



Editor's Choice

Wide range double photoionisation spectra of N₂ and CO₂

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ABSTRACT

Using a magnetic bottle time-of-flight electron spectrometer we have measured double photoionisation spectra of N₂ and CO₂ covering the range from threshold up to the triple ionisation energies. The experiments demonstrate the use of a new asynchronous chopper in eight-bunch mode of the synchrotron radiation source SOLEIL. For CO₂²⁺ some broad bands in the Auger spectra are found to have multiple resolved counterparts in the photoionisation spectrum. All the bands in the Auger spectra have counterparts in the photoionisation spectra, where extra bands attributed to triplet states are present. In the spectrum of N₂²⁺ we suggest reassignment of one band.

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1. Introduction

Spectra of doubly charged molecular ions have long been recorded at relatively low resolution by spectroscopy of Auger electrons [1]. More recently the low-lying doubly ionised states of many molecules have been measured with vibrational resolution by magnetic-bottle electron–electron coincidence spectroscopy (TOF-PEPECO) [2] using atomic HeII ionising radiation. Similar spectra of the dication states of important molecules have also been measured by threshold photoelectrons coincidence (TPEsCO) [3,4], by charge exchange spectroscopy [5] and by Doppler-free kinetic energy release spectroscopy [6]. We now show that by using the TOF-PEPECO technique with soft X-rays from a synchrotron radiation source we can record double photoionisation spectra over the whole range from threshold up to the triple ionisation energies, which typically lie between 60 and 100 eV for almost all molecules. The new spectra extend into the range where outer-valence and inner valence electrons are accessed, and show triplet states of the ions as well as the singlet states emphasised in Auger spectra. We find that in the cases of N₂ and CO₂ distinct signatures are seen in

the double photoionisation spectra for most of the leading 2-hole configurations.

There has been extensive previous work on the formation and properties of the dications of both nitrogen and carbon dioxide. We defer reference to the relevant publications to the sections where each molecule is discussed individually.

2. Experimental methods

The measurements were made on the PLEIADES beamline (see Supplementary Information of Ref. [7]) at SOLEIL using a magnetic bottle electron spectrometer which has already been described in detail [8]. The important characteristics of the apparatus for the present experiment are that electrons of all energies are detected simultaneously with a numerical resolution of $E/\Delta E$ of about 50. The detection efficiency is independent of energy and amounts to about 50% of the electrons formed in the source region. Briefly, ionisation takes place where an effusive gas jet from a 0.5 mm needle intersects the wavelength-selected beam of ionising light. The ionisation zone is located on axis in the strongly divergent magnetic field (ca. 0.5 T) of a conically tipped cylindrical permanent magnet, which directs most of the photoelectrons into the guiding field (ca. 10⁻³ T) of a long (2 m) solenoid taking them to a Z-stack microchannel plate detector. In eight-bunch operating mode, the SOLEIL synchrotron provides sub-nanosecond pulses at 148 ns

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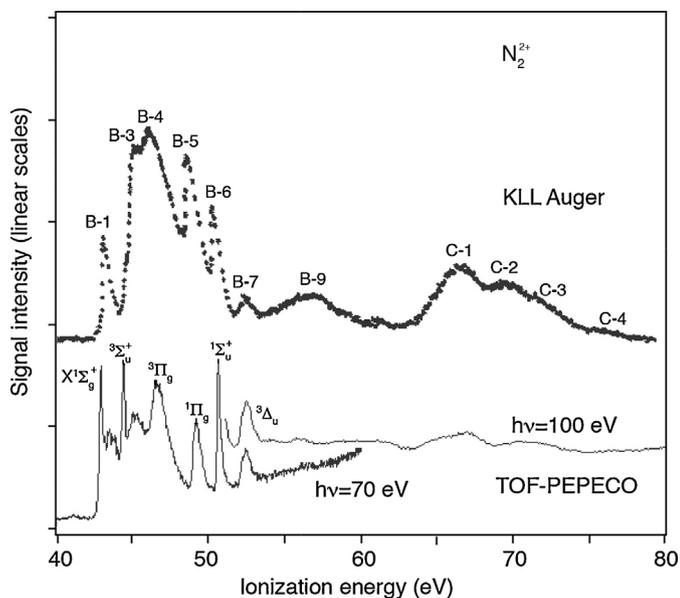


Figure 1. Double photoionisation spectra of nitrogen taken at 70 and 100 eV photon energy compared with the electron-impact induced Auger spectrum [10] (for X-ray excited Auger spectra, please see Ref. [11]). State identifications are those given by Ahmad et al. [12].

intervals, whereas the flight time of the electrons to the detector is between 100 and 5000 ns. To select individual light pulses at usefully long intervals, we place a new chopper at the light beam focus, before the electron spectrometer. The chopper consists of a Ti disc of 200 mm diameter shaped to minimise strain when rotating at 1000 Hz. There are 120 slits of 80 μm width at the periphery of the disc, which together with a fixed 80 μm slit provide opening times of about 125 ns at 8.33 μs intervals. The chopper was run in asynchronous rotation relative to the ring pulses, so the rate of single light pulses actually passing the chopper to register at the light detector as possible START signals for electron timing was about 100 kHz. An electronic circuit arrangement was used to inhibit data collection on the rare occasions when two successive light pulses managed to pass through to the light detector with an interval of 148 ns between them. By comparison with the chopper that some of us developed earlier [9] this chopper is superior in the shorter opening time of 125 ns compared with ca. 400 ns as each moving slit passes a fixed slit located at the beam focus. This has been achieved mainly by increasing the diameter of the spinning disc bearing the moving slits, essentially up to the limit imposed by the tensile strength of titanium.

3. Results

Spectra were gathered at the photon energies 65, 70 and 100 eV for N_2 and at 65 and 85 eV for CO_2 . Because the TOF spectrometer provides better energy resolution at lower electron (and thus photon) energies, we show a composite spectrum for N_2 to cover the whole range. The relative intensities of the major peaks vary only slightly over the photon energy range used. We show the spectra in Figures 1 and 2 with redrawn Auger spectra [10] for comparison, and list their features in Tables 1 and 2.

3.1. Nitrogen

Comparison of the photoionisation and Auger spectra of N_2^{2+} in Figure 1 immediately confirms three general features common to such spectra. First, the lower energy resolution in the Auger spectrum, caused by the short 1s hole lifetime makes broad bands stand

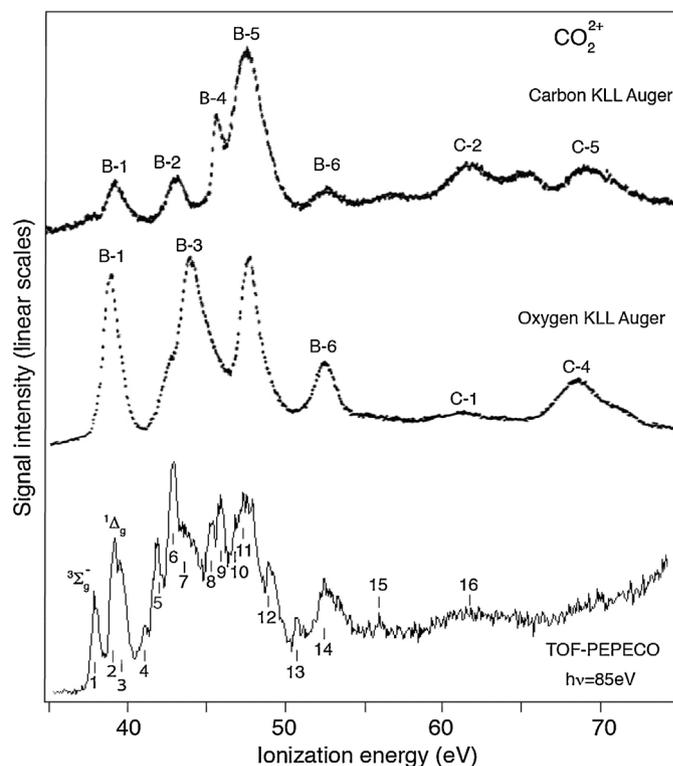


Figure 2. Double photoionisation spectrum of carbon dioxide at 85 eV photon energy compared with the oxygen and carbon KLL Auger spectra [10] redrawn on the same scale and shifted to make the first bands match the lowest $^1\Delta_g$ state of CO_2^{2+} .

out more strongly relative to sharp bands. Secondly, higher energy states are relatively more strongly populated in the Auger spectrum than in photoionisation at the comparatively low photon energies used here. Thirdly, triplet states of the dication are less strongly populated in the Auger spectrum than in photoionisation.

The low energy states of N_2^{2+} have been thoroughly explored with vibrational resolution by TPESCO and TOF-PEPECO combined [12], by charge exchange [5] and by Doppler-free kinetic energy release [13]. Some of the states have been studied with rotational resolution by optical and laser spectroscopic methods e.g. Refs. [14,15]. A full list of the many techniques employed is given by Lundqvist et al. [13] and a full listing of old and new work, both experimental and theoretical devoted to N_2^{2+} is included in a recent review [16]. The lower energy part of the N_2 KLL Auger spectrum has recently been remeasured with vibrational resolution [17] at different photon energies. The relative band intensities vary little with photon energy and are similar to those recorded under electron impact. The results of all these techniques agree on

Table 1
Band energies and assignments for N_2^{2+} .

State	Energy	
	Ahmad et al. [12]	This work
$X^1\Sigma_g^+$	42.88	42.9
$a^3\Pi_u$	42.99	–
$b^3\Sigma_g^-$	43.84	43.5
$A^1\Pi_u$	44.38	44.4
$^1\Delta_g$	44.43	–
		45.2
$C^3\Sigma_u^+$	44.52	–
$d^3\Pi_g$	46.43	46.7
$B^1\Pi_g$	49.5	49.2
$D^1\Sigma_u^+$	50.8	50.6
$^3\Delta_u$	52.71	52.5

Table 2
Assignment^a of bands in the spectrum of CO₂²⁺.

Feature	Energy (eV)		State	Ionisation
	This work	Slattery et al. [18]		
1	37.5	37.34	X ³ Σ _g ⁻	1π _g ⁻²
2	38.7	38.52	a ¹ Δ _g	1π _g ⁻²
3	39.3	39.16	b ¹ Σ _g ⁺	1π _g ⁻²
4	40.6	40.1	c ¹ Σ _u ⁻	1π _u ⁻¹ 1π _g ⁻¹
5	41.5	41.43	D ³ Π _u	3σ _u ⁻¹ 1π _g ⁻¹
6	42.5	42.3	d ¹ Π _u	3σ _u ⁻¹ 1π _g ⁻¹
		42.65	E ³ Π _g	3σ _u ⁻¹ 1π _u ⁻¹
		42.82	e ¹ Π _g	3σ _u ⁻¹ 1π _g ⁻¹
7	43.7	1Π _g	3σ _u ⁻¹ 1π _u ⁻¹	
8	45.1	? ¹ Δ _u	1π _u ⁻¹ 1π _g ⁻¹	
9	45.7	1Σ _g ⁺	1π _u ⁻² + 3σ _u ⁻²	
10	46.9			
11	47.5	1Δ _g	1π _u ⁻²	
12	49.0	? ³ Γ		
13	50.9	? ³ Γ		
14	52.8	1Σ _u ⁺	4σ _g ⁻¹ 3σ _u ⁻¹	
15	56.8	1Σ _g ⁺	4σ _g ⁻²	
16	62.1		2σ _u ⁻¹ π ⁻¹	

^a Gamma represents an unknown angular momentum.

the character and identification of all the clearly resolved states. The general character of the states in different regions of the spectrum is also understood from simple orbital considerations and more detailed theory [1] and has been explored in Auger electron-fragment ion coincidence experiments [19]. In this work our purpose is to complement this existing knowledge with data from photoionisation, particularly on the states whose lifetimes are too short to produce resolved vibrational structure or fluorescence emission. To set the scene we begin with consideration of the electron configuration of neutral N₂, which can be written:

$$1s\sigma_g^2 1s\sigma_u^2 2s\sigma_g^2 2s\sigma_u^2 2p\pi_u^4 2p\sigma_g^2$$

Eighteen states to be expected in double ionisation are generated by removing two electrons from the valence and inner valence orbitals, thus:

Orbital	States	Sum of orbitals energies + 12 eV	Observed
2pσ _g ⁻²	1Σ _g ⁺	43.0 (as 2 × 15.5 + 12)	43.0
2pπ _u ⁻¹ 2pσ _g ⁻¹	3Π _u , 1Π _u	44.3	43.5, 45
2pπ _u ⁻²	3Σ _g ⁻ , 1Δ _g , 1Σ _g ⁺	45.6	43.8 (3Σ _g ⁻)
2pσ _g ⁻¹ 2sσ _u ⁻¹	3Σ _u ⁺ , 1Σ _u ⁺	46.1	?, 51.2
2pπ _u ⁻¹ 2sσ _u ⁻¹	3Π _g , 1Π _g	47.4	47, 49.5
2sσ _u ⁻²	1Σ _g ⁺	49.2	
2pσ _g ⁻¹ 2sσ _g ⁻¹	3Σ _g ⁺ , 1Σ _g ⁺	64.7	
2pπ _u ⁻¹ 2sσ _g ⁻¹	3Π _u , 1Π _u	66.1	
2sσ _u ⁻¹ 2sσ _g ⁻¹	3Σ _u ⁺ , 1Σ _u ⁺	67.9	
2sσ _g ⁻²	1Σ _g ⁺	86.6	94.5

The 12 eV added to the orbital ionisation energy sums in this list is a crude representation of the expected Coulomb repulsion energy, chosen to give the correct double ionisation energy of the ground state of the dication. Few real states have such simple unmixed configurations, of course, and additional states can arise from excitation ('shake up') to normally unoccupied orbitals. Of the eighteen double-hole states, seven have been measured in resolved spectra and are discussed in detail in the most recent TPESCO and TOF-PEPECO paper [12]. Two have been vibrationally resolved in the latest Auger work [17] where their assignments were confirmed. The eighth state identified [12] as ³Δ_u, would have to have a leading configuration from shake-up, of which the simplest possibility would be 2pπ_u⁻³2pπ_g⁺¹. High level calculations of potential energy curves for the states of N₂²⁺ have been carried out by several authors and those of Senekowitsch et al. [13,20] are particularly useful. They show that the states with strong contributions from

configurations where bonding electrons have been removed are mainly repulsive in the Franck–Condon zone of neutral N₂. Such states will appear in the spectra as unstructured broad bands, and risk being overlooked as background in the regions where many states overlap.

The region of the spectrum attributed to removal of two valence electrons (from 2sσ_u², 2pπ_u⁴ and 2pσ_g²) extends from 43 to about 50 eV. Three expected states not yet resolved in this region, namely 1Σ_g⁺, 3Σ_u⁺ and a second 1Σ_g⁺ presumably contribute to the considerable unstructured intensity beneath the clear peaks in this region of both the photoionisation spectrum and the Auger spectrum. While the singlet states identified in Figure 1 in the photoionisation spectrum (1Σ_g⁺, 1Π_g and 1Σ_u⁺) and the corresponding states in the Auger spectrum (B-1, B-5 and B-6) show the same relative intensity pattern in the two spectra, the relative intensity in the 45–48 eV range of the Auger spectrum is very much higher. This is in spite of the expected absence of triplet states, and most probably arises from strong population of the 1Δ_g state as suggested by the calculations of Wetmore and Boyd [21]. States of this symmetry are strongest from π⁻² ionisations in almost all clearly recorded spectra [2,22]. The identification of the state near 53 eV as ³Δ_u by Ahmad et al. [12] and by Besnard et al. [23] also derives from Wetmore and Boyd's calculations, although the theoreticians point out in the text that the assignment is not definitive. The intensity (area) of the '³Δ_u' band in the TOF-PEPECO spectrum relative to that of the nearby 1Σ_u⁺ state is greater than the equivalent area ratio B-7/B-6 in Auger; this is consistent with the idea that the state involved is a triplet. On the other hand, triplet states are usually much weaker than singlets in Auger spectra as can be seen, for instance, in the spectra of CO₂²⁺ below. On this basis the identification of the state at 53 eV as the missing 1Σ_g⁺ state from 2sσ_u⁻² ionisation in accordance with Ågren's empirical calculations [1] seems more probable.

The spectral region from 54 to 80 eV ionisation energy presents the greatest difficulty for detailed interpretation. States in this region may have mixed configurations but gain intensity in the spectra mainly from ionisations of one electron from a valence orbital and one from an inner valence orbital. The pattern of three features at 67.1, 70.4 and 72.1 eV designated as C-1, C-2 and C-3 in the Auger spectrum and also visible in photoionisation is reminiscent of the pattern of valence orbitals in the photoelectron spectrum. One is therefore tempted to identify them in a broad-brush manner as ionisations from 2sσ_g and each

outer valence orbital in turn; this assignment is in essence supported by Ågren's calculations [1] as well as by the simple orbital energy sums. It was used by Eberhardt et al. [19] in connection with the dissociation properties of ions in these states. Unfortunately the more recent high-level theoretical calculations of Senekowitsch et al. [20], Taylor et al. [24] and Olsson et al. [25] do not extend to the high energies involved. The double photoionisation spectrum in this high energy region parallels the Auger spectrum, showing bands corresponding to B-9, C-1 and C-2. We cannot do better than to accept Ågren's interpretation of these bands as deriving their main intensity from $2s\sigma_u^{-2}$, $2s\sigma_g^{-1}3s\sigma_g^{-1}$ and $2s\sigma_g^{-1}2s\sigma_u^{-1}$ respectively, though presumably with greater contribution from triplets than in the Auger spectra.

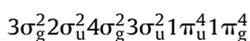
Finally we note how surprisingly well the simple sums of orbital energies and Ågren's empirical model fit both the experimental data and more sophisticated calculations.

3.2. Carbon dioxide

The dication states of carbon dioxide have been studied intensively, if not quite so intensively as those of nitrogen. Recent spectroscopic work combining TPESCO and TO-PEPECO spectra with mass spectrometric measurements [18] led to identification of eight resolved states at energies up to 43 eV. The lower energy part of the carbon KLL Auger spectrum has been remeasured with vibrational resolution by Puettner et al. [26], who in consequence of their experimental and theoretical analysis reinterpreted some of the band assignments in the earlier work of Slattery et al. [18]. An even more recent work by Zhang et al. [27], directed mainly towards examination of the dissociations of CO_2^{2+} , included new theoretical calculations with assignments consistent with those of Slattery et al. [18].

In the PEPECO spectrum taken at 85 eV we distinguish 16 features, numbered in Figure 2, for comparison with the CK and OK Auger spectra [10]. The states identified by Slattery et al. [18] and in the earlier TOF-PEPECO work [22] below 43 eV are visible despite the lower energy resolution caused by our higher photon and consequent electron energies, though 3 of them form an unresolved complex near 42 eV (bands 6 and 7). The bands whose assignments are disputed are numbers 5 and 6 with others hidden within band 7; because of the band congestion and low resolution our spectrum cannot contribute to solution of the assignment question. The low-energy bands are supplemented by several intense peaks in the range from 43 to 55 eV, of which some have clear counterparts in the Auger spectra. The very sharp Auger peak resolved by Puettner et al. [26] at an Auger energy equivalent to 45.7 eV ionisation energy has a counterpart in the PEPECO spectrum as the sharp and intense band 9 at exactly the same energy. A few other states are thought to have been detected in charge-transfer experiments [5] within the region up to 46 eV and others have been calculated in the same region [1,28–30]. Unfortunately the most recent and highest level calculations have been restricted to low-lying states of CO_2^{2+} and provide no help with interpretation of the bulk of the spectrum at higher energy.

As with nitrogen, we can get a preliminary idea of the dication states to be expected by consideration of the orbital structure of CO_2 , as revealed in its photoelectron spectrum. Its configuration outside the K shells is:



Of these $3\sigma_g$ and $2\sigma_u$ give a single broad photoelectron band at about 37 eV binding energy and constitute the inner valence orbitals; the others are valence orbitals with energies between 14 and 20 eV. Removal of 2 electrons from the valence orbitals and

addition of 10 eV notional Coulomb repulsion energy predicts 23 dication states with energies between 38 and 50 eV. Combination of valence orbitals with inner valence predicts 16 more states between 60 and 70 eV and inner valence state combinations give a final 4 states above 85 eV. Many of these states, including all the singlets, have been calculated by Ågren [1] in interpretation of the Auger spectra.

Because the Auger spectra have the selective advantages of emphasising singlet states and states localised on particular atoms, we approach the identification of features in the wide range TOF-PEPECO spectrum with help from the Auger data.

Features 1–3: The first three states are clearly identified as $^3\Sigma_g^-$, $^1\Delta_g$ and $^1\Sigma_g^+$ arising from $1\pi_g^{-2}$ ionisation. Of these the two singlet states both contribute to the first peak in both the carbon and oxygen Auger spectra. Since $1\pi_g$ is located purely on the oxygen atoms in linear CO_2 , it is natural that the peak is relatively weak in the carbon Auger spectrum.

Feature 4: The feature with maximum at 40.6 eV can be identified with the $^1\Sigma_u^-$ state found at 40.1 eV by Slattery et al. [18]. This is the lowest energy state arising from $1\pi_u^{-1}1\pi_g^{-1}$ ionisation and has a fairly pure configuration according to Millié et al. [28]. But it is rather surprising that as a singlet it is not seen in the Auger spectra, and we have to surmise that it is concealed within the B-1 or B-2 bands. In this context, and generally, we must remember that the Franck–Condon envelope in Auger spectra may be very different from that in direct photoionisation, because of nuclear relaxation in the intermediate core-hole state.

Feature 5: The peak at 41.5 eV can be identified with the $^3\Pi_u$ state located by Slattery et al. [18] at 41.4 and based mainly on $3\sigma_u^{-1}1\pi_g^{-1}$ ionisation [28]. It is absent from the Auger spectra, as expected.

Features 6 and 7: The strong peak at 42.5 eV and the broad band around 43.7 eV cover a number of states seen in the TPESCO and TOF-PEPECO spectra [18], namely $^3\Pi_g$, $^1\Pi_g$ and $^1\Pi_u$. The corresponding strong peaks B-2 and B-3 in the carbon and oxygen Auger spectra are probably dominated by $^1\Pi_u$ and $^1\Pi_g$ as assigned by Ågren [1].

Feature 8 at 45.1 eV may be the $^1\Delta_u$ state derived from $1\pi_u^{-1}1\pi_g^{-1}$ ionisation, because peak B-4 in the early Auger spectrum was so assigned [1]. But no peak appears at this energy in the better resolved Auger spectrum of Puettner et al. [26]. By the calculation of Millié et al. [28] the $^1\Delta_u$ state should appear 1 eV lower in energy, whereas the other assigned state from this configuration, $^1\Sigma_u^-$, is calculated only 0.4 eV lower than our observed peak, so this assignment is questionable. As it appears in photoionisation but not in Auger, band 8 is most likely to represent a triplet state.

Feature 9: At 45.7 eV the rather strong peak in photoionisation has its counterpart in the Auger spectra in the very sharp peak seen at 45.7 eV in the well-resolved Auger spectrum of Puettner et al. [26] and assigned to a $^1\Sigma_g^+$ state of mixed configuration. Two sharp peaks at 45.71 and 45.94 were seen in the early TOF-PEPECO spectrum using 48.4 eV light [22], but could not be assigned at that time. They must come from a bound state at this energy. Because the first of these is an exact match in energy to band 9 and a rough match in width to the Auger line, we can be fairly confident in assigning it now to the same state.

Feature 10 is a possibly dubious shoulder, which we refrain from assigning. It adjoins the intense peak of *feature 11* at 47.5 eV, whose counterparts B-5 in the C and O Auger spectra are assigned as $^1\Delta_g$, from $1\pi_u^{-2}$. This assignment seems relatively safe.

Features 12 and 13 at 49.0 eV and 50.9 eV cannot be assigned at this time. They are probably triplets as they do not appear in the Auger spectra, and they lie close in energy to 8 states (5 triplets) calculated by Millié et al. [28,31].

Feature 14 coincides in energy and roughly in shape with the B-6 bands in both Auger spectra, assigned as $^1\Sigma_u^+$ by Ågren [1] from $4\sigma_g^{-1} 3\sigma_u^{-1}$. This seems reasonable.

Feature 15 at 56.8 eV may possibly be the counterpart to the weak band B-7 in the O Auger spectrum or B-8 in the C Auger spectrum. Ågren assigns these as $^1\Sigma_u^+$ from $4\sigma_g^{-1} 3\sigma_u^{-1}$ and $^1\Sigma_g^+$ from $4\sigma_g^{-2}$ respectively.

Feature 16 at about 62 eV clearly involves an inner valence orbital. It can be associated with either C-1 or C-2 in the Auger spectra, which simple orbital energy sums and Ågren's calculations attribute to $2\sigma_u^{-1}$ ionisation together with removal of an electron from one of the π orbitals.

4. Conclusions

The measurements have successfully demonstrated the use of a new fast chopper to isolate single soft X-ray pulses from SOLEIL's synchrotron light in 8-bunch mode. We suggest that the highest energy distinct band in the spectrum of N_2^{2+} should be identified as a $^1\Sigma_g^+$ state instead of $^3\Delta_u$ as at present. For CO_2^{2+} we suggest identifications of several states at higher energy than those hitherto seen in photoionisation. In both cases there is close correspondence between the double photoionisation spectra and both the long-standing and new Auger spectra, apart from the different intensity of triplet states.

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