



## Carbon K-shell photoionization of CO: Molecular frame angular distributions of normal and conjugate shakeup satellites

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### ABSTRACT

We have measured the molecular frame angular distributions of photoelectrons emitted from the Carbon K-shell of fixed-in-space CO molecules for the case of simultaneous excitation of the remaining molecular ion. Normal and conjugate shakeup states are observed. Photoelectrons belonging to normal  $\Sigma$ -satellite lines show an angular distribution resembling that observed for the main photoline at the same electron energy. Surprisingly a similar shape is found for conjugate shakeup states with  $\Pi$ -symmetry. In our data we identify shake rather than electron scattering (PEVE) as the mechanism producing the conjugate lines. The angular distributions clearly show the presence of a  $\Sigma$  shape resonance for all of the satellite lines.

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## 1. Introduction

The present paper combines two vibrantly discussed topics: molecular frame angular distributions of innershell photoelectrons and few body processes induced by a single photon. We will ask how molecular frame angular distributions are influenced by the involvement of other active electrons and in turn what we can learn about few electron processes from molecular frame angular distributions. Before we discuss our experiment we give a brief summary on the background of both topics.

### 1.1. Photon induced many electron transitions

Photoionization of atoms and molecules leads in many cases to a simultaneous excitation of the remaining ion [1,2]. Such ionization excitations manifest themselves in satellites lines to the main photoelectron line in the electron energy distribution. As this process is inherently a many electron process its description becomes particularly challenging: a widely used two-step model for ionization excitation implies that either the photon leads to the emission of the photoelectron by a primary *dipole* transition followed by a *monopole* transition inside the molecular ion (normal shakeup). Alternatively the photon may excite the molecule in a *dipole* tran-

sition and subsequently an electron is shaken off to the continuum in a *monopole* transition (conjugate shakeup). At high excess energies conjugate shakeup dies off and only molecular ion states with the same symmetry as the ground state are populated. Conjugate shakeup however contributes significantly at low electron energies.

The word “shakeup” was introduced in the context of the sudden approximation. It refers to a “*mechanism*” by which the excitation proceeds. It can be formalized as a Feynman-diagram in many body perturbation theory [3–5]. In an intuitive picture of that description the photon induces a sudden single active electron transition in which it gives its angular momentum either to the ejected or the excited electron. This ionization or excitation step changes the potential and hence the eigenstates of the system. As the wave functions of the remaining electrons relax to the new eigenstates of the altered potential, they have a non-zero overlap to excited or even continuum states to which they are “shaken up” or “shaken off”. This simple picture, however, does not answer the question how the photon energy is partially transferred from the first electron, which absorbed the photon, to the shake electron, but it permits calculation of the shake probabilities as simple overlap integrals without an operator [2].

Within the framework of many body perturbation theory a second mechanism of electron–electron scattering, which actually has a classical analog, can lead to a two electron transition upon absorption of a single photon. This mechanism comes at a variety of names like TS1 [4], knock-off [6,7] or PEVE (photoelectron valence electron interaction) [8–10]. It is also related to the rescattering

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mechanism in the multiphoton context [11]. The wording mechanism is certainly a simplification as the depicted scenario describes contributions to a transition amplitude. The details of these amplitudes have been worked out in great detail for the two electron process of single photon double ionization of helium [12].

Similar to the shakeup mechanism, PEVE can be “normal” or “conjugate” which means that it can either lead to the same symmetry or to a different symmetry of the molecular ion compared to that of the main line. Such a change of symmetry is possible since the electrons can exchange angular momentum in the internal collision. For the case of a conjugate process PEVE and shake can be experimentally separated by examining the orientation of the molecular axis to the polarization [8]: if e.g. in the conjugate shakeup the photon induces an excitation from a  $\Sigma$  to a  $\Pi$  orbital the molecular axis has to be perpendicular to the polarization during the photo absorption.

### 1.2. Molecular frame angular distributions

Angular distributions of photoelectrons emitted from molecules exhibit a very rich structure in the laboratory frame, if the molecular axis is fixed in space [13,14]. What is the physical origin of this structure? From the perspective of angular momentum one may say that the outgoing photoelectron wave is a coherent superposition of several angular momentum states, even within the dipole approximation where only  $1\hbar$  is deposited by the photon into the system. These high angular momenta in the continuum electron wave function are compensated by a rotational excitation of the molecular ion left behind, which can also be measured directly [15]. One may say that the photoionization process splits the many body wave function of electrons and nuclei of the neutral molecule into an angular momentum entangled wave function of a free electron carrying angular momentum in the angular distribution and a molecular ion carrying the equivalent angular momentum in rotation. A simplistic and mechanistical way to understand the creation of these high angular momentum states is suggested by the multiple scattering picture: a dipolar photoelectron wave is created in the K-shell of the molecule. On the way through the molecule this wave is multiply scattered at the multi-center potential of the molecule. It is this multiple scattering which creates the angular momentum in the rotational degrees of freedom of the molecular ion and in the electron wave itself. In a particle picture the minima and maxima in the electron angular distribution are then interpreted as destructive or constructive interference between different pathways of the electron through the molecular environment. In a wave formulation they are the interference pattern of the direct dipolar electron wave with all multiply scattered electron waves. Such multiple scattering effects can be employed to use the photoelectron angular distribution to illuminate a molecule from within [16]. Particularly rich patterns arise when the electron wave resonates inside the structure of the multi-centric potential giving rise to a *shape resonance* [14,17]. For homonuclear molecules, there is a second mechanism which gives rise to higher order angular momenta: the coherent emission of the primary electron wave from two or more centers. Even if multiple scattering is small, as it is, e.g. the case for protons as scatterers in  $H_2$ , this potentially delocalized nature of the photoeffect [18] alone can create diffraction structures in the angular distributions [13,19–22] and hence also rotationally excite the ions.

### 1.3. Carbon K-shell ionization of CO

In the remainder of this paper we have chosen the example of Carbon K-shell ionization of fixed-in-space CO to investigate the interplay between creation of satellite lines via excitation with the molecular frame angular distributions. It is certainly tempting to try

**Table 1**

CO C 1s ionized ground and excited electronic states (from Ref. [24]). The assignment of the type of shakeup state is taken from the  $\beta$  parameter of the photoelectron from Ref. [24]. States assigned as “conjugate” are those for which a  $\beta$  close to zero has been observed.

Peak	Assignment	Binding energy (eV)	Type
0	$2\sigma^{-1}2\Sigma^+$	296.20	Main
1	$2\sigma^{-1}5\sigma^{-1}2\pi^1(S' = 1)^2\Pi$	304.10	Conjugate
2	$2\sigma^{-1}1\pi^{-1}2\pi^1(S' = 1)^2\Sigma^+$	304.85	Normal
3	$2\sigma^{-1}1\pi^{-1}2\pi^1\Delta, ^2\Sigma^-$	306.31	Conjugate
4	$2\sigma^{-1}4\sigma^{-1}2\pi^1\Pi$	308.97	Conjugate
5	$2\sigma^{-1}1\pi^{-1}2\pi^1(S' = 0)^2\Sigma^-$	311.29	Normal
6	Unknown	313.30	Conjugate
7	$2\sigma^{-1}5\sigma^{-1}6\sigma^1(S' = 1)^2\Sigma^+$	313.97	Normal
8	$2\sigma^{-1}5\sigma^{-1}6\sigma^1(S' = 0)^2\Sigma^+$	315.37	Normal
9	$2\sigma^{-1}5\sigma^{-1}7\sigma^1(S' = 1)^2\Sigma^+$	316.25	Normal
10	Unknown	317.14	Normal

to understand the angular distribution of the satellites as being created by two steps: first an initial *p*-wave or *s*-wave of an outgoing electron is created by shake or conjugate shake process respectively and in a second step this low angular momentum wave is multiply scattered in the molecular potential where higher angular momenta are added. This simplistic picture, however, neglects the molecular symmetry of the wave functions. Our data show that an alternative view, also put forward in Ref. [23] is more appropriate. The *s*-wave character for the shaken off electron in the atomic case refers to the fact that no angular momentum is transferred from the photon to the shaken off electron. For the molecular case, where *s* is not a good quantum number, that idea can be generalized to shakeup in which the  $\Sigma$  and  $\Pi$  character of the bound state wave function is conserved upon the transition to the continuum.

The Carbon K satellite spectrum of CO has been studied in detail experimentally [23–29,47] and theoretically [29–33]. Two major satellite features S0 and S1 corresponding to singlet and triplet coupled excitations have been observed [27] and calculated [32]. They show a very different photon energy dependence. High resolution studies have then resolved the various states contributing to these two main features (see Fig. 1 below and Table 1). Hemmers et al. [24] have measured the  $\beta$  parameters of the electron for these lines. They found that – as expected by the simple picture above – the satellite lines fall into two groups: those with  $\beta = 0$  which are conjugate shakeup satellites and those whose  $\beta$  is similar to the one of the main line which are direct (i.e. normal shakeup) satellites. In our study presented here we measure the molecular ion angular distribution in addition. As outlined above this will clearly allow us to also pin down not only the symmetry (normal or conjugate) but also the excitation mechanism (shake versus PEVE). As a further step we will then investigate the electron angular distributions in the body fixed frame. This will in particular allow identification of possible shape resonances.

## 2. Experiment

The experiment has been performed at beamline BL4 of the Advanced Light Source at Lawrence Berkeley National Laboratory using the COLTRIMS technique [34–36]. The photon energies employed were in a region of 290–320 eV, in all cases the light was linearly polarized. We have set the monochromator to a resolution of about 100 meV, sufficient to resolve the major features of the satellite spectrum. The photon beam is crossed at right angle with a supersonic CO beam. The photoelectron and both ions are guided by weak electric (12.3 V/cm) and magnetic (8 G) fields towards two large area position and time sensitive micro-channel plate detectors equipped with delayline position readout [37,38].

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