i>	36 282.3	(² Π _{g3/2})7 <i>f</i>
34 747.3	(² Π _{g3/2})4 <i>f</i>	36 283.1	(² Π _{g3/2})7 <i>f</i>
34 750.2	(² Π _{g3/2})4 <i>f</i>	36 284.0	(² Π _{g3/2})7 <i>f</i>
34 768.9	(² Π _{g1/2})4 <i>f</i>	36 284.9	(² Π _{g3/2})7 <i>f</i>
34 782.1	(² Π _{g1/2})4 <i>f</i>	36 285.6	(² Π _{g3/2})7 <i>f</i>
34 785.4	(² Π _{g1/2})4 <i>f</i>	36 285.9	(² Π _{g3/2})7 <i>f</i>
34 800.9	(² Π _{g1/2})4 <i>f</i>	36 286.7	(² Π _{g3/2})7 <i>f</i>
34 802.0	(² Π _{g1/2})4 <i>f</i>	36 289.7	(² Π _{g3/2})7 <i>f</i>
34 803.9	(² Π _{g1/2})4 <i>f</i>	36 291.4	(² Π _{g3/2})7 <i>f</i>
34 805.3	(² Π _{g1/2})4 <i>f</i>	36 292.4	(² Π _{g3/2})7 <i>f</i>
35 144.6	(² Π _{g3/2})4 <i>f</i> 1 ₀	36 339.0	(² Π _{g1/2})7 <i>f</i>
35 206.6	(² Π _{g1/2})4 <i>f</i> 1 ₀	36 461.5	(² Π _{g3/2})8 <i>f</i>
35 552.8	(² Π _{g3/2})5 <i>f</i>	36 488.3	(² Π _{g1/2})6 <i>f</i> 1 ₀
35 560.8	(² Π _{g3/2})5 <i>f</i>	36 511.3	(² Π _{g1/2})8 <i>f</i>
35 563.3	(² Π _{g3/2})5 <i>f</i>	36 512.8	(² Π _{g1/2})8 <i>f</i>
35 571.6	(² Π _{g3/2})5 <i>f</i>	36 515.1	(² Π _{g1/2})8 <i>f</i>
35 576.1	(² Π _{g3/2})5 <i>f</i>	36 581	(² Π _{g3/2})9 <i>f</i>
35 606.9	(² Π _{g1/2})5 <i>f</i>	36 635	(² Π _{g1/2})9 <i>f</i>
35 614.8	(² Π _{g1/2})5 <i>f</i>	36 669	(² Π _{g3/2})10 <i>f</i>
35 616.2	(² Π _{g1/2})5 <i>f</i>	36 780	(² Π _{g3/2})12 <i>f</i>
35 624.3	(² Π _{g1/2})5 <i>f</i>	36 785	(² Π _{g3/2})12 <i>f</i>
35 626.0	(² Π _{g1/2})5 <i>f</i>	36 822	(² Π _{g3/2})13 <i>f</i>
35 627.1	(² Π _{g1/2})5 <i>f</i>	36 834	(² Π _{g1/2})12 <i>f</i>
35 628.7	(² Π _{g1/2})5 <i>f</i>	36 840	(² Π _{g1/2})12 <i>f</i>
35 975.6	(² Π _{g3/2})5 <i>f</i> 1 ₀		
36 013.6	(² Π _{g3/2})6 <i>f</i>		
36 019.3	(² Π _{g3/2})6 <i>f</i>		

ment with the one-photon work of Cossart-Magos *et al.*¹² In agreement with earlier REMPI studies we find that rather high laser powers (in the order of 0.5 mJ per pulse) have to be used to observe the *nf* resonances.^{48–52} The (²Π_{g3/2},²Π_{g1/2})4*f*, (²Π_{g3/2},²Π_{g1/2})5*f*, and (²Π_{g3/2})6*f* resonances are relatively strong. However, in the high-energy part of the excitation spectrum [(²Π_{g1/2})6*f* and higher members] it is extremely difficult to produce a signal and, as a consequence, very high laser powers (in the order of 1.5 mJ per pulse) have to be used. In this very high-power laser field several secondary processes, not observed for REMPI *via* the lower *nf* states, may become important in the case of the higher *nf* states (*vide infra*).

Excitation spectra have also been measured using the “magnetic bottle” spectrometer in the mass-resolved ion detection mode, by which C⁺, O⁺, CO⁺, and CO₂⁺ ions could be observed. When the O⁺, CO⁺, and CO₂⁺ ions are monitored over the *nf* resonances of CO₂ similar spectra as in Figs. 1–4 are obtained. It is seen that the ratio CO⁺/CO₂⁺ becomes larger as *n* increases, in agreement with earlier observations.^{48,51} In these studies very small O⁺ ion yields were measured, whereas we observe on the (²Π_{g3/2,1/2})*nf* Rydberg resonances an O⁺ production which is typically one order of magnitude larger. At high *n* the CO₂⁺ ion signal becomes small, but it is nevertheless always clearly visible.

The ratio CO⁺/O⁺ is about constant for all *nf* states measured in the present study. In contrast to the wavelength dependence observed for the O⁺, CO⁺, and CO₂⁺ ions, the C⁺ signal only follows the *nf* resonances of CO₂ to a very limited extent.

Similar excitation spectra as recorded with nanosecond laser excitation have been obtained using picosecond laser excitation. In these experiments, in which a 3 ps laser pulse with significantly higher peak power is employed, excitation spectra obtained using either electron or ion detection are again comparable. The main difference between the nanosecond and picosecond results is found in the fragmentation ratios. Typical ion yields in, e.g., the (²Π_{g3/2})6*f* ion spectrum obtained with nanosecond excitation are CO₂⁺:CO⁺:O⁺=0.13:0.73:0.14, while picosecond excitation results in the yields 0.50:0.35:0.15. We thus observe that with picosecond excitation considerably less fragmentation occurs, while also the ratio of CO⁺ to O⁺ ions is changed dramatically.

In the one-photon absorption study of Cossart-Magos *et al.*,¹² several *ns*, *np*, and *nd* Rydberg states have been assigned in the energy region of the present study, whereas the 3*p* Rydberg states have been observed in (3+1) REMPI in a different energy region.^{48,51} We have not observed Rydberg series other than the *nf* series, which might indicate that their predissociation rates are higher than for the *nf* Rydberg states. Neither have we observed resonant features in the excitation spectra that can be attributed to one-, two-, or four-photon resonant transitions.

B. Carbon atom resonances and background peaks

In a previous REMPI study the various sharp resonant features on the high-energy side of the 4*f* and 5*f* resonances of CO₂ have been attributed to neutral CO₂ states above the lowest ionization limit in a resonant process requiring four photons.^{49,50} In agreement with this study we have observed these sharp resonances as well, as can be seen in Figs. 1 and 2. However, we have assigned these features to (2+1) REMPI of carbon atoms, i.e., a secondary process, on the basis of the following considerations.

- (1) The observed transition energies of the peaks close to the CO₂ 4*f* and 5*f* resonances are in excellent agreement with the calculated energies from the atomic 2*s*²2*p*² ³P_{0,1,2}^e → 2*s*²2*p*3*p* ³D_{1,2,3}^e transitions and the atomic 2*s*²2*p*² ³P_{0,1,2}^e → 2*s*²2*p*3*p* ³P_{0,1,2}^e transitions, respectively.^{56–58} The first manifold of transitions has been studied with (2+1) REMPI previously,⁵⁹ but the second manifold has never been observed before with multiphoton excitation. The peak positions measured in both the quadrupole setup and the electron spectrometer are in good agreement, and are given in Table II together with their assignments.
- (2) Using the electron spectrometer in mass-resolved ion mode confirms that ions with *m/e*=12 are responsible for the sharp features.
- (3) The photoelectron spectra taken at the sharp features show only one peak, corresponding to the

TABLE II. Observed (2+1) REMPI transitions in atomic carbon. Frequencies are given in cm^{-1} .

Observed photon energy	Literature photon energy ^a	Assignment
34 823.1	34 823.0	$2s^2 2p^2 \ ^3P_2^e \rightarrow 2s^2 2p3p \ ^3D_1^e$
34 833.6	34 833.6	$2s^2 2p^2 \ ^3P_2^e \rightarrow 2s^2 2p3p \ ^3D_2^e$
34 836.5	34 836.5	$2s^2 2p^2 \ ^3P_1^e \rightarrow 2s^2 2p3p \ ^3D_1^e$
Not observed	34 844.7	$2s^2 2p^2 \ ^3P_0^e \rightarrow 2s^2 2p3p \ ^3D_1^e$
34 847.2	34 847.1	$2s^2 2p^2 \ ^3P_1^e \rightarrow 2s^2 2p3p \ ^3D_2^e$
34 850.3	34 850.3	$2s^2 2p^2 \ ^3P_2^e \rightarrow 2s^2 2p3p \ ^3D_3^e$
34 855.3	34 855.3	$2s^2 2p^2 \ ^3P_0^e \rightarrow 2s^2 2p3p \ ^3D_2^e$
34 863.9	34 863.8	$2s^2 2p^2 \ ^3P_1^e \rightarrow 2s^2 2p3p \ ^3D_3^e$
Not allowed $\Delta J = +3$	34 872.0	$2s^2 2p^2 \ ^3P_0^e \rightarrow 2s^2 2p3p \ ^3D_3^e$
35 185.6	35 185.1	$2s^2 2p^2 \ ^1D_2^e \rightarrow 2s^2 2p4p \ ^1P_1^e$
35 363.8	35 363.8	$2s^2 2p^2 \ ^3P_1^e \rightarrow 2s^2 2p3p \ ^3S_1^e$
35 654.6	35 654.6	$2s^2 2p^2 \ ^3P_2^e \rightarrow 2s^2 2p3p \ ^3P_0^e$
35 660.8	35 660.8	$2s^2 2p^2 \ ^3P_2^e \rightarrow 2s^2 2p3p \ ^3P_1^e$
Not observed	35 668.1	$2s^2 2p^2 \ ^3P_1^e \rightarrow 2s^2 2p3p \ ^3P_0^e$
35 671.0	35 671.0	$2s^2 2p^2 \ ^3P_2^e \rightarrow 2s^2 2p3p \ ^3P_2^e$
35 674.2	35 674.3	$2s^2 2p^2 \ ^3P_1^e \rightarrow 2s^2 2p3p \ ^3P_1^e$
35 676.2	35 676.3	$2s^2 2p^2 \ ^3P_0^e \rightarrow 2s^2 2p3p \ ^3P_0^e$
Not observed	35 682.5	$2s^2 2p^2 \ ^3P_0^e \rightarrow 2s^2 2p3p \ ^3P_1^e$
35 684.6	35 684.5	$2s^2 2p^2 \ ^3P_1^e \rightarrow 2s^2 2p3p \ ^3P_2^e$
35 692.8	35 692.7	$2s^2 2p^2 \ ^3P_0^e \rightarrow 2s^2 2p3p \ ^3P_2^e$
35 788.6	35 788.6	$2s^2 2p^2 \ ^1D_2^e \rightarrow 2s^2 2p4p \ ^1D_2^e$
36 029.5	36 029.5	$2s^2 2p^2 \ ^1D_2^e \rightarrow 2s^2 2p4p \ ^1S_0^e$
36 863.5	36 863.5	$2s^2 2p^2 \ ^1D_2^e \rightarrow 2s^2 2p4f \ F(5/2)_{2,3}$
36 866.8	36 866.8	$2s^2 2p^2 \ ^1D_2^e \rightarrow 2s^2 2p4f \ F(7/2)_{3,4}$
36 896.9	36 896.9	$2s^2 2p^2 \ ^1D_2^e \rightarrow 2s^2 2p4f \ G(7/2)_{3,4}$
36 910.5	36 910.4	$2s^2 2p^2 \ ^1D_2^e \rightarrow 2s^2 2p4f \ D(5/2)_{2,3}$
36 911.8	36 911.7	$2s^2 2p^2 \ ^1D_2^e \rightarrow 2s^2 2p4f \ G(9/2)_{4,5}$
36 921.9	36 921.9	$2s^2 2p^2 \ ^1D_2^e \rightarrow 2s^2 2p4f \ D(3/2)_{1,2}$

^aReferences 56–58.

$2s^2 2p^2 \ ^3P_J^e \rightarrow 2s^2 2p3p \ (^3D_{J'}^e, \ ^3P_{J'}^e) \rightarrow 2s^2 2p \ ^2P_{1/2,3/2}^o(2+1)$ ionization process in atomic carbon. The kinetic energy of the electrons is about 1.699 eV for the carbon resonances near the CO_2 4f resonances, depending a little (± 5 meV) on the transition and the excitation energy, and about 2.006 eV at the carbon resonances near the CO_2 5f resonances. In the previous REMPI-PES study the photoelectron spectrum of the sharp structure near the 4f resonance was reported to show a single peak at 1.994 eV.^{50,51} The reason for this discrepancy is not clear at present, but may have resulted from a less accurate calibration of the absolute kinetic energy in the previous study.

- (4) Several other carbon atom (2+1) REMPI transitions out of the $2s^2 2p^2 \ ^3P_{0,1,2}^e$ and especially the $2s^2 2p^2 \ ^1D_2^e$ states have also been observed in the present study, some of which to our knowledge have never been observed before using REMPI. All transition energies and assignments are given in Table II. The $2s^2 2p4f$ atomic carbon states are best described in an intermediate coupling scheme. The labels $L(K)_{J_1, J_2}$ in Table II have been taken from Johansson.⁵⁶

If the suggested carbon atom assignments are accepted, the next question concerns the source of the atoms in the $2s^2 2p^2 \ ^3P_{0,1,2}^e$ ground and the $2s^2 2p^2 \ ^1D_2^e$ first excited

state. As mentioned before, when the yield of C^+ ions is monitored as a function of the wavelength, an excitation spectrum is observed that is completely different from the spectra observed monitoring O^+ , CO^+ , or CO_2^+ ions. Moreover, it turns out that the carbon atom resonances near the 4f state of CO_2 are present with virtually identical intensity when no CO_2 gas is admitted into the spectrometer and the pressure drops to the background pressure. All other carbon atom resonances decrease in intensity only by about 10% when the CO_2 gas inlet is closed. It therefore seems that the presence of the carbon atoms is hardly correlated with CO_2 . Possibly most of the $\text{C}(^3P_{0,1,2}^e)$ and $\text{C}(^1D_2^e)$ atoms are produced by fragmentation of large organic molecules (e.g., pump oil) present in the ionization chamber. Nevertheless, the photoelectron spectra obtained for ionization of CO_2 via the $(^2\Pi_{g3/2,1/2})nf$ Rydberg states (*vide infra*) show that a small fraction of $\text{C}(^3P_{0,1,2}^e)$ atoms is produced by fragmentation of CO_2 . In these photoelectron spectra distinct peaks are present, which can be attributed to the ionization of $\text{C}(^3P_{0,1,2}^e)$ to the $\text{C}^+(^2P_{1/2,3/2}^o)$ ionic manifold, and which disappear completely when no CO_2 gas is present in the spectrometer.

Other background gases like O_2 or N_2 might interfere with our CO_2 measurements at high laser power as well, e.g., O_2 shows a very strong $\text{X}^3\Sigma_g^-(v''=0)$

$\rightarrow \rightarrow \text{C } 3s\sigma_g^3 \Pi_g(v'=2) (2+1)$ REMPI transition at the resonance wavelength for excitation of the $4f$ Rydberg states of CO_2 .⁶⁰⁻⁶³ Fortunately, the $4f$ Rydberg states are relatively strong as well, so that with the laser power used to investigate these states the signals due to O_2 are only minor. Additionally, we have inspected this O_2 resonance in a follow-up study using pure O_2 to confirm earlier conclusions which indicated that electrons produced *via* this transition have kinetic energies below 0.9 eV.⁶⁰ Since photoelectrons produced in the ionization *via* the $4f$ Rydberg states of CO_2 have kinetic energies considerably larger than 0.9 eV, we conclude that this O_2 transition does not interfere with our results on these states. We have further confirmed that other O_2 resonances in the wavelength region investigated by us, e.g., the transitions to the $\text{C } 3s\sigma_g^3 \Pi_g(v'=3,4)$ levels,⁶² similarly do not disturb our results on CO_2 .

In our excitation spectra obtained with mass-resolved ion detection a strong signal at $m/e=28$ is observed. This signal has to a large extent the same excitation spectrum as CO_2 and would therefore logically be assigned to CO^+ . However, since N_2^+ has the same m/e ratio, part of the signal might also be due to ionization of background N_2 . We have confirmed in a separate study on pure N_2 , however, that N_2^+ ions and electrons deriving from ionization of N_2 do not interfere with our CO_2 measurements in the present wavelength region, even though several strong resonant features of N_2 are present.⁶⁴⁻⁶⁶

CO is interesting from another point of view, since it may be produced by dissociation of CO_2 or CO_2^+ . It is well known that dissociation products need not be in their electronic, vibrational, or rotational ground states. In order to investigate whether our wavelength or photoelectron spectra reveal the presence of CO in its $X^1\Sigma^+(v''=0)$ ground state, produced by the photodissociation of CO_2 or CO_2^+ , we have recorded the REMPI and photoelectron spectra of pure CO in the wavelength region of the current study on CO_2 . The strongest resonances of CO in this region are the $X^1\Sigma^+(v''=0) \rightarrow A^1\Pi(v'=3,4) (2+2)$ REMPI transitions. The $X^1\Sigma^+(v''=0) \rightarrow A^1\Pi(v'=1,2,3)$ transitions have been investigated in a previous study.⁶⁷ Additionally, we have measured the photoelectron spectra for ionization *via* several of these CO transitions. From the excitation and photoelectron spectra it can be concluded that in our measurements on CO_2 signals deriving from $\text{CO } X^1\Sigma^+(v''=0)$ are not observed. However, this does not exclude the generation of CO *via* photodissociation of CO_2 or CO_2^+ in the wavelength region of the present study, since ionization of $\text{CO } X^1\Sigma^+(v''=0)$ produced from photodissociation might require too many photons to be observed or CO might be produced in electronically and vibrationally excited states.

C. Oxygen atom resonances

Atomic oxygen is one of the possible photodissociation products of CO_2 . Recently Pratt *et al.* have reported transitions which probe the oxygen atom in its excited $2s^22p^4^1D_2^e$ state *via* two-photon transitions to the *even* $2s^22p^33p^1^1P_1^e$ and $2s^22p^33p^1^1F_3^e$ levels above the first ionization energy.⁶⁸ After population of these states, two processes might occur: either "LS-coupling forbidden" autoioniza-

FIG. 5. (a) Excitation spectrum of atomic oxygen using electron detection showing the five $(3+1)$ REMPI transitions listed in Table III which originate from the $2s^22p^4^1D_2^e$ state. (b) $(3+1)$ photoelectron spectrum obtained at the $2s^22p^4^1D_2^e \rightarrow 2s^22p^33d^1^1F_3^e$ transition at a one-photon energy of $36\,153.5\text{ cm}^{-1}$, showing the dominance of photon absorption from the excited state resulting in ions in the $2s^22p^3^2D_{3/2,5/2}^e$ state over autoionization resulting in ions in the $2s^22p^3^4S_{3/2}^e$ state.

tion into the $2s^22p^3^4S_{3/2}^e$ ionization continuum, i.e., the autoionization process proceeds *via* spin-spin, spin-orbit, or other interactions, or absorption of one extra photon followed by ionization into one of the $2s^22p^3^2D_{3/2,5/2}^e$ ionization continua. The $1P_1^e$ state showed only autoionization into the $4S_{3/2}^e$ continuum, while the $1F_3^e$ state showed both processes. For the $1F_3^e$ state the extra photon absorption process could be enhanced by increasing the laser power, so that at the maximum laser power used in that study both processes had comparable intensities.

In our experiments on CO_2 we have observed several three-photon transitions starting from the $2s^22p^4^1D_2^e$ state of the oxygen atom to *odd* states above the lowest ionization energy. The excitation spectrum of these states obtained using kinetic energy resolved electron detection is shown in Fig. 5(a). Mass-resolved ion detection confirms that these resonances originate from atomic oxygen. Excitation of a $2p$ electron from $2s^22p^4^1D_2^e$ into the $3d'$ orbital results in five singlet states:^{69,70} $1S_0^o$, $1P_1^o$, $1D_2^o$, $1F_3^o$, and $1G_4^o$. Figure 5(a) consists of two parts. The right part has been measured with relatively low laser power and shows the $3d' 1F_3^o$ and $3d' 1D_2^o$ states. The left part, observed with higher laser power shows the $3d' 1S_0^o$ and $3d' 1G_4^o$ states, as well as some extra structure that may derive from the $3d' 1P_1^o$ level.⁶⁹ The peak positions and assignments are given in Table III. These states have never been observed before using REMPI, and like the $3p'$ states measured by Pratt *et al.*,⁶⁸ they may be

TABLE III. Observed (2+1) and (3+1) REMPI transitions in atomic oxygen. The (3+1) transitions are singlet-singlet transitions, whereas the (2+1) transitions involve a singlet-triplet transition. Frequencies are given in cm^{-1} .

Observed photon energy	Literature photon energy	Assignment
(3+1) REMPI		
36124.8	36124.9 ^a	$2s^2 2p^4 \ ^1D_2 \rightarrow 2s^2 2p^3 3d' \ ^1S_0 \rightarrow 2s^2 2p^3 \ ^2D_{3/2,5/2}^o$
36131.8	36130.3 ^a	$2s^2 2p^4 \ ^1D_2 \rightarrow 2s^2 2p^3 3d' \ ^1G_4 \rightarrow 2s^2 2p^3 \ ^2D_{3/2,5/2}^o$
36136.3	36135.4 ^b	$2s^2 2p^4 \ ^1D_2 \rightarrow 2s^2 2p^3 3d' \ ^1P_1^o \rightarrow 2s^2 2p^3 \ ^2D_{3/2,5/2}^o$
36151.3	36150.4 ^a	$2s^2 2p^4 \ ^1D_2 \rightarrow 2s^2 2p^3 3d' \ ^1D_2 \rightarrow 2s^2 2p^3 \ ^2D_{3/2,5/2}^o$
36153.5	36153.0 ^a	$2s^2 2p^4 \ ^1D_2 \rightarrow 2s^2 2p^3 3d' \ ^1F_3^o \rightarrow 2s^2 2p^3 \ ^2D_{3/2,5/2}^o$
(2+1) REMPI		
36 381.1	36 381.4–36381.7 ^c	$2s^2 2p^4 \ ^1D_2 \rightarrow 2s^2 2p^3 3p^3 P_{0,1,2}^e \rightarrow 2s^2 2p^3 \ ^4S_{3/2}^o$

^aReference 70.

^bReference 69.

^cReference 71.

used for monitoring the presence of the oxygen atom in the $2s^2 2p^4 \ ^1D_2$ state using three-photon absorption, but in a different wavelength region than the two-photon absorption to the $3p'$ states. The photoelectron spectrum obtained for ionization via the $3d' \ ^1F_3$ level is shown in Fig. 5(b) and demonstrates that absorption of one extra photon and subsequent ionization into the $^2D_{3/2,5/2}^o$ ionization continua dominates the ionization dynamics. We therefore conclude that under our experimental circumstances (1 mJ per pulse vs 25 μJ per pulse by Pratt *et al.*) the role of autoionization is almost negligible. This behavior is observed for all $3d'$ excited states listed in Table III.

Another weak peak deriving from atomic oxygen is present at an excitation energy of 36381.1 cm^{-1} . This energy agrees quite well with the $2s^2 2p^4 \ ^1D_2 \rightarrow 2s^2 2p^3 3p^3 P_{0,1,2}^e$ two-photon transitions.⁷¹ The photoelectron spectrum shows subsequent ionization into the $2s^2 2p^3 \ ^4S_{3/2}^o$ ionization continuum, i.e., a (2+1) REMPI process. The assignment of this resonance would imply a spin-forbidden transition, which can only occur if singlet character is mixed into the wave function of the triplet states. Similar mixing has been suggested previously for higher energy levels.^{69,70}

All resonances of the oxygen atom listed in Table III disappear completely when no CO_2 gas is introduced into the spectrometer. Unlike the carbon atom, the oxygen atoms do not result therefore from ionization of background gases, but are produced by the dissociation of CO_2 or CO_2^+ .

The $\text{O}(2s^2 2p^4 \ ^1D_2)$ fragment can be produced at all photon levels except the first, as the lowest dissociation limit leading to this atom with CO in its $X \ ^1\Sigma^+$ ($v''=0$) ground state is only 7.420 eV above the ground state of CO_2 . Very high quantum yields for $\text{O}(^1D_2)$ have been observed for one-photon excitation in a region corresponding to the two-photon energy of the present study.^{72,73} If the production of $\text{O}(^1D_2)$ would occur at our two-photon level, we would have to conclude that the accompanying CO fragment is not observed, because ionization of $\text{CO } X \ ^1\Sigma^+$ requires too many photons to be detectable.

Resonances originating from the $2s^2 2p^4 \ ^3P_{0,1,2}^e$ ground state of the oxygen atom have not been observed in our ex-

citation spectra, even though several three-photon allowed Rydberg series are present in the energy region of the present study.⁵⁸ The odd triplet series converging to the lowest $^4S_{3/2}^o$ ionization limit, i.e., the $ns \ ^3S_1^o$, $nd \ ^3D_{1,2,3}$ and $ng \ ^3G_{3,4,5}$ series are allowed in three-photon absorption, and subsequent absorption of an additional photon should ionize the atom into the $^4S_{3/2}^o$ continuum. No electrons deriving from ionization of oxygen atoms have been observed in the photoelectron spectra of CO_2 that can be attributed to ionization of the triplet ground state into the $^4S_{3/2}^o$ continuum. From these observations it can be concluded that below the three-photon level no oxygen atoms are produced in their $^3P_{0,1,2}^e$ ground state, since otherwise the aforementioned resonances to the triplet states should have been observed. If such atoms would result from dissociation processes at higher photon levels, they are unlikely to be observed in the present experiments. They would probably only be generated via the CO_2 ($^2\Pi_{g3/2,1/2}$) nf resonances, at which energies a subsequent ionization of $\text{O}(^3P_{0,1,2}^e)$ would be a nonresonant four-photon process.

D. Photoelectron spectra

In the preceding section photoelectron spectra have been used to confirm the assignments of atomic carbon and oxygen signals. Here we will be concerned with the (3+1) REMPI photoelectron spectra of CO_2 obtained for ionization via the CO_2 molecular nf Rydberg states for $n=4-7$. These photoelectron spectra and partial assignments are shown in Figs. 6–14. The kinetic energy resolution of the electrons in the present study is about 15 meV (FWHM), but the positions of the peaks can be determined with an accuracy of about 7 meV. The lowest ionic state of CO_2 ($X \ ^2\Pi_g$) is located 13.776 eV above the ground state.^{15,16,18,41,45–47} The splitting between the two spin-orbit components ($^2\Pi_{g3/2}$ and $^2\Pi_{g1/2}$) has been determined to be 20 meV.^{14–16,18–21,41,45,46} With the present resolution it is therefore possible to distinguish between these two spin-orbit components in the photoelectron spectra. In agreement with the assignments of Cossart-Magos *et al.*¹² all nf Rydberg states having a $^2\Pi_{g3/2}$ core only show the lowest spin-orbit component in their

photoelectron spectra, while Rydberg states with $^2\Pi_{g1/2}$ cores only show the upper component. A first inspection of the photoelectron spectra of Figs. 6–14 shows that most spectra contain a great number of resolved peaks covering a kinetic energy region of at least 2 eV. A small number of these peaks can be attributed to ionization of the carbon atom, in particular in the photoelectron spectra recorded near carbon resonances in the excitation spectrum (see Table II).

Since the mass-resolved ion spectra only show minor CO_2^+ signals and larger C^+ , O^+ , and CO^+ signals, part of the photoelectrons might be assumed to result from ionization processes of neutral fragments produced *via* dissociation of CO_2 or CO_2^+ . Oxygen atoms resulting from the photodissociation of CO_2 or CO_2^+ may be in either the $2s^22p^4\ ^3P_{0,1,2}^e$ triplet ground state or in one of the $2s^22p^4\ ^1D_2^e$ or $^1S_0^e$ lower excited states. Ionization from these states requires the absorption of at least four photons. In the preceding section we have concluded that there is no indication in the excitation and photoelectron spectra for oxygen atoms in their triplet ground state. These same spectra, on the other hand, clearly showed the presence of oxygen atoms in the $2s^22p^4\ ^1D_2^e$ state. Alternatively, (pre)dissociation of CO_2 has been shown^{34,74} to produce oxygen atoms in several higher excited states, e.g., $2s^22p^33p\ ^3P_{0,1,2}^e$ and $2s^22p^33s\ ^3S_1^e$, which can be ionized by one- or two-photon absorption, leaving the O^+ ion in the $2s^22p^3\ ^4S_{3/2}^o$ or $2s^22p^3\ ^2D_{3/2,5/2}^o$ ionic states. As a result of the large number of energetically allowed transitions some individual peaks in the spectra of Figs. 6–14 could be attributed to ionization of the oxygen atom. Inspection of the assignments and the photoelectron peaks that are then left unaccounted for, however, shows that these assignments do not lead to a consistent picture. In the same way it is energetically possible that highly excited carbon atoms are created which are subsequently ionized by one extra photon into the $^2P_{1/2,3/2}^o$ ionization continua, but similar to the case of the oxygen atom a consistent overall assignment can not be obtained in this way.

In the preceding section we investigated the possibility that CO is produced in its $X\ ^1\Sigma^+(v''=0)$ ground state, and concluded that the excitation and photoelectron spectra do not reveal the presence of this species in the excitation spectra or in the photoelectron spectra. Several one-photon VUV studies on CO_2 have shown, however, that photodissociation of CO_2 may well produce CO molecules which are electronically, vibrationally and rotationally highly excited.^{31,34,35,38,44,75–77} These states can subsequently be ionized to different electronic, vibrational and rotational levels of the CO^+ ion by a number of photons which ranges from 1–5, depending upon the specific excited and ionic states. Nevertheless, we conclude that such ionization processes are not responsible for the majority of the photoelectron peaks in the spectra of Figs. 6–14. This conclusion is based on the following observations. First, in order to investigate whether electrons are observed from ionization of excited CO, we have calculated the kinetic energies of electrons associated with ionization of the $v=0$ –8 vibrational levels of the $X\ ^1\Sigma^+$, $a\ ^3\Pi_r$, $a'\ ^3\Sigma^+$, $d\ ^3\Delta_i$, $e\ ^3\Sigma^-$, $A\ ^1\Pi$, $I\ ^1\Sigma^-$, and $D\ ^1\Delta$ states of CO to the $v^+=0$ –8 vibrational levels of both the $X\ ^2\Sigma^+$ ionic ground state and the $A\ ^2\Pi$,

first electronically excited state of CO^+ . The level energies and ω_e and $\omega_e x_e$ parameters have been adopted from Huber and Herzberg.⁷⁸ This procedure results in a vast number of predicted electron energies, but a consistent assignment of large groups of electron peaks in the photoelectron spectra of Figs. 6–14 cannot be obtained in this way. Secondly, the photoelectron spectra recorded with picosecond excitation are very similar to the spectra observed using nanosecond excitation, even though the mass-resolved ion spectra obtained with picosecond excitation show a considerably smaller $\text{CO}^+/\text{CO}_2^+$ ratio than the spectra recorded with nanosecond excitation.

On the basis of the aforementioned considerations we believe that the electron peaks shown in Figs. 6–14 do not result from ionization of the dissociation products of CO_2 such as C, O, or CO, but from ionization of CO_2 itself. The peaks form long vibrational progressions that are seen to extend to over 1.5 eV in some cases (see, for example, Figs. 7, 11, and 13). This has also been reported in an earlier REMPI-PES study on the $4f$ and $5f$ Rydberg states of CO_2 .⁵¹

Ionization of CO_2 *via* the $(^2\Pi_{g3/2,1/2})nf$ Rydberg states would normally be expected to terminate on the rovibronic levels of the $X\ ^2\Pi_{g3/2,1/2}$ ionic state. Indeed, no electron peaks corresponding to ionization to the excited $A\ ^2\Pi_u$, $B\ ^2\Sigma_u^+$, and $C\ ^2\Sigma_g^+$ states, whose excitation energies are well known,^{15,16,18–20,45,46} are observed in the present study. The photoelectron peaks in Figs. 6–14 should consequently be ascribed to ionization to vibrational levels of the $X\ ^2\Pi_g$ ground ionic state. Assignment of these peaks is hampered by the relatively limited knowledge on vibrational levels with energies which exceed 0.4 eV. As the vibrational state density in the ion increases rapidly with higher vibrational excitation, it therefore becomes progressively more difficult to assign photoelectron peaks in this energy region, while at the same time the possibility to compare the assignments with other studies becomes minimal. The assignment of the peaks in the photoelectron spectra shown in Figs. 6–14 are given in Tables IV–XII. Photoelectron peaks near the origin can be confidently assigned, bearing the aforementioned

FIG. 6. Photoelectron spectrum obtained at the $(^2\Pi_{g3/2})4f$ origin transition at a one-photon energy of $34\,731\text{ cm}^{-1}$. The photoelectron peak labeled 5 is discussed in the text. The assignments of the photoelectron peaks are given in Table IV.

FIG. 7. Photoelectron spectra obtained at 34 771, 34 781, 34 791, 34 804, and 34 811 cm^{-1} (lower to upper trace) which correspond to different positions in the three-photon resonance line of the $(^2\Pi_{g/2})4f$ origin transition. The two main progressions $^2\Pi_{g/2}(v_1^+, 0, 0)$ and $^2\Pi_{g/2}(v_1^+, 0, 2)$, present in all five spectra, have been labeled. The assignments of the photoelectron peaks are given in Table V.

remarks in mind, but for vibrational excitations exceeding 0.4 eV peaks can be assigned to various $^2\Pi_g(v_1, v_2, v_3)$ combinations. From these possible assignments the most consistent ones have been chosen on the basis of the following criteria.

First, for all members of the nf Rydberg series in CO_2 we observe core preservation in the vibrationless origin photoelectron peak, and core preservation was therefore main-

FIG. 8. Photoelectron spectrum obtained at the $(^2\Pi_{g/2})4f1_0$ transition at a one-photon energy of 35 207 cm^{-1} showing primarily $\Delta v=0$ ionization behavior. The photoelectron peak labeled 5 is discussed in the text. The assignments of the photoelectron peaks are given in Table VI.

FIG. 9. Photoelectron spectrum obtained at the $(^2\Pi_{g/2})5f$ origin transition at a one-photon energy of 35 562 cm^{-1} . The photoelectron peaks labeled 1–5 are discussed in the text. The assignments of the photoelectron peaks are given in Table VII.

tained in the assignment of the entire vibrational progression in a specific photoelectron spectrum. Secondly, it should be realized that transitions involving an *odd* number of quanta in the nontotally symmetric vibrations ω_2 (degenerate bend) and ω_3 (asymmetric stretch) in the $X\ ^2\Pi_g$ ground ionic state are formally forbidden.¹ This selection rule has been taken into consideration in the assignments of the photoelectron spectra, but in some cases photoelectron peaks can *only* be assigned if this selection rule is violated, for example, the (0,1,0) vibration in Fig. 7 (Table V) and the (0,0,1) vibration in Fig. 8 (Table VI). Finally, in the photoelectron kinetic energy region corresponding to highly rovibronically excited ions in the $X\ ^2\Pi_g$ ground ionic state, the photoelectron peaks are preferably fitted into vibrational progressions as much as possible. For example, the assignment of a photoelectron peak to (4,0,0) is reinforced if the (3,0,0) and (5,0,0) vibrations can also be assigned in the same photoelectron spectrum.

In the present study the resolution is insufficient to discriminate between close-lying Renner–Teller states within the $v_2=1$ or $v_2=2$ manifolds like $\mu\ ^2\Sigma_u^+1/2$, $^2\Delta_u5/2$, and $^2\Delta_u3/2$, $\kappa\ ^2\Sigma_u^-1/2$ in $v_2=1$ and $\mu\ ^2\Pi_{g/2}3/2$, $^2\Phi_{g/2}7/2$ and $^2\Phi_{g/2}5/2$,

FIG. 10. Photoelectron spectrum obtained at the $(^2\Pi_{g/2})5f$ origin transition at a one-photon energy of 35 616 cm^{-1} . The photoelectron peaks labeled 1 and 3–5 are discussed in the text. The assignments of the photoelectron peaks are given in Table VIII.

FIG. 11. Photoelectron spectrum obtained at the $(^2\Pi_{g3/2})6f$ origin transition at a one-photon energy of $36\,013\text{ cm}^{-1}$. The photoelectron peak labeled 3 is discussed in the text. The two main progressions $^2\Pi_{g3/2}(v_1^+, 0, 0)$ and $^2\Pi_{g3/2}(v_1^+, 0, 2)$ have also been labeled. The assignments of the photoelectron peaks are given in Table IX.

$\kappa^2\Pi_{g1/2,3/2}$ in $v_2=2$. As indicated in the assignments, it is, however, possible in some cases to discriminate between the lower 2(3) and the upper 2(3) Renner-Teller components in the $v_2=1(2)$ states, because these groups are separated by approximately the spin-orbit splitting of the $X\ ^2\Pi_g$ ionic state (20 meV).

The photoelectron spectrum of the $(^2\Pi_{g1/2})4f$ state shown in Fig. 7 is one of the most complicated spectra, and its assignment procedure will therefore be described as a representative example for the other photoelectron spectra. The photoelectron spectra of the $(^2\Pi_{g1/2})4f$ state have been recorded with identical laser powers at different positions in the excitation spectrum of the $(^2\Pi_{g1/2})4f$ (see also Fig. 1). Apart from the trivial fluctuations in integrated intensity, it is observed that the vibrational activity changes dramatically in going from low to high excitation energy in Fig. 7. Two photoelectron peaks can easily be assigned: the highest energy peak corresponds in all traces to the vibrationless $X\ ^2\Pi_{g1/2}$ origin, while the peak around 1.7 eV can be attributed to atomic carbon. The carbon signal is present in the CO_2 photoelectron spectra because of the near-lying atomic

FIG. 13. Photoelectron spectrum obtained at the $(^2\Pi_{g3/2})7f$ origin transition at a one-photon energy of $36\,282\text{ cm}^{-1}$. The photoelectron peaks labeled 1–5 are discussed in the text. The assignments of the photoelectron peaks are given in Table XI.

carbon resonances in the excitation spectrum (see Fig. 1). Inspection of the highly vibrationally excited region ($E_{\text{vib}} > 0.4\text{ eV}$) in the spectrum measured at a photon energy of $34\,781\text{ cm}^{-1}$ reveals several peaks, which are separated by regular intervals. These regular distances have been extrapolated to the energy region closer to the origin where weak peaks are found at the expected positions. This progression is identified as a $(v_1, 0, 0)$ progression and is observed up to $v_1=14$. For such high values of the vibrational quantum number the vibrational energies can no longer be calculated accurately within the harmonic approximation, but the anharmonicity constant x_{11} should be taken into account. Indeed, it is observed that in this energy region the intervals are by no means constant. With the v_1 numbering established the peaks have been fitted to the equation $E_{\text{vib}} = E_{\text{s.o.}} + \omega_1 v_1 + x_{11} v_1^2$ which results in values for ω_1 and x_{11} of 0.159 and $-1.5 \times 10^{-3}\text{ eV}$, respectively. $E_{\text{s.o.}}$ stands for a fixed offset and its value depends on whether the progression is in the $^2\Pi_{g3/2}$ or $^2\Pi_{g1/2}$ ionic potential. For the present $(v_1, 0, 0)$ progression in the $^2\Pi_{g1/2}$ potential $E_{\text{s.o.}}$ is fixed at 20 meV. The value obtained for ω_1 is in good agreement with values reported in more accurate studies.^{14–18,20,21,46} The

FIG. 12. Photoelectron spectrum obtained at the $(^2\Pi_{g1/2})6f$ origin transition at a one-photon energy of $36\,065\text{ cm}^{-1}$. The peaks labeled 1–5 are discussed in the text. The assignments of the photoelectron peaks are given in Table X.

FIG. 14. Photoelectron spectrum obtained at the $(^2\Pi_{g1/2})7f$ origin transition at a one-photon energy of $36\,340\text{ cm}^{-1}$. The photoelectron peaks labeled 1–5 are discussed in the text. The assignments of the photoelectron peaks are given in Table XII.

TABLE IV. Observed peaks and vibrational energies in the photoelectron spectrum obtained at the (${}^2\Pi_{g3/2}$)4*f* origin transition at a one-photon energy of 34 731 cm⁻¹.

Observed electron energy (eV)	Observed vibrational energy (eV)	Ionic state
3.451	-0.003	${}^2\Pi_{g3/2}(0,0,0)$ FWHM 40 meV
3.279	0.169	${}^2\Pi_{g3/2}(1,0,0)$
		${}^2\Pi_g(0,2,0)\kappa^2\Pi_{g1/2,3/2}$
3.262	0.186	${}^2\Pi_{g3/2}(0,0,1)$
3.213	0.235	${}^2\Pi_g(0,1,1)\mu^2\Sigma_u^+, {}^2\Delta_{u5/2}$
3.125	0.323	${}^2\Pi_{g3/2}(2,0,0)$
		${}^2\Pi_g(1,2,0)\kappa^2\Pi_{g1/2,3/2}$
3.103	0.345	${}^2\Pi_{g3/2}(1,0,1)$
3.072	0.376	${}^2\Pi_{g3/2}(0,0,2)$
		peak 5; see the text
2.976	0.472	${}^2\Pi_{g3/2}(3,0,0)$
		${}^2\Pi_g(0,2,2)\mu^2\Pi_{g1/2,3/2}$
		${}^2\Pi_{g3/2}(2,0,1)$
		${}^2\Pi_g(2,2,0)\kappa^2\Pi_{g1/2,3/2}$
2.890	0.558	${}^2\Pi_{g3/2}(0,0,3)$
2.619	0.829	${}^2\Pi_{g3/2}(3,0,2)$
2.483	0.965	${}^2\Pi_{g3/2}(4,0,2)$

value obtained for x_{11} is of the same order as the x_{11} value for the ground state of CO₂, which amounts to -0.5×10^{-3} eV.⁷⁹

The intense peak at a vibrational energy of 0.387 eV can readily be assigned to ${}^2\Pi_{g1/2}(0,0,2)$. Combining this peak with the ${}^2\Pi_{g1/2}(v_1,0,0)$ progression reveals a second progression, viz., ${}^2\Pi_{g1/2}(v_1,0,2)$. These two progressions dominate the lower two traces in Fig. 7 and are present as well in the other three traces.

The middle trace of Fig. 7 shows peaks close to the ${}^2\Pi_{g1/2}(0,0,0)$ origin which can be assigned to the ${}^2\Pi_{g1/2}(0,1,0)$ vibration. The intensity of these peaks can be as large as or even larger than the intensity of the origin peak, as can be seen in the upper two traces of Fig. 7. The remaining peaks in the upper three traces of Fig. 7 can be attributed to ${}^2\Pi_{g1/2}(v_1,1,0)$ and ${}^2\Pi_{g1/2}(v_1,1,2)$ progressions. Some members of these progressions are observed to coincide with members of the ${}^2\Pi_{g1/2}(v_1,0,0)$ and ${}^2\Pi_{g1/2}(v_1,0,2)$ progressions, which may give rise to variations in the intensities.

The assignments of the (${}^2\Pi_{g1/2}$)4*f* photoelectron spectra as well as the procedure described above have been used to assign the remaining photoelectron spectra in a similar way. The (${}^2\Pi_{g3/2}$)6*f* and (${}^2\Pi_{g3/2}$)7*f* photoelectron spectra shown in Figs. 11 and 13 and tabulated in Tables IX and XI, respectively, also show long progressions based on the symmetric stretch ω_1 . The progression in the (${}^2\Pi_{g3/2}$)6*f* spectrum can be observed up to $v_1=16$ and fitting of the vibrational energies as described above for the (${}^2\Pi_{g1/2}$)4*f* state ($E_{s.o.}$ is now set to 0) results in values for ω_1 and x_{11} of 0.158 and -1.2×10^{-3} eV, respectively.

The ω_2 activity in the photoelectron spectra of (${}^2\Pi_{g1/2}$)4*f* is observed for the partially resolved rotational structure on the high energy side of (${}^2\Pi_{g1/2}$)4*f* in the excitation spectrum. As these structures are also observed in the excitation spectra of the (${}^2\Pi_{g3/2}$)4*f* and (${}^2\Pi_{g3/2,1/2}$)5*f* states, ω_2 activity might have been expected in these photo-

electron spectra as well, but inspection of the photoelectron spectra shows that such is not the case. The (${}^2\Pi_{g3/2}$)7*f* state, on the other hand, also shows ω_2 activity in the photoelectron spectrum on the high-energy side of the partially resolved rotational contour.

When we compare the above results obtained with kinetic energy resolved electron detection with the results obtained with mass-resolved ion detection, it becomes clear that the two techniques yield complementary results. The photoelectron spectra are dominated by electrons deriving from the ionization of CO₂, whereas mass-resolved ion detection reveals that the CO₂⁺ ion is only a minor product of the excitation and ionization processes: the fragment ions CO⁺ and O⁺ are formed in considerably larger abundances. The observation that the yields of CO⁺ and O⁺ follow the (${}^2\Pi_{g3/2,1/2}$)*nf* resonances of CO₂ on the three-photon level and that off-resonance no CO⁺ or O⁺ ions are generated, together with the apparent absence of electrons deriving from the ionization of CO and O in the photoelectron spectra of the (${}^2\Pi_{g3/2,1/2}$)*nf* states would seem to indicate that the fragment ions result from dissociative absorption processes in the CO₂⁺ ion.^{29,51,80} Such processes would require the absorption of at least six photons: four photons to ionize CO₂ and, subsequently, two photons to access the dissociative continua in the ionic manifold leading to the fragment ions. The dissociation into CO⁺ ions is accompanied by the production of O atoms in most probably the $2s^22p^4\ ^3P_{0,1,2}$ or $2s^22p^4\ ^1D_2^e$ state. The dissociation into O⁺ ions is accompanied by the generation of CO fragments in their X¹ Σ^+ ground state. As concluded previously, the ionization of these neutral fragments is not observed because an additional four photons would need to be absorbed.

The photoelectron spectra and their assignments obtained in the present high-resolution REMPI-PES study on the (${}^2\Pi_{g3/2,1/2}$)4*f* and (${}^2\Pi_{g3/2,1/2}$)5*f* Rydberg states differ in several important aspects from the previous low-resolution (3+1) REMPI-PES studies of Wu *et al.*⁴⁹⁻⁵² In these studies photoelectrons were assigned deriving from a (3+2) process terminating on the C² Σ_g^+ ionic state. Such ionization processes have definitely not been observed in the present study. Given the observation of the previous study that these processes were enhanced when tuning to the sharp resonances at the high-energy side of the molecular (${}^2\Pi_{g1/2}$)4*f* resonance,⁵⁰ and given our conclusion that these sharp resonances should be attributed to atomic carbon, we feel that as the result of the low resolution these photoelectron peaks have not been assigned correctly. Wu *et al.* also tentatively came to the conclusion that ionization processes might occur to a hitherto unobserved ionic state.⁵⁰ Electrons that can be attributed to such processes are not observed in the present study. Finally, the long progressions observed in the (3+1) REMPI-PES studies of Wu *et al.* were to a major extent assigned to even $v_3\omega_3$ progressions.⁵¹ Our high-resolution photoelectron spectra do not allow for the assignment of such progressions. In contrast, it is observed that the dominant progressions present in the photoelectron spectra are based on the symmetric stretch vibration ω_1 .

TABLE V. Observed peaks and vibrational energies in the photoelectron spectra obtained at the (${}^2\Pi_{g1/2}$) $4f$ origin transition for one-photon energies of 34 771, 34 781, 34 791, 34 804, and 34 811 cm^{-1} . In the photoelectron spectrum obtained with a one-photon energy of 34 811 cm^{-1} the ($v_1, 1, 0$) progression, which nearly coincides with the ($v_1-2, 0, 2$) progression, may be present. The listed progressions are present in all five traces of Fig. 7. The absolute energies given are obtained from the photoelectron spectrum measured at one-photon energy of 34 771 cm^{-1} . (a) Additional peaks observed in the photoelectron spectrum obtained with a one-photon energy of 34 771 cm^{-1} . (b) Additional peaks observed in the photoelectron spectrum obtained with a one-photon energy of 34 791 cm^{-1} . (c) Additional peaks observed in the photoelectron spectrum obtained with a one-photon energy of 34 811 cm^{-1} .

Observed electron energy (eV)	Observed vibrational energy (eV)	Ionic state
3.448	0.020	${}^2\Pi_{g1/2}(0,0,0)$ FWHM 30 meV
3.296	0.172	${}^2\Pi_{g1/2}(1,0,0)$ Only in 34 804 and 34 811 cm^{-1}
3.141	0.327	${}^2\Pi_{g1/2}(2,0,0)$ Only in 34 804 and 34 811 cm^{-1}
3.081	0.387	${}^2\Pi_{g1/2}(0,0,2)$
2.983	0.485	${}^2\Pi_{g1/2}(3,0,0)$
2.914	0.554	${}^2\Pi_{g1/2}(1,0,2)$
		${}^2\Pi_{g1/2}(0,0,3)$
2.839	0.629	${}^2\Pi_{g1/2}(4,0,0)$
2.785	0.683	${}^2\Pi_{g1/2}(2,0,2)$
2.703	0.765	${}^2\Pi_{g1/2}(5,0,0)$
		${}^2\Pi_{g1/2}(0,0,4)$
2.639	0.829	${}^2\Pi_{g1/2}(3,0,2)$ Only in 34 811 cm^{-1}
2.558	0.910	${}^2\Pi_{g1/2}(6,0,0)$
2.498	0.970	${}^2\Pi_{g1/2}(4,0,2)$
2.413	1.055	${}^2\Pi_{g1/2}(7,0,0)$
2.373		Background peak
2.270	1.198	${}^2\Pi_{g1/2}(8,0,0)$
2.212	1.256	${}^2\Pi_{g1/2}(6,0,2)$
2.152	1.316	${}^2\Pi_{g1/2}(9,0,0)$
2.026	1.442	${}^2\Pi_{g1/2}(10,0,0)$
1.896	1.572	${}^2\Pi_{g1/2}(11,0,0)$
1.763	1.705	${}^2\Pi_{g1/2}(12,0,0)$
1.66	1.81	${}^2\Pi_{g1/2}(13,0,0)$ not visible: coincides with C peak
1.557	1.911	${}^2\Pi_{g1/2}(14,0,0)$
(a)		
3.270	0.198	${}^2\Pi_{g1/2}(0,0,1)$
3.237	0.231	${}^2\Pi_g(0,1,1)\mu^2\Sigma_{u1/2}^+, {}^2\Delta_{u5/2}$
1.665		$C(2s^22p^2\ ^3P_{0,1,2}^o \rightarrow 2s^22p\ ^2P_{1/2,3/2}^o)$
(b)		
3.420	0.058	${}^2\Pi_g(0,1,0)\mu^2\Sigma_{u1/2}^+, {}^2\Delta_{u5/2}$
3.404	0.074	${}^2\Pi_g(0,1,0){}^2\Delta_{u3/2}, \kappa^2\Sigma_{u1/2}^-$
3.253	0.225	${}^2\Pi_g(1,1,0)\mu^2\Sigma_{u1/2}^+, {}^2\Delta_{u5/2}$
3.064	0.414	${}^2\Pi_g(0,1,2)\mu^2\Sigma_{u1/2}^+, {}^2\Delta_{u5/2}$
3.037	0.441	${}^2\Pi_g(0,1,2){}^2\Delta_{u3/2}, \kappa^2\Sigma_{u1/2}^-$
1.697		$C(2s^22p^2\ ^3P_{0,1,2}^o \rightarrow 2s^22p\ ^2P_{1/2,3/2}^o)$
(c)		
3.431	0.057	${}^2\Pi_g(0,1,0)\mu^2\Sigma_{u1/2}^+, {}^2\Delta_{u5/2}$
3.253	0.235	${}^2\Pi_g(1,1,0)\mu^2\Sigma_{u1/2}^+, {}^2\Delta_{u5/2}$
		${}^2\Pi_g(1,1,0){}^2\Delta_{u3/2}, \kappa^2\Sigma_{u1/2}^-$
3.210	0.278	${}^2\Pi_g(1,2,0)\mu^2\Pi_{g3/2,1/2}, {}^2\Phi_{g7/2}$
3.048	0.440	${}^2\Pi_g(0,1,2)\mu^2\Sigma_{u1/2}^+, {}^2\Delta_{u5/2}$
		${}^2\Pi_g(0,1,2){}^2\Delta_{u3/2}, \kappa^2\Sigma_{u1/2}^-$
2.88	0.61	${}^2\Pi_g(1,1,2)$ coincides with ${}^2\Pi_{g1/2}(4,0,0)$
2.737	0.751	${}^2\Pi_g(2,1,2)$ coincides with ${}^2\Pi_{g1/2}(5,0,0)$
2.59	0.90	${}^2\Pi_g(3,1,2)$
2.44	1.05	${}^2\Pi_g(4,1,2)$
1.692		$C(2s^22p^2\ ^3P_{0,1,2}^o \rightarrow 2s^22p\ ^2P_{1/2,3/2}^o)$

E. One-photon ionization peaks

When the kinetic energies of, for instance, the ${}^2\Pi_{g3/2}(0,0,0)$ photoelectron peaks are monitored over a wide range of photon energies, they follow the following equation:

$$(E_{\text{kin}})_{3/2(0,0,0)} = 4 \cdot E_{\text{photon}} - IE, \quad (1)$$

with $IE = 13.776$ eV, where all variables are given in eV.

TABLE VI. Observed peaks and vibrational energies in the photoelectron spectrum obtained at the ($^2\Pi_{g1/2}$) $4f1_0$ transition at a one-photon energy of 35 207 cm^{-1} .

Observed electron energy (eV)	Observed vibrational energy (eV)	Ionic state
3.674	0.013	$^2\Pi_{g1/2}(0,0,0)$
3.517	0.170	$^2\Pi_{g1/2}(1,0,0)$
3.480	0.207	$^2\Pi_{g1/2}(0,0,1)$
		$^2\Pi_g(1,1,0)\mu^2\Sigma_u^+, ^2\Delta_{u5/2}$
3.355	0.332	$^2\Pi_{g1/2}(2,0,0)$
3.192	0.495	$^2\Pi_{g1/2}(3,0,0)$
		$^2\Pi_{g1/2}(2,0,1)$
3.134	0.553	$^2\Pi_{g1/2}(0,0,3)$
		$^2\Pi_{g1/2}(1,0,2)$
		peak 5; see the text
3.096		$C(2s^22p^2\ ^1D_2 \rightarrow 2s^22p\ ^2P_{1/2,3/2}^o)$
2.810	0.877	peak 4; see the text
2.713	0.974	$^2\Pi_{g1/2}(4,0,2)$
2.427	1.260	$^2\Pi_{g1/2}(6,0,2)$
1.941		
1.838		$C(2s^22p^2\ ^3P_{0,1,2}^o \rightarrow 2s^22p\ ^2P_{1/2,3/2}^o)$
1.770		peak 3; see the text
1.597		peak 2; see the text
1.320		
0.704		peak 1; see the text

TABLE VIII. Observed peaks and vibrational energies in the photoelectron spectrum obtained at the ($^2\Pi_{g1/2}$) $5f$ origin transition at a one-photon energy of 35 616 cm^{-1} .

Observed electron energy (eV)	Observed vibrational energy (eV)	Ionic state
3.868	0.019	$^2\Pi_{g1/2}(0,0,0)$
3.739	0.148	$^2\Pi_g(0,2,0)^2\Phi_{g5/2}, \kappa^2\Pi_{g1/2,3/2}$
3.653	0.234	$^2\Pi_g(0,1,1)\mu^2\Sigma_u^+, ^2\Delta_{u5/2}$
3.520	0.367	$^2\Pi_{g1/2}(1,0,1)$
		$^2\Pi_{g1/2}(0,0,2)$
3.371	0.516	$^2\Pi_g(0,2,2)^2\Phi_{g5/2}, \kappa^2\Pi_{g1/2,3/2}$
3.181	0.706	$^2\Pi_{g1/2}(2,0,2)$
		peak 5; see the text
3.069	0.818	$^2\Pi_g(2,2,2)^2\Phi_{g5/2}, \kappa^2\Pi_{g1/2,3/2}$
		$^2\Pi_{g1/2}(4,0,1)$
		$^2\Pi_{g1/2}(3,0,2)$
2.855	1.032	$^2\Pi_{g1/2}(3,0,3)$
		peak 4; see the text
2.772	1.115	$^2\Pi_{g1/2}(5,0,2)$
		$^2\Pi_g(4,2,2)^2\Phi_{g5/2}, \kappa^2\Pi_{g1/2,3/2}$
2.558	1.329	$^2\Pi_{g1/2}(9,0,0)$
2.195		
1.978		$C(2s^22p^2\ ^3P_{0,1,2}^o \rightarrow 2s^22p\ ^2P_{1/2,3/2}^o)$
1.814		peak 3; see the text
0.776		peak 1; see the text

The slope 4 results from the fact that the ionization process requires four photons, while IE is the lowest $\text{CO}_2\ X\ ^2\Pi_{g3/2}$ ionization energy.

When the same procedure is followed for the peaks labeled 1–5 in Figs. 6–14, it turns out that their kinetic energies can be fitted to

$$\text{Peak 1: } (E_{\text{kin}})_1 = 1 \cdot E_{\text{photon}} - 3.627, \quad (2a)$$

$$\text{Peak 2: } (E_{\text{kin}})_2 = 1 \cdot E_{\text{photon}} - 2.757, \quad (2b)$$

$$\text{Peak 3: } (E_{\text{kin}})_3 = 1 \cdot E_{\text{photon}} - 2.594, \quad (2c)$$

$$\text{Peak 4: } (E_{\text{kin}})_4 = 1 \cdot E_{\text{photon}} - 1.565, \quad (2d)$$

TABLE VII. Observed peaks and vibrational energies in the photoelectron spectrum obtained at the ($^2\Pi_{g3/2}$) $5f$ origin transition at a one-photon energy of 35 562 cm^{-1} .

Observed electron energy (eV)	Observed vibrational energy (eV)	Ionic state
3.861	0.000	$^2\Pi_{g3/2}(0,0,0)$
3.683	0.178	$^2\Pi_{g3/2}(0,0,1)$
3.566	0.294	$^2\Pi_{g3/2}(2,0,0)$
		$^2\Pi_g(1,2,0)\mu^2\Pi_{g1/2,3/2}, ^2\Phi_{g7/2}$
		$^2\Pi_g(0,2,1)\mu^2\Pi_{g1/2,3/2}, ^2\Phi_{g7/2}$
3.521	0.340	$^2\Pi_{g3/2}(1,0,1)$
3.172	0.689	$^2\Pi_{g3/2}(2,0,2)$
		peak 5; see the text
2.835	1.026	$^2\Pi_{g3/2}(3,0,3)$
		peak 4; see the text
		$C(2s^22p^2\ ^3P_{0,1,2}^o \rightarrow 2s^22p\ ^2P_{1/2,3/2}^o)$
1.958		
1.910		
1.804		peak 3; see the text
1.652		peak 2; see the text
0.769		peak 1; see the text

$$\text{Peak 5: } (E_{\text{kin}})_5 = 1 \cdot E_{\text{photon}} - 1.233. \quad (2e)$$

The first step in the fitting procedure consisted of varying both the slope and the offset. From this it was established that the slope is a number close to 1 (± 0.05). In the second step the slope was fixed at 1 in order to obtain an accurate

TABLE IX. Observed peaks and vibrational energies in the photoelectron spectrum obtained at the ($^2\Pi_{g3/2}$) $6f$ origin transition at a one-photon energy of 36 013 cm^{-1} .

Observed electron energy (eV)	Observed vibrational energy (eV)	Ionic state
4.084	0.000	$^2\Pi_{g3/2}(0,0,0)$
4.008	0.076	$^2\Pi_g(0,1,0)$
3.906	0.178	$^2\Pi_{g3/2}(0,0,1)$
3.723	0.361	$^2\Pi_{g3/2}(0,0,2)$
3.614	0.470	$^2\Pi_{g3/2}(3,0,0)$
3.571	0.513	$^2\Pi_{g3/2}(1,0,2)$
3.423	0.661	$^2\Pi_{g3/2}(2,0,2)$
3.316	0.768	$^2\Pi_{g3/2}(5,0,0)$
3.186	0.898	$^2\Pi_{g3/2}(6,0,0)$
3.033	1.051	$^2\Pi_{g3/2}(7,0,0)$
2.901	1.183	$^2\Pi_{g3/2}(8,0,0)$
2.766	1.318	$^2\Pi_{g3/2}(9,0,0)$
2.653	1.431	$^2\Pi_{g3/2}(10,0,0)$
2.517	1.567	$^2\Pi_{g3/2}(11,0,0)$
2.389	1.695	$^2\Pi_{g3/2}(12,0,0)$
2.259	1.825	$^2\Pi_{g3/2}(13,0,0)$
2.123	1.961	$^2\Pi_{g3/2}(14,0,0)$
		$C(2s^22p^2\ ^3P_{0,1,2}^o \rightarrow 2s^22p\ ^2P_{1/2,3/2}^o)$
1.998	2.086	$^2\Pi_{g3/2}(15,0,0)$
1.863	2.221	$^2\Pi_{g3/2}(16,0,0)$
		peak 3; see the text
0.856		peak 1; see the text

TABLE X. Observed peaks and vibrational energies in the photoelectron spectrum obtained at the ($^2\Pi_{g1/2}$)6*f* origin transition at a one-photon energy of 36 065 cm⁻¹.

Observed electron energy (eV)	Observed vibrational energy (eV)	Ionic state
4.095	0.015	$^2\Pi_{g1/2}(0,0,0)$
4.011	0.099	$^2\Pi_g(0,1,0)^2\Delta_{u3/2}, \kappa^2\Sigma_{u1/2}^-$
3.984	0.126	$^2\Pi_g(0,2,0)\mu^2\Pi_{g1/2,3/2}, ^2\Phi_{g7/2}$
3.942	0.168	$^2\Pi_g(0,2,0)^2\Phi_{g5/2}, \kappa^2\Pi_{g1/2,3/2}$
3.922	0.188	$^2\Pi_{g1/2}(1,0,0)$
		$^2\Pi_{g1/2}(0,0,1)$
3.873	0.237	$^2\Pi_g(0,1,1)\mu^2\Sigma_{u1/2}^+, ^2\Delta_{u5/2}$
		$^2\Pi_g(1,1,0)^2\Delta_{u3/2}, \kappa^2\Sigma_{u1/2}^-$
3.817	0.293	$^2\Pi_g(0,1,1)$
		$^2\Pi_g(1,2,0)$
		$^2\Pi_g(0,2,1)$
3.744	0.366	$^2\Pi_{g3/2}(0,0,2)$ possibly from ($^2\Pi_{g3/2}$)6 <i>f</i>
3.575	0.535	$^2\Pi_{g3/2}(1,0,2)$ possibly from ($^2\Pi_{g3/2}$)6 <i>f</i>
3.427	0.683	$^2\Pi_{g3/2}(2,0,2)$ possibly from ($^2\Pi_{g3/2}$)6 <i>f</i>
3.312	0.798	$^2\Pi_{g3/2}(5,0,0)$ possibly from ($^2\Pi_{g3/2}$)6 <i>f</i>
3.216	0.894	$^2\Pi_{g3/2}(6,0,0)$ possibly from ($^2\Pi_{g3/2}$)6 <i>f</i>
		peak 5; see the text
2.897	1.213	$^2\Pi_{g3/2}(8,0,0)$ possibly from ($^2\Pi_{g3/2}$)6 <i>f</i>
		peak 4; see the text
2.130		
1.877		peak 3; see the text
1.719		peak 2; see the text
1.522		
0.837		peak 1; see the text

value for the offset. Equations (2a)–(2e) indicate that these photoelectron peaks result from the ionization of a highly excited species by a one-photon ionization process. The one-photon ionization peaks can only be seen in the photoelectron spectra under relatively high laser power conditions and are therefore not observed in photoelectron spectra obtained for ionization *via* the CO₂ ($^2\Pi_{g3/2}$)4*f*, ($^2\Pi_{g1/2}$)4*f*, and ($^2\Pi_{g3/2}$)6*f* Rydberg states where the regular CO₂ signals dominate the spectra. Moreover, it is observed that they have in most cases significantly larger widths than the regular CO₂ peaks (see, for example, Fig. 12) and sometimes show more structure (see, for example, Fig. 14, peaks 2 and 3). A study of the excitation wavelength dependence of the one-photon ionization photoelectron peaks is largely restricted by the high laser powers that need to be used, but it would appear that their intensities only follow the CO₂ ($^2\Pi_g$)*nf* resonances to a limited extent. The only clue available for establishing the origin of these one-photon ionization photoelectron peaks is given by the offsets found in equations (2a)–(2e). The offset represents the energy difference between the unknown ionization limit and the unknown excited state from which ionization takes place by one-photon absorption. Since it is not known from which species the photoelectron peaks arise, we have tried various possibilities, similar to the procedure adopted in the assignment of the regular photoelectron peaks as has been described earlier.

In a previous REMPI-PES study on the Rydberg states of methyl iodide photoelectron peaks have been observed with a similar one-photon ionization behavior.⁵⁴ In this case it was suggested that this process finds its origin in the mix-

ing of 6*p* and 7*s* character into higher-lying Rydberg states. If we assume a similar mixing of Rydberg states as the origin for the one-photon photoelectrons in CO₂ we should be able to relate the offsets in Eqs. (2a)–(2e) to known highly excited states of CO₂. Such does not appear to be possible.

Similarly, it is found that a meaningful and consistent overall assignment cannot be obtained under the assumption that the photoelectrons derive from the ionization of highly excited carbon and/or oxygen atoms to the lower lying ionic states of these atoms. Such an assignment would moreover be at odds with the observed large widths (in some cases as large as 90 meV) of the photoelectron peaks, since atomic ionization would be expected to give rise to peaks in the photoelectron spectrum with the spectrometer limited width of about 15 meV.

Recently ion-pair dissociation according to CO₂⁺⁺(*R_C*) → CO⁺(*X* $^2\Sigma^+$) + O⁻($^2P_{1/2,3/2}^\circ$) has been observed to occur.⁴² The electron affinity of the oxygen atom is 1.462 eV,⁸¹ which would imply that ionization of O⁻($^2P_{1/2,3/2}^\circ$) might occur by a one-photon absorption process. None of the one-photon ionization photoelectron peaks matches, however, such a process and we thus conclude that ion-pair dissociation with subsequent ionization of O⁻ is not observed in our experiments.

When we assume, on the other hand, that the CO molecule is responsible for the presence of the one-photon ionization photoelectron peaks, it turns out that the five peaks can be related to one-photon ionization processes of lower Rydberg states of CO to the *X* $^2\Sigma^+(v^+)$ continua.^{78,82} These tentative assignments are given in Table XIII. Rotational excitation within these highly excited CO Rydberg states could be responsible for the large widths of the one-photon ionization photoelectron peaks.

The assignments of Table XIII all concern strong $\Delta v = 0$ ionization processes, i.e., the vibrational quantum numbers of the neutral and ionic states are the same, except for the weak peak 2, which can only be assigned to a $\Delta v = +1$ ionization process. This would seem peculiar as the $\Delta v = 0$ photoelectron peak of the same transition cannot be observed. From the lowest energy thresholds for dissociation processes leading to the CO fragments it can be concluded that at least four photons are required to produce the fragments responsible for peaks 1–3, while peaks 4 and 5 can only occur if at least five photons are absorbed.

F. Two-color experiments

In the preceding sections we have observed that the photoelectron spectra obtained with (3+1) REMPI-PES *via* the ($^2\Pi_{g3/2,1/2}$)*nf* Rydberg states exhibited dramatic variations from state to state. Such behavior might in principle arise at either the three-photon level, i.e., it could find its origin in differences in the electronic character of the various Rydberg states or in the dynamic processes occurring at this energy level, or at the four-photon level, where autoionization and (pre)dissociation could be of crucial importance. In order to investigate the relative influence of the three- and four-photon levels on the measured photoelectron spectra we have performed two-color REMPI-PES experiments.

TABLE XI. Observed peaks and vibrational energies in the photoelectron spectrum obtained at the $(^2\Pi_{g3/2})7f$ origin transition for one-photon energies of 36 282 and 36 297 cm^{-1} .

Observed electron energy (eV)	Observed vibrational energy (eV)	Ionic state
4.218	0.000	$^2\Pi_{g3/2}(0,0,0)$
4.042	0.176	$^2\Pi_g(0,2,0)\kappa^2\Pi_{g1/2,3/2}$
		$^2\Pi_{g3/2}(0,0,1)$
3.942	0.277	$^2\Pi_g(0,1,1)^2\Delta_{u3/2}, \kappa^2\Sigma_{u1/2}^-$
		$^2\Pi_g(1,2,0)\mu^2\Pi_{g1/2,3/2}, ^2\Phi_{g7/2}$
3.906	0.312	$^2\Pi_{g3/2}(2,0,0)$
3.757	0.461	$^2\Pi_{g3/2}(3,0,0)$
3.644	0.574	$^2\Pi_{g3/2}(0,0,3)$
3.600	0.618	$^2\Pi_{g3/2}(4,0,0)$
3.453	0.765	$^2\Pi_{g3/2}(5,0,0)$
3.310	0.908	$^2\Pi_{g3/2}(6,0,0)$
		$^2\Pi_{g3/2}(0,0,5)$
3.262	0.956	$^2\Pi_{g3/2}(4,0,2)$
		peak 5; see the text
3.113	1.105	$^2\Pi_{g3/2}(5,0,2)$
3.012	1.206	$^2\Pi_{g3/2}(8,0,0)$
2.919	1.299	$^2\Pi_{g3/2}(9,0,0)$
		peak 4; see the text
2.818	1.400	$^2\Pi_{g3/2}(7,0,2)$
2.608		
2.520		
2.375		
2.325		
2.227		
1.903		peak 3; see the text
1.731		peak 2; see the text
1.596		
0.869		peak 1; see the text
0.714		
Additional ω_2 activity in photoelectron spectrum obtained with a one-photon energy of 36 297 cm^{-1}		
4.173	0.052	$^2\Pi_g(0,1,0)\mu^2\Sigma_{u1/2}^+, ^2\Delta_{u5/2}$
4.143	0.082	$^2\Pi_g(0,1,0)^2\Delta_{u3/2}, \kappa^2\Sigma_{u1/2}^-$

In these experiments two photons of the first color ν and one photon of the second color ν' are used to resonantly excite a $(^2\Pi_{g3/2,1/2})nf$ Rydberg state, which is subsequently ionized by the absorption of a fourth photon of either color. Since the ionizing photon can have an energy of either $h\nu$ or $h\nu'$, the two-color photoelectron spectrum is in principle the composite of two separate photoelectron spectra:

$$E_{\text{kin},1} = (2h\nu + h\nu') + h\nu - \text{IE}, \quad (3a)$$

$$E_{\text{kin},2} = (2h\nu + h\nu') + h\nu' - \text{IE}, \quad (3b)$$

where IE stands for an ionization energy. Since the transition probability for excitation scales roughly as $I^2(\nu) \cdot I(\nu')$ and, hence, higher laser powers are required for color ν than for ν' , one would expect the contribution of process (3a) to be larger than that of process (3b). Indeed, similar two-color (3+1) REMPI-PES experiments on excited states of the krypton atom clearly demonstrated the dominance of process (3a). In the case of krypton the variation of $I(\nu)$ and $I(\nu')$ allowed for the suppression of the contribution of process (3b), although it always remained present to some extent.

If we assume for the moment that process (3a) dominates the ionization dynamics, two experiments can be performed, which separately probe the influence of the nature of the three- and four-photon levels. In a constant ionic state

TABLE XII. Observed peaks and vibrational energies in the photoelectron spectrum obtained at the $(^2\Pi_{g1/2})7f$ origin transition at a one-photon energy of 36 340 cm^{-1} .

Observed electron energy (eV)	Observed vibrational energy (eV)	Ionic state
4.228	0.019	$^2\Pi_{g1/2}(0,0,0)$
4.062	0.185	$^2\Pi_{g1/2}(1,0,0)$
		$^2\Pi_{g1/2}(0,0,1)$
3.954	0.293	$^2\Pi_g(0,1,1)^2\Delta_{u3/2}, \kappa^2\Sigma_{u1/2}^-$
		$^2\Pi_g(1,2,0)$
		$^2\Pi_g(0,2,1)$
3.778	0.470	$^2\Pi_g(0,1,2)^2\Delta_{u3/2}, \kappa^2\Sigma_{u1/2}^-$
		$^2\Pi_{g1/2}(3,0,0)$
3.626	0.621	$^2\Pi_{g1/2}(4,0,0)$
3.275	0.972	$^2\Pi_{g1/2}(4,0,2)$
		peak 5; see the text
2.941		peak 4; see the text
2.104		
2.021		
1.901		peak 3; see the text
1.763		peak 2; see the text
1.641		
1.606		
1.478		
0.880		peak 1; see the text

TABLE XIII. Assignments of one-photon ionization peaks to CO Rydberg states.

Peak 1	$b\ 3s\sigma\ ^3\Sigma^+(v'=0)$	$\rightarrow$	$X\ ^2\Sigma^+(v^+=0)$	$\Delta v=0$
Peak 2	$E\ 3p\pi\ ^1\Pi(v'=0)$	$\rightarrow$	$X\ ^2\Sigma^+(v^+=1)$	$\Delta v=+1$
Peak 3	$C\ 3p\sigma\ ^1\Sigma^+(v'=0)$	$\rightarrow$	$X\ ^2\Sigma^+(v^+=0)$	$\Delta v=0$
	$c\ 3p\pi\ ^3\Pi(v'=0)$	$\rightarrow$	$X\ ^2\Sigma^+(v^+=0)$	$\Delta v=0$
Peak 4	$h\ 4s\sigma\ ^3\Sigma^+(v'=0)$	$\rightarrow$	$X\ ^2\Sigma^+(v^+=0)$	$\Delta v=0$
Peak 5	$K,H\ 4p\sigma\ ^1\Sigma^+(v'=0)$	$\rightarrow$	$X\ ^2\Sigma^+(v^+=0)$	$\Delta v=0$
	$L\ 4p\pi\ ^1\Pi(v'=0)$	$\rightarrow$	$X\ ^2\Sigma^+(v^+=0)$	$\Delta v=0$

(CIS) experiment the photon energies $h\nu$ and $h\nu'$ are scanned simultaneously in such a way that the three-photon level is scanned over a resonance, while at the same time the four-photon level remains constant. Alternatively, in a constant excited state (CES) experiment $h\nu$ and $h\nu'$ are scanned such that the three-photon level remains at a constant energy, whereas the four-photon level changes. Photoelectron spectra obtained in the CIS and CES mode consequently may elucidate the role of the three- and four-photon levels, respectively. If the vibrational branching ratios upon ionization are predominantly determined by processes at the four-photon level, the CES photoelectron spectra are expected to exhibit major variations, whereas the CIS photoelectron spectra should remain more or less the same. If processes at the three-photon level, on the other hand, are responsible for the vibrational branching ratios, the reverse can be expected.

In our one-color REMPI-PES experiments we have observed that the photoelectron spectra obtained for (3+1) ionization *via* the $(^2\Pi_{g3/2})4f$ Rydberg state are characterized by a dominant $\Delta v=0$ transition with a limited contribution of ionization to vibrationally excited ions. Ionization *via* the $(^2\Pi_{g1/2})4f$ Rydberg state, on the other hand, results in a large vibrational activity in the photoelectron spectra, which is moreover rapidly changing as a function of the excitation wavelength. We have therefore performed CIS and CES experiments on CO₂ at the three- and four-photon levels pertinent to excitation and ionization of the $(^2\Pi_{g3/2,1/2})4f$ manifold. In these experiments the $(^2\Pi_{g3/2})4f$ Rydberg state is excited by two-color excitation, while ionization according to process (3a) subsequently occurs in the four-photon energy region previously accessed in the one-color REMPI-PES experiments on the $(^2\Pi_{g1/2})4f$ Rydberg state. If dynamic processes at the one-color four-photon level of the $(^2\Pi_{g1/2})4f$ state would be responsible for the non-Franck-Condon ionization behavior *via* this state, then one expects that the two-color photoelectron spectra *via* the $(^2\Pi_{g3/2})4f$ state will demonstrate a vibrational activity different from the one-color photoelectron spectra *via* this state, and, more importantly, strongly depend on the energy of the two-color four-photon level.

By scanning one of the two photon energies and collecting all electrons irrespective of their kinetic energies it was confirmed that the two-color excitation spectra are very similar to the one-color excitation spectrum of Fig. 1. This indicates that all resonant molecular features in this excitation spectrum derive from the three-photon level, since all other photon levels are now different from the ones of the one-color experiment.

FIG. 15. Two-color photoelectron spectra forming a CES series. The three-photon level is fixed at the $(^2\Pi_{g3/2})4f$ origin resonance at 104 187 cm⁻¹, while the four-photon level is at 139 120 cm⁻¹ in the lowest trace and 139 250 cm⁻¹ in the uppermost trace. Every trace upwards increases the four-photon level by 10 cm⁻¹. The spectra have been recorded at a fixed retarding voltage of -2.5 V. The photoelectron peaks labeled with an asterisk derive from ionization to the vibrationless $X\ ^2\Pi_g$ ionic state according to process (3b) (see the text).

As a result of the low signal intensities it was not possible to measure the photoelectron spectra in these CIS and CES two-color experiments in our standard fashion, i.e., by varying the retarding voltage on the flight tube. We have therefore recorded the spectra by transformation of the time-of-flight (TOF) spectra using a fixed retarding voltage of -2.5 V. This implies that only electrons with kinetic energies larger than about 2.5 eV can be detected. The photoelectron spectra obtained in this way show peaks with significantly larger widths and thus less resolution than in the normal photoelectron spectra, but, as will be shown, it is still possible to monitor the relative changes in the spectra quite well.

A series of CES photoelectron spectra is shown in Fig. 15. The three-photon level in these spectra is fixed at the excitation energy of the $(^2\Pi_{g3/2})4f$ Rydberg state at 104 187 cm⁻¹, which would correspond to a one-photon energy of 34 729 cm⁻¹ in the one-color experiments, while the four-photon level is at 139 120 cm⁻¹ in the lowest trace and 139 250 cm⁻¹ in the uppermost trace. Each vertical trace increases the four-photon level by 10 cm⁻¹, which is thus scanned across the four-photon level accessed in the one-color experiments on the $(^2\Pi_{g1/2})4f$ Rydberg state. The photoelectron peak to the right in the photoelectron spectra of Fig. 15 can be assigned to the transition to the unresolved vibrationless spin-orbit components of the lowest ionic

FIG. 16. Two-color photoelectron spectra forming a CIS series are shown on the left-hand side. The four-photon level is fixed at $139\,220\text{ cm}^{-1}$, corresponding to the one-color four-photon level of the $(^2\Pi_{g/2})4f$ origin state. The three-photon level changes from $104\,131\text{ cm}^{-1}$ in the bottom trace to $104\,231\text{ cm}^{-1}$ in the uppermost trace, increasing by 10 cm^{-1} in each trace. The three-photon level is thus scanned over the $(^2\Pi_{g/2})4f$ origin resonance. The photoelectron peaks labeled with an asterisk derive from ionization to the vibrationless $X\ ^2\Pi_g$ ionic state according to process (3b) (see the text). On the right-hand side, on the same horizontal level the one-color photoelectron spectra with corresponding three-photon levels, but different four-photon levels are shown. The spectra have been recorded at a fixed retarding voltage of -2.5 V .

state, $^2\Pi_g$, by process (3a). As yet, we have assumed that the photoelectron spectrum can be well described by process (3a). Under the experimental conditions of full laser power necessary to obtain these spectra it is, however, to be expected that process (3b) cannot be neglected. Indeed, analysis of the photoelectron spectra in Fig. 15 demonstrates that the peaks marked with an asterisk can only be assigned consistently under the assumption that they derive from ionization to the $^2\Pi_g$ ionic origin by process (3b). We notice that process (3b) also results in CES spectra, although a different part of the ionization continuum is addressed, namely from $138\,507\text{ cm}^{-1}$ in the lowest trace to $138\,247\text{ cm}^{-1}$ in the uppermost trace. As a result of the lower resolution, the assignment of the photoelectron peaks other than the transitions to the ionic origins by processes (3a) and (3b) is more difficult. Only the two peaks around 3.1 eV can be assigned with reasonable confidence to the transitions to the $^2\Pi_g(0,0,2)$ and $^2\Pi_g(0,1,2)$ ionic levels by process (3a).

Figure 16 (left-hand side) shows a series of photoelectron spectra obtained in the CIS mode. In these spectra the four-photon level according to process (3a) is fixed at $139\,220\text{ cm}^{-1}$, corresponding to the one-color four-photon level of the $(^2\Pi_{g/2})4f$ excitation. The three-photon level

changes, from $104\,131\text{ cm}^{-1}$ in the bottom trace to $104\,231\text{ cm}^{-1}$ in the uppermost trace, by increments of 10 cm^{-1} , i.e., the $(^2\Pi_{g/2})4f$ resonance is scanned. Process (3b), which is again prominently present as can be deduced from the photoelectron peak around 3.4 eV marked with an asterisk, can in this case not be considered to give rise to either CIS or CES spectra, since both the three- and four-photon levels change. For comparison Fig. 16 (right-hand side) shows the one-color photoelectron spectra when the three-photon energy is scanned over the $(^2\Pi_{g/2})4f$ resonance. Left- and right-hand traces on identical horizontal levels correspond to the same three-photon levels, but the four-photon levels are different.

Even though not all of the photoelectron peaks in the CIS and CES photoelectron spectra can be assigned conclusively, a qualitative inspection of Figs. 15 and 16 already demonstrates a large difference between the influence of the three- and four-photon levels on the vibrational branching ratios. The spectra obtained in the CES mode exhibit dramatic changes, which are most apparent in the relative intensities of the ionic origin and the peaks which have been tentatively assigned to the $^2\Pi_g(0,0,2)$ and $^2\Pi_g(0,1,2)$ levels by process (3a). The photoelectron spectra in the CIS mode, in contrast, remain more or less the same. This indicates that the ionization dynamics are to a major extent determined by processes at the four-photon level.

IV. DISCUSSION

The results of the one- and two-color REMPI-PES studies discussed earlier demonstrate unambiguously that $(3+1)$ REMPI via the $(^2\Pi_{g/2,1/2})nf$ Rydberg states results in ionization processes which are to a major extent determined by what occurs at the four-photon level. Moreover, the observation of multiphoton ionization of fragments has enabled the identification of the electronic states in which such fragments are formed and might contribute to an understanding of the dissociation processes occurring at various photon levels. In the following it will be shown that our experimental data are in agreement with *a priori* expectations that the direct ionization pathway of $(^2\Pi_{g/2,1/2})nf$ Rydberg states should give rise to a dominant $\Delta v=0$ propensity. The flagrant deviations from this behaviour observed in several photoelectron spectra will subsequently be ascribed to autoionization processes which can effectively compete with the direct ionization pathway. The observation of strong transitions to the “forbidden” odd levels of the degenerate bending and asymmetric stretch vibrations in the $X\ ^2\Pi_g$ ionic state will highlight the various vibronic coupling mechanisms, to which the ionic manifold is subject.

A. Molecular ionization processes

As discussed in Sec. I, CO_2 has various valence states which have been predicted in a number of theoretical studies to be located well below the lowest $(^2\Pi_{g/2,1/2})4f$ Rydberg states.^{7–11} The influence of these valence states on the higher lying np and nf Rydberg states has been investigated in detail by Cossart-Magos *et al.*¹² From this study it is known that the np Rydberg states interact strongly with valence states of the same symmetry resulting in diffuse band shapes

indicating short lifetimes for all np Rydberg states, except for the $3p\pi_u\ ^3\Sigma_u^-$ transition, which shows rotational resolution in one-photon absorption studies.^{4,6} In the energy region of the present study several np states ($n \geq 5$) are expected but not observed, which might imply that the predissociation rates of these states are so large that ionization by additional one-photon absorption does not compete effectively. The (3+1) REMPI-PES spectra via the $3p$ states investigated by Wu *et al.* show long vibrational progressions which might derive in part from such interactions.⁵¹ In contrast to the np Rydberg series, the nf Rydberg series can be observed in the excitation spectrum with several narrow, partially resolved, rotational features up to high values of the principal quantum number in both the one-photon absorption¹² as well as the present REMPI study. The narrow, partially resolved rotational structures indicate relatively long lifetimes for these states. Furthermore, the one-photon excitation spectra of Cossart-Magos *et al.* demonstrated that the quantum defect of the members of the nf Rydberg series is almost constant. These observations indicate that the nf series is unperturbed, or at least considerably less perturbed than the np Rydberg series, by the lower lying bound or dissociative valence states. We therefore do not expect that photoelectron spectra via the $(^2\Pi_{g3/2,1/2})nf$ Rydberg series will be influenced by coupling with valence states.

The nf Rydberg series are described in the $(\Omega_c)nf$ coupling scheme in which the nf Rydberg electron is almost completely decoupled from the molecular axis.¹² The nf Rydberg series under investigation in the present study converge to the lowest $X\ ^2\Pi_{g3/2,1/2}$ ionic states. The similarity of the potential energy surfaces of the $(^2\Pi_{g3/2,1/2})nf$ Rydberg states and the $X\ ^2\Pi_{g3/2,1/2}$ ionic states would lead one to infer that the ionization process will occur with a $\Delta v = 0$ propensity, i.e., the change in vibrational quantum numbers in going from the lower excited state to the upper ionic state should be zero. Such behavior is indeed what is principally observed in the photoelectron spectrum of the $(^2\Pi_{g1/2})4f1_0$ state (Fig. 8 and Table VI). This photoelectron spectrum shows a very small vibrationless origin and a dominant contribution from ionization to the $^2\Pi_{g1/2}(1,0,0)$ ionic level. Quite in contrast to this photoelectron spectrum and our *a priori* expectations we observe long vibrational progressions extending to well over 1 eV in the (3+1) REMPI-PES spectra via other nf Rydberg states. All CO_2^+ vibrations are active in the spectra of Figs. 6–14, and $^2\Pi_g(v_1,0,0)$ progressions can be observed up to very high values of v_1 : $v_1=14$ in the $(^2\Pi_{g1/2})4f$ and $v_1=16$ in the $(^2\Pi_{g3/2})6f$ photoelectron spectra.

In a (3+1) REMPI experiment spurious resonances at the one- or two-photon level can in principle influence the photoelectron spectra. The valence states mentioned before are expected at energies that correspond approximately to the two-photon level in our experiment. (2+2) or (2+1+1) REMPI processes could therefore contribute to the photoelectron signals. Since no evidence for such processes can be found in either the excitation spectrum or in the power dependence of the photoelectron spectra of Figs. 6–14, such an explanation for the observed deviations from Franck–

Condon behavior in the photoelectron spectra can be ruled out.

The photoelectron spectra obtained with two-color excitation of the $(^2\Pi_{g3/2})4f$ Rydberg state provide strong evidence that processes occurring at the four-photon level are of crucial importance for an explanation of the non-Franck–Condon behavior. A similar conclusion was reached in the (3+1) REMPI-PES study of Wu *et al.*, in which several explanations for the observed deviations from the $\Delta v = 0$ behavior were considered.⁵¹ From the absence of a laser power dependence of the photoelectron spectra it was inferred that autoionization and dissociation processes on the four-photon level were responsible for these deviations.⁵² Our results using picosecond excitation independently corroborate this scenario, since no fundamental differences could be observed between the photoelectron spectra obtained with nanosecond and picosecond excitation, even though considerably higher peak powers were used in the picosecond excitation experiments.

The four-photon level is therefore expected to play an important role in the photoelectron spectra. Within 6 eV above the lowest electronic $\text{CO}_2^+(X\ ^2\Pi_g)$ state three electronically excited ionic states can be found, viz., $A\ ^2\Pi_u$, $B\ ^2\Sigma_u^+$, and $C\ ^2\Sigma_g^+$. The neutral Rydberg states converging to each of these limits, denoted by R_A , R_B , and R_C respectively, have been the subject of numerous studies, based on nonresonant one-photon absorption in combination with photoelectron spectroscopy^{32,33} or resonant one-photon absorption in combination with different detection techniques.^{24,28–31,34–44} On the basis of these studies we can conclude that in the present work we access an energy region at the four-photon level close to the $A\ ^2\Pi_u$ ($v_1^+=0-7$) ionic limits, where the density of Rydberg states converging to these limits can be expected to be particularly high. Moreover, the one-photon excitation studies show that in this energy region also Rydberg states are present which converge to the $B\ ^2\Sigma_u^+$ ($v_1^+=0,1$) ionic limits as well as a few Rydberg states converging to the $C\ ^2\Sigma_g^+$ ionic limit. In the previous one-photon studies such neutral superexcited states were excited by one-photon absorption from the $X\ ^1\Sigma_g^+$ ground state of CO_2 . It is important to realize that in the present study excitation can in effect be considered as a one-photon excitation from the $(^2\Pi_{g3/2,1/2})nf$ Rydberg states. As a consequence we do not necessarily excite the same R_A , R_B , and R_C superexcited states as in the one-photon excitation studies from the ground state.

Because of the high state density at the four-photon level, the photoelectron spectra may change rapidly as a function of the photon energy as different close-lying superexcited states exert their influence. The $(^2\Pi_{g1/2})4f$ photoelectron spectra may in this respect serve as an example. The four-photon level in this case is close to the R_A TO ($n=9, v_1=1$) and Henning sharp R_B ($n=5, v_1=0$) levels.²⁹ As the photon energy is increased (Fig. 7), various superexcited states, which might converge to different ionic limits, come into (near) resonance and the photoelectron spectra change rapidly, showing for example an increasing ω_2 activity.

B. Processes occurring at the four-photon level

The question that naturally arises is how we can rationalize the main characteristics of our photoelectron spectra, i.e., the long ω_1 progressions and in some cases the unusually intense "forbidden" transitions to ungerade vibrational levels in the lowest ionic state $X^2\Pi_g$, on the basis of processes occurring in neutral superexcited states. Several one-photon excitation studies indicate that electronic autoionization and neutral dissociation are two decay channels of the CO_2 superexcited states which may manifest themselves prominently.^{29,31-44} In low-resolution photoelectron spectra obtained after one-photon excitation of superexcited states in the energy region that corresponds to our four-photon level vibrational progressions, based mainly on the $^2\Pi_g(v_1, 0, 0)$ progression, are present.^{32,33,39,41,43} The observation that the intensities of the photoelectron peaks in these progressions are in reasonable agreement with the Franck-Condon factors between the ionic ground state and the excited ionic state to which the neutral superexcited state converges indicates a central role for autoionization. A similar conclusion is reached on the basis of one-photon excitation spectra of this energy region in which the $A^2\Pi_u \rightarrow X^2\Pi_g$ and $B^2\Sigma_u^+ \rightarrow X^2\Pi_g$ ionic fluorescence emissions are monitored, and which are observed to be modulated by the R_A , R_B , and R_C series.^{36,37,44} Moreover, the same modulations are observed when the $A^1\Pi \rightarrow X^1\Sigma^+$ emission of CO is monitored, demonstrating that dissociation is an important decay channel as well.^{34,35,38,44}

The importance of autoionization also becomes clear from the threshold photoelectron and photoionization efficiency spectra measured by Baer and Guyon.⁴¹ In this study two types of autoionization were invoked to explain the measured excitation spectra: direct autoionization of Rydberg states converging to higher lying ionic limits and resonance autoionization of such states *via* neutral dissociative valence states. The major difference between these two types of autoionization is that in resonance autoionization a significant amount ($\sim 8\%$) of zero kinetic energy electrons was observed to be produced. In the present study it is not possible to observe electrons with a kinetic energy below 0.1 eV, and we can therefore not analyze our results in this respect. Dissociative valence states might, however, be of importance in the present study. These states cannot be excited directly as the result of unfavorable Franck-Condon factors, but they might very well influence the electronic character of the regular R_A , R_B , and R_C Rydberg states. In the threshold studies of Baer and Guyon resonances have been observed which have been attributed to a long $(0, v_2, 0)$ progression deriving from a bent neutral valence state. Such states have been invoked frequently and might also influence the present study.^{29,41,46,47}

From fluorescence spectroscopy on the CO_2^+ ion it is known that the C-O distance in the $A^2\Pi_u$ ionic state (1.2274 Å) is considerably larger than in the $X^2\Pi_g$ ionic ground state (1.1769 Å).²⁰ As a result, the $A^2\Pi_u \rightarrow X^2\Pi_g$ fluorescence spectra exhibit strong vibrational activity in the symmetric stretch vibration ω_1 .²³ It can thus be expected that when a Rydberg state converging to the $A^2\Pi_u$ ionic state comes into (near) resonance in our experiments, electronic

autoionization would give rise to vibrational progressions based on ω_1 . Such autoionization processes might well explain the long vibrational progressions observed in the photoelectron spectra *via* the $(^2\Pi_{g1/2})4f$ and $(^2\Pi_{g3/2})6f$ Rydberg states. In the first instance one would be tempted to correlate the four-photon levels associated with these excitations with the excitation energies of R_A states determined in one-photon excitation studies. We emphasize, however, once again that it is very probable that other R_A states are excited in the present study, since excitation effectively is performed with the $(^2\Pi_{g3/2,1/2})nf$ Rydberg state as the initial state instead of the ground state. Indeed, we find that, while the four-photon level of the $(^2\Pi_{g1/2})4f$ excitation is (near) resonant with the R_A TO ($n=9, v_1=1$) state, the four-photon level of the $(^2\Pi_{g3/2})6f$ excitation is not close to any known R_A Rydberg state.^{24,29}

Alternatively, the ω_1 progressions might result from dissociation processes occurring in neutral superexcited states. In this case, however, one would expect to observe long progressions based on the asymmetric stretch vibration ω_3 as well. In the present photoelectron spectra such progressions are not present. It seems consequently unlikely that dissociation processes lie at the basis of the long ω_1 progressions.

While autoionization under the influence of R_A Rydberg states would appear to account satisfactorily for the observation of long ω_1 progressions, autoionization processes do not seem to be able to explain the observation of strong transitions to the $^2\Pi_g(0,1,0)$ and $^2\Pi_g(0,0,1)$ ionic levels, since within the Born-Oppenheimer approximation transitions to odd levels of the ungerade vibrational modes are not allowed in an even-photon ionization process.

The $^2\Pi_g(0,1,0)$ peak has been observed before in one-photon photoelectron spectra^{15-18,21} and in a recent one-photon ZEKE-PFI study,⁴⁷ but never with the intensity observed in the present work. In HeI and NeI photoelectron spectra this peak has an intensity of only a few percent of the strongest peak, the $^2\Pi_g(0,0,0)$ vibrationless origin.^{15-18,21} In the one-photon threshold photoelectron study of Baer and Guyon this intensity rises to 26% of the $^2\Pi_g(0,0,0)$ peak.⁴¹ In the present work, however, we find that for some excitations the $^2\Pi_g(0,1,0)$ peak dominates the complete photoelectron spectrum. The $(^2\Pi_{g1/2})4f$ photoelectron spectra (Fig. 7) show, for example, a $^2\Pi_g(0,1,0)$ peak (at 3.431 eV), which is twice as strong as the origin band. The photoelectron spectrum of the $(^2\Pi_{g1/2})6f$ state provides another example in which the $^2\Pi_g(0,1,0)$ band (at 4.011 eV) has considerable intensity (Fig. 12).

If the $X^2\Pi_g$ ionic state would have a bent geometry, as suggested in the past,⁸³ the selection rule mentioned would not be valid anymore. The ω_2 vibration has a_1 symmetry in the C_{2v} point group and transitions to odd numbers of this mode then become allowed. Recent calculations⁸⁴ indicate, however, that the four lowest electronic ionic states $X^2\Pi_g$, $A^2\Pi_u$, $B^2\Sigma_u^+$ and $C^2\Sigma_g^+$ are all linear. The bent valence states invoked previously might in this respect be of importance.^{29,41,46,47} If the neutral superexcited states involved in autoionization processes in the present study would actually belong to this class of states, or be coupled to them, one might expect ω_2 activity. However, the study of

Baer and Guyon⁴¹ has shown that excitation of such a state from the ground state leads to an excitation spectrum with not only activity of $\omega_2=1$, but rather with a long progression in this vibration. For direct autoionization processes to the ionic $X^2\Pi_g$ ground state one would conversely expect such a progression as well. In the photoelectron spectra of the $(^2\Pi_{g1/2})4f$ and $(^2\Pi_{g1/2})6f$ states, such progressions cannot be assigned. This would consequently seem to rule out an explanation of the intensity of $\omega_2=1$ on merely autoionization under the influence of bent valence states.

An alternative explanation of the strong $^2\Pi_g(0,1,0)$ activity involves vibronic coupling between the $X^2\Pi_g$ and $B^2\Sigma_u^+$ ionic states via the ω_2 bending vibration.^{16,21,46,47} In this mechanism the transition to $^2\Pi_g(0,1,0)\mu^2\Sigma_{u1/2}^+$ gains intensity through the transition to the $B^2\Sigma_u^+(0,0,0)$ state. Transitions to the other components of the Renner-Teller quartet ($^2\Delta_{u5/2}$, $^2\Delta_{u3/2}$, and $\kappa^2\Sigma_{u1/2}^-$) are expected to be weaker, because they are only allowed through the weaker transitions to the $B^2\Sigma_u^+(0,v_2,0)$, $v_2=2,4,\dots$ levels, as has been confirmed in the ZEKE study of Merkt *et al.*⁴⁷ The same vibronic interaction that couples the ionic states will also couple the neutral superexcited Rydberg states R_B converging to the $B^2\Sigma_u^+$ ionic limit to the $X^2\Pi_g(0,1,0)$ ionic level plus the continuum electron. As a result of this vibronic coupling it can then be expected that autoionization of R_B states, excited at the four-photon level in the present study, will lead to activity of the ω_2 vibration in the $X^2\Pi_g$ ionic ground state. The photoelectron spectra obtained for ionization via the $(^2\Pi_{g1/2})4f$ state (Fig. 7), show an increasing ω_2 activity as the photon energy is increased. This is in nice agreement with the fact that the four-photon level is then approaching the $(n=5, v_1=0)$ member of the Henning sharp R_B series.^{24,29} In the middle trace of Fig. 7, the $^2\Pi_g(0,1,0)$ quartet is visible as two unresolved doublets, one containing the transitions to the $\mu^2\Sigma_{u1/2}^+$ and $^2\Delta_{u5/2}$ states (at 3.420 eV) and one containing the transitions to the $^2\Delta_{u3/2}$ and $\kappa^2\Sigma_{u1/2}^-$ states (at 3.404 eV). In the other traces this splitting is not as well resolved, presumably as the result of an uneven intensity distribution over the two doublets. In the photoelectron spectrum of the $(^2\Pi_{g1/2})6f$ state (Fig. 12) the $^2\Pi_g(0,1,0)$ quartet has an intensity which is about half the intensity of the transition to the ionic $^2\Pi_g$ vibrationless origin. In this case, however, the splitting is not observed. From the energy difference with the ionic origin one would tend to conclude that the dominant intensity is in the doublet containing the $^2\Delta_{u3/2}$ and $\kappa^2\Sigma_{u1/2}^-$ states. Inspection of the excitation energies of the known Rydberg series converging to the $B^2\Sigma_u^+$ ionic state reveals that at the four-photon level of the transition to the $(^2\Pi_{g1/2})6f$ state the $(n=9, v_1=0)$ member of the Henning diffuse R_B series is closeby,^{24,29} which might explain the ω_2 activity. Following the same line of reasoning ω_2 activity would be expected as well in the photoelectron spectrum of the $(^2\Pi_{g3/2})6f$ state (Fig. 11), for which the four-photon level coincides with the $(n=9, v_1=0)$ member of the Henning sharp R_B series.^{24,29} Such activity is, however, not observed.

While transitions to the $\omega_2=1$ level in the $X^2\Pi_g$ ionic state have been reported in other studies, the transition to the $\omega_3=1$ asymmetric stretch level in the $X^2\Pi_g$ has not been

observed before in one-photon ionization studies from the ground state. In the present work this transition shows up with unprecedented intensity in several photoelectron spectra, most notably if ionization occurs via the $(^2\Pi_{g3/2})5f$ state (Fig. 9), where the intensity of the $^2\Pi_g(0,0,1)$ vibration (at 3.683 eV) is about a third of the $^2\Pi_g(0,0,0)$ transition (at 3.861 eV). The diode-laser absorption work of Kawaguchi has shown that the $X^2\Pi_g$ and $A^2\Pi_u$ states in CO_2^+ are vibronically coupled via the ω_3 asymmetric stretch vibration.¹³ This vibronic coupling might lend intensity to the transition to the $^2\Pi_g(0,0,1)$ vibration.^{16,17,21} A possible mechanism that explains the $\omega_3=1$ activity in the photoelectron spectra of the present study involves a similar vibronic coupling between the R_A superexcited states converging to the $A^2\Pi_u$ ionic limit and the $X^2\Pi_g$ ionic state plus the continuum electron. Once again, it can be expected that ω_3 activity in the photoelectron spectra is enhanced under the influence of an R_A member excited at the four-photon level.

The previous discussion has shown that the ionization process via $(^2\Pi_{g3/2,1/2})nf$ Rydberg states in CO_2 is rather complex. Qualitatively speaking, the photoelectron spectra can be considered to result from two competing processes. On the one hand, a direct ionization process contributes which exhibits a dominant $\Delta v=0$ behavior as has become apparent most clearly from the photoelectron spectrum obtained via the $(^2\Pi_{g1/2})4f$ 1_0^1 transition. On the other hand, the two-color photoelectron spectra have shown a dramatic dependence on processes at the four-photon level. Under the influence of autoionizing neutral superexcited states severe deviations from $\Delta v=0$ have been observed to occur. These deviations manifest themselves as long vibrational progressions in the symmetric stretch vibration and activity of "forbidden" vibrational levels in the $X^2\Pi_g$ ionic state. One can reasonably account for such observations by invoking autoionization of Rydberg states converging to the $A^2\Pi_u$ ionic limit as well as vibronic couplings between the $X^2\Pi_g$ and the $A^2\Pi_u$ and $B^2\Sigma_u^+$ ionic states. However, elucidating the exact details of such processes is severely hindered by the fact that the states, which are accessible by one-photon excitation from $(^2\Pi_g)nf$ Rydberg states, have not been studied as yet.

V. CONCLUSIONS

Three-photon resonance enhanced multiphoton ionization in combination with high-resolution photoelectron spectroscopy has allowed for a comprehensive study of the processes occurring in the $(3+1)$ ionization of the CO_2 $(^2\Pi_{g3/2,1/2})nf$ Rydberg states. In agreement with the conclusions of previous $(3+1)$ ionization studies on the $(^2\Pi_{g3/2,1/2})4f$ and $(^2\Pi_{g3/2,1/2})5f$ states the photoelectron spectra obtained for ionization via the $n=4-7$ members show that strong deviations from the *a priori* expected Franck-Condon behavior may occur. The high resolution in the present study leads, however, to important reinterpretations, since our photoelectron spectra show that previous assignments of photoelectron peaks were not correct. The picture that emerges from our photoelectron spectra and from two-color REMPI-PES experiments, in which the influence of processes occurring at the four-photon level has been in-

vestigated, is one in which electronic autoionization competes effectively with direct ionization. As a result, the photoelectron spectra in some cases exhibit long vibrational progressions in the symmetric stretch vibration ω_1 , while in other cases the photoelectron peaks corresponding to the degenerate bending vibration $\omega_2=1$ and the asymmetric stretch vibration $\omega_3=1$ in the $X^2\Pi_g$ ionic state show unprecedented large intensities. It is suggested that vibronic coupling within the ionic manifold may be a significant contributor to the activity of these two ungerade vibrations.

In the excitation spectra several resonances have been observed which are attributed to multiphoton excitation of atomic fragments. In particular, it has been shown that resonances previously assigned to four-photon excitation of autoionizing CO_2 states in fact derive from (2+1) REMPI of atomic carbon, which is produced almost exclusively from photodissociation of background gas under the high laser intensity conditions necessary in a (3+1) REMPI study on CO_2 . Additionally, we have observed for the first time (3+1) REMPI transitions starting from the $2s^22p^4\ ^1D_2'$ state of atomic oxygen, deriving from the photodissociation of CO_2 , via states above the lowest atomic ionization energy. Finally, indications have been found in the photoelectron spectra that three-photon excitation and subsequent ionization of ($^2\Pi_{g3/2,1/2}$) nf Rydberg states of CO_2 results in the production of highly excited neutral CO molecules.

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