INNER VALENCE SATELLITE STRUCTURE IN HIGH RESOLUTION X-RAY EXCITED PHOTOELECTRON SPECTRA OF N_2 AND CO

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Abstract

The high resolution X-ray excited (hν = 1487 eV) valence photoelectron spectra of N_2 and CO are presented. The spectra show a rich line structure down to 65 eV binding energy due to electron correlation effects. Several new structures are observed and new assignments are made from comparisons with calculations, monochromatized HeII excited photoelectron spectra and resonance Auger electron spectra .

INTRODUCTION

Photoelectron spectroscopy is an important tool to study the electron structure of molecules and atoms. For the outermost valence electrons UV-photoelectron spectroscopy (UPS) has been used extensively. For the excitation of the spectra both laboratory sources providing Ne(I), Ne(II), He(I) and He(II) resonance lines and synchrotron radiation have been employed. These studies have provided a deep understanding of the vertical and adiabatic ionization energies, the vibrational structure of the levels in the singly ionized molecules, the potential energy curves for the states involved, the symmetry of the orbitals and also about more intricate phenomena such as predissociation. The independent particle model is normally adequate to assign the outer valence electrons and the assignment of states using *ab-initio* or semi-empirical calculations can be performed on a routine basis.

In contrast to this, many unsolved problems remain for the inner valence states. The binding energies in this region range from ca 20 eV to ca 100 eV. The He(II) radiation has an energy of 40.8 eV, but gives without monochromatization access to states with a binding energy not larger than ca 27 eV. It also has a much lower intensity than He(I) sources and a limited number of highly resolved spectra have been published. The most extensive recent spectroscopic work on the inner valence levels of molecules has so far been done using angular resolved synchrotron radiation excited photoelectron spectroscopy (SRPS) and X-ray excited photoelectron spectroscopy (XPS). The resolution obtainable with these experimental methods is, however, substantially lower than the resolution in a typical He(II) UPS experiment. The theoretical description of the inner valence levels is difficult since normally the independent particle model is inadequate. Correlation plays an important role for the electron structure in this region and in some cases even the Born-Oppenheimer approximation breaks down [1,2,3].

However, recent experimental results make it possible to discuss the electron structure in the inner valence region of molecules in greater detail than hitherto. In a recent report a monochromator for He II UV-radiation has been described and applied to photoelectron spectroscopy studies of several small molecules [4]. Furthermore, high energy monochromators for synchrotron radiation have opened up the possibility to study the phenomenon of resonant autoionization, where the initial state in the autoionization process contains a core hole which subsequently decays. Normally the kinetic energy distribution of the electrons emitted in the autoionization process is measured. This experiment is sometimes referred to as autoionization (resonance) spectroscopy [5], but it is also called deexcitation spectroscopy (DES) [6] and resonance Auger spectroscopy [7]. Another method to obtain autoionization spectra is from electron-electron coincidence spectroscopy at threshold [8,9]. Moreover, in electron beam excited Auger electron spectra autoionization lines can be studied as satellites. Very highly resolved autoionization spectra have been obtained in such spectra of CO [10]. The autoionization process leads to the same final states as the direct photoionization process. It is interesting to compare the results obtained in autoionization and photoelectron spectra.

In Fig.1 we illustrate the different processes leading to main and satellite lines in resonant autoionization and direct photoionization. Depending on whether the excited electron takes part in the autoionization transition or not, the final state will become a single hole state (participant decay) or a 2 holes - 1 particle state (spectator decay). In the photoionization process, the so-called main lines correspond to single hole final states, while the 2 holes - 1 particle final states are referred to as correlation satellites or shake-up lines. The latter concept should strictly be used only to the so-called monopole excitation process [11]. However, in the spectroscopic terminology shake-up lines is often used more generally for different types of satellites. In addition to these processes we have to consider shake-off processes (direct double ionization), where two electrons leave the system and also so-called double and triple shake-up processes which leave the system in 3 holes - 2 particle states etc.

In photoelectron spectra of the inner valence region the strong satellites must have the same symmetry to mix with one of the close lying single hole states. This usually gives a large number of possibilities for states to be seen in an electron spectrum with reasonable intensity. The resonance autoionization process tends to select different symmetries, as will be discussed below. Especially it is found that the processes involving a so called spectator electron (the excited electron does not take part in the autoionizing transition) give strong lines in the spectra. The corresponding satellites in the photoelectron spectra are often weak and therefore a very high signal-to-noise ratio is needed in the photoelectron experiment. As an example of the use of this method we may take the assignment of the $4s4p^5 5p$ and $4s^0 4p^6 5p$ satellites in the X-ray excited photoelectron spectrum of Kr [12] using corresponding resonance Auger data [7]. It should be pointed out that the lines in the X-ray excited spectrum are extraordinary weak and cannot be observed without monochromatization.

In this study we present new monochromatized X-ray excited photoelectron spectra of the N_2 and CO molecules and make assignments of the inner valence satellites using data from different other investigations including autoionization spectra. To facilitate reading, the assignments are made in terms of single final state configurations. In general, these correspond in each case to the leading configuration in a CI picture. Several states with high binding energy are observed for the first time in the present study.

EXPERIMENTAL

The spectra were recorded using an electrostatic X-ray photoelectron spectrometer described previously [13]. This instrument is provided with a quartz crystal monochromator and a rotating anode to obtain high resolution and high intensity. The gases were obtained commercially of spectral purity. The pressure in the sample compartment was held at a few mtorrs. Several recordings were made on the spectra and calibration was obtained using known UPS values for the outer valence lines.

RESULTS AND DISCUSSION

The N_2 molecule

In the upper part of Fig.2 we show the full valence photoelectron spectrum of N_2 excited with monochromatized X-rays (photon energy = 1487 eV). The outermost $2\sigma_u$, $1\pi_u$ and $3\sigma_g$ orbitals are easily identified with binding energies below 20 eV. At higher energies a large number of lines can be seen. Some of these lines between 20 eV and 45 eV have been observed earlier by synchrotron radiation [2]. The structures below 30 eV have also been observed in He(II) excited photoelectron spectra [4,14,15]. Most calculations of the inner valence spectrum have been performed using the sudden approximation which is appropriate to the excitation energy in the present XPS study. Ågren *et al* [16] have published results from a CI calculation on the X-ray photoelectron spectrum. The energies and intensities in this report agree well with the observed spectrum. However, it is known that vibronic coupling plays an important role to describe the inner valence region in N_2 [2]. This effect was not included by Ågren *et al* and much work remains to be done on this problem. Nichols *et al* have also performed a large scale calculation on the inner valence spectrum of N_2 using a multiconfigurational electron propagator model [17]. Schirmer and Walter have performed two particle - 1 hole Tamm Dancoff calculations using the Greens function formalism [18]. CI calculations have been performed by Okuda and Jonathan [19].

In the lower part of Fig. 3 we show a more highly resolved detail of the XPS of N_2. The different observed structures in Figs. 2 and 3 are classified and the binding energies are given in Table I together with assignments. It should be noted that the classification of the lines differ considerably from the standard notation, since, when considering both XPS, UPS and DES spectra a general revision has to be made of the earlier assignments.

Eberhardt *et al* [20] have published a DES (resonance Auger) spectrum of N_2. This spectrum is indicated in the lower part of Fig.2 and has been aligned according to the binding energies of the outer states. It should be noticed that the strong autoionization processes in this case takes place in the presence of a "spectator" $1\pi_g$ electron.

As can be seen the resonance Auger spectrum favours different final states compared to the photoelectron spectrum. This is of course due to the fact that the intensities in the photoelectron spectrum are determined by the dipole moment integrals whereas the resonance Auger intensities depend on the Couloumb integrals. It is interesting to discuss this difference from an experimental point of view. In particular, the dominating line in the outer valence single - hole region of the resonance Auger spectrum is due to a transition to the $1\pi_u{}^{-1}$ state, while all identified $^2\Sigma$ final states apparently acquire very low intensity. This experimental finding seems to be applicable both to the inner and outer valence regions of N_2 and CO. This empirical relationship will be used below together with information from high resolution UPS to assign the spectra and seems to give a consistent description of all types of spectra discussed here.

The low intensity for the $1\pi_u{}^{-1}$ state in the photoelectron spectrum is due to the fact that the $1\pi_u$ orbital, from symmetry reasons, is composed entirely of atomic N2p orbitals and the photoionization cross section for these atomic orbitals is low. Accordingly related shake-up and correlation lines in the XPS spectrum are expected to be very weak. In contrast the states that have a contribution from the N2s atomic orbital dominate the XPS spectrum since the cross section for this atomic orbital is high. As another striking example the $2\ \sigma_u{}^{-1}$ state corresponds to the most dominating line in the photoelectron spectrum whereas it cannot even be observed above the background in the resonance Auger spectrum.

In the energy range between 25 and 30 eV three lines can be observed in the DES. These lines correspond to 2 holes - 1 particle states and the excited electron lies in the $1\pi_g{}^*$ orbital in the DES. In the corresponding region in the XPS only two strong lines are observed at 25.0 and 28.8 eV. A weak component can be seen at ca 30 eV on the high binding energy tail of the 28.8 eV structure. The well known C $^2\Sigma_u{}^+$ state is associated with the 25.0 eV line. The main configuration of this state is $3\sigma_g{}^{-1}\ 1\pi_u{}^{-1}1\pi_g{}^1$. At this energy two more states are predicted [16-19] corresponding to the $3\sigma_g{}^{-2}\ 1\pi_g{}^1$ and $1\pi_u{}^{-2}\ 1\pi_g{}^1$ configurations. These have $^2\Pi$ symmetry and are calculated to have zero intensity in the XPS. However, these three states have been observed in a recent high resolution monochromatized HeII excited photoelectron spectrum [4] which shows one strong progression corresponding to the C state with vertical energy at 25.3 eV. In the same study another band, corresponding to the D state, was observed on the low binding energy side of this band. The vertical energy of this progression was found to be approximately 24.5 eV. This energy coincides with the energy of the first strong structure in the inner valence region in the DES. This is expected since the corresponding state has $^2\Pi$ symmetry. From the DES intensity the strongest peak in the 25-30 eV region of the DES therefore, probably, does not correspond to the C-state but to the other $^2\Pi$ state. This state is also inferred in the same recent HeII study as a progression of very weak lines on the high binding energy tail of the C-band. This band is associated with the E state.

Already from the assignment of these states it is seen that previous classifications of the states in the inner valence region of N_2 has to be revised. We therefore propose a new classification which will be performed in analogy with the states in the isoelectronic molecule CO, as discussed below. In this scheme we will place the C-E states around 25 eV, cf. Table 1. This classification is in agreement with Gilmore's potential curves [21] for singly ionized N_2.

In the photoelectron spectrum we recognize the $2\sigma_u^{-1}\ 1\pi_u^{-1}\ 1\pi_g^{1}\ {}^2\Sigma_g^+$ state around 28.8 eV which is approximately 1.5 eV below the calculated value of 30.4 eV [16]. The value of 28.8 eV agrees with the value obtained earlier by Krummacher *et al* [2]. Adopting an experimental interpretation, as discussed above, this ${}^2\Sigma_g^+$ state is expected to have low intensity in the DES. An intense DES structure has its maximum around 30 eV which fits well with the weak structure on the high binding energy tail of the 28.8 eV peak. Ågren *et al* [16] have calculated a $2\sigma_u^{-1}\ 3\sigma_g^{-1}\ 1\pi_g^{1}\ {}^2\Pi_u$ state at ca 0.8 eV higher binding energy than the ${}^2\Sigma_g^+$ state. We classify these states as F and G, respectively.

The high binding energy side of the 30 eV structure in the DES is unsymmetrical, suggesting contributions from other components of ${}^2\Pi$ symmetry. According to the calculations in ref [16] the next state of this symmetry has a binding energy 3.5 eV higher binding energy than our G-state. This splitting is probably exaggerated in the calculations and the DES spectrum indicates an energy close to 31.5 eV. We classify this state tentatively as the H-state. This state is not seen in the XPS. Since our G and H states have the same leading configuration and symmetry we expect that the H-state should be very weak in the XPS as is the case for our G-state. Moreover, in the recent vibrationally resolved monochromatized HeII excited UPS a weak vibrational progression can be inferred at about 30.4 eV superimposed on the weak G-state progression.

In the calculations the next state, which we refer to as the I state, is a $3\sigma_g^{-1}\ 1\pi_u^{-1} 1\pi_g^{1}$ ${}^2\Sigma_u^+$ state. It is predicted to be seen in the XPS at ca 5 eV above our F-state. The corresponding line in our spectrum is relatively intense and is seen at 31.9 eV, which is ca 3 eV above our F-state. Hence, the calculations probably exaggerate the splitting between the states in this energy region. The DES intensity in this region is quite low, which agrees with the experimental interpretation made above. Furthermore, this state is reflected by rather strong vibrational progression centered at approximately 31.9 eV in the recent UPS study [4].

In the photoelectron spectrum the next peak appears at 33.1 eV. We denote this state as the J-state. The calculation [16] indicates that the $3\sigma_g^{-1}\ 1\pi_u^{-2}\ 1\pi_g^{2}\ {}^2\Sigma_g^+$ double shake-up state is mainly responsible for this peak. This assignment also agrees with the low intensity in the DES.

The next $^2\Sigma_g{}^+$ state in the calculations is dominated by a $2\sigma_u{}^{-1}\ 1\pi_u{}^{-1}\ 1\pi_g{}^1$ configuration. It is predicted to have a slightly lower intensity than our F-state which has the same leading configuration. This state probably corresponds to the hitherto unobserved structure in the photoelectron spectrum around 34.0 eV, which we assign as the K-state. Slightly above our K-state several closely lying $^2\Pi$ states are predicted [16]. In the DES an increased intensity can be found at about 36 eV. These states are expected to be weak in the XPS but are probably responsible for e.g. the small structure that can be inferred around 36 eV on the low binding energy side of the $2\sigma_g{}^{-1}$ structure (*cf* Fig.3).

The large $2\sigma_g{}^{-1}$ line in the photoelectron spectrum has earlier been investigated in synchrotron radiation studies [2,22]. In the X-ray photoelectron spectrum we observe two main components at 37.0 and 37.9 eV, respectively, which seem to agree with the two calculated $2\sigma_g{}^{-1}$ states [16]. However, the situation is complex in this energy region since it has been shown that vibronic coupling plays a very important role for inner valence states of this type [1,2]. These two main structures are also seen in synchrotron radiation excited spectra, where the photon energy has been varied from 44 - 55 eV. At the high binding energy side of the $2\sigma_g{}^{-1}$ main line a component can be clearly seen at around 40.8 eV. This structure has also been reported by Grimm and Carlsson [22]. At a slightly lower binding energy, close to 40.1 eV, another weak component may be inferred. At 42.5 and 44.0 eV binding energy two other components can be seen. The $2\sigma_g{}^{-1}$ line and the components close to it , as discussed above, are only weakly represented in the DES. This indicates that $2\sigma_g{}^{-1}$ single hole states dominate in this energy region. The inferred 40.1 eV structure could be explained by the $2\sigma_u{}^{-1}\ 1\pi_u{}^{-2}1\pi_g{}^2$ $^2\Sigma_u{}^+$ double shake-up state predicted by Ågren *et al* [16] at a binding energy slightly higher than the $2\sigma_g{}^{-1}$ single hole state. The 40.8 eV structure could be explained as originating from the $3\sigma_g{}^{-1}\ 1\pi_u{}^{-1}2\pi_u{}^1\ {}^2\Sigma_g{}^+$ state. The relatively high intensity of this state is due to configuration mixing with the $2\sigma_g{}^{-1}$ single hole state.

At binding energies above the double ionization energy at about 43 eV several new weak structures are observed. These structures can be discussed using resonance Auger data. The two weak and narrow lines at 46.3 eV and 48.1 eV are seen in all runs of the spectrum and are clearly above the noise level. These structures correspond to strong lines in the DES and are therefore probably associated to $^2\Pi$ states. At this high binding energy excited Rydberg orbitals must be involved. Slightly below 50 eV a broad feature can be seen in the DES. This feature is probably caused by converging Rydberg series of $^2\Pi$ states. Coupling between the discrete singly ionized states and the double ionization continuum may give rise to broad structures. This may explain the large width of the structure, centered around 50.5 eV.

Around 62 eV we observe a weak and broad structure in the photoelectron spectrum of Fig.2. This structure could be explained by a σ - σ^* shake-up transition associated with the $2\sigma_g{}^{-1}$ "main" line. Such a state would also interact with a number of shake-off continua of $^2\Sigma$ symmetry and would thus form a shake-off resonance [23].

The CO molecule.

In the upper part of Fig.4. we show the high resolution X-ray excited valence photoelectron spectrum of CO. Some of the lines have been observed earlier by synchrotron radiation [24]. In the lower part of the same figure we display the resonance Auger spectrum taken at 287 eV photon energy from ref. [20]. The two spectra from CO are obviously very similar to those in Fig.2 showing results from N_2. In particular we recognize the same differences in the intensity for the singly ionized states in the outer valence region. Thus, the $1\pi^{-1}$ line is weak in the photoelectron spectrum and strong in the resonance Auger spectrum. For the $4\sigma^{-1}$ state a small line is discerned in the resonance Auger spectrum whereas the corresponding line is to weak to be observed in the case of N_2. The same arguments as above can thus be used to assign the states in the spectra.

At around 23.7 eV binding energy we observe the so called C-state in the photoelectron spectrum. At approximately 0.5 - 1 eV lower binding energy we find a very strong line in the DES [20] . This line has earlier been observed by Correia *et al* in the electron impact excited autoionization spectrum [10]. Moreover, in the vibrationally resolved HeII excited photoelectron spectrum Åsbrink *et al* [15], Potts and Williams [14] and Carlsson-Göthe *et al* [4] have found two different states in this energy region centered at 22.7 eV and 23.4 eV.

Evidently different states are favoured in the high energy photoelectron spectrum and in the resonance Auger spectrum, as was discussed above. In the X-ray excited photoelectron spectrum the $^2\Sigma$ states dominate and the structure at 23.7 eV binding energy is thus assigned to the $5\sigma^{-1}\ 1\pi^{-1}\ 2\pi^1\ ^2\Sigma$ state which can be considered as a normal monopole shake-up state that gets intensity by configuration interaction with the $4\sigma^{-1}$ state. The strong line in the DES at about 22.7 eV can be associated with the $5\sigma^{-2}\ 2\pi^1\ ^2\Pi$ state. This agrees with the Green's function calculations by Freund and Liegener [5] who obtained a very high intensity for this $^2\Pi$ state and a rather low intensity for the $^2\Sigma$ state in the autoionization spectrum. Whereas this line in the DES has no counterpart in the XPS, an extensive vibrational progression in the HeII excited spectrum with maximum intensity at the expected energy of about 22.7 eV, can obviously be associated with this line. In the study by Potts and Williams the same assignment was given based on CI calculations by Okuda and Jonathan [19]. The state was referred to as the D state. The same type of classification has been adopted also for N_2, as discussed above. Since the final electronic state has $^2\Pi$ symmetry the structure in the photoelectron spectrum must be described as a correlation satellite borrowing intensity from the $1\pi^{-1}$ single hole state at 16 eV. In the X-ray excited spectrum this intensity is expected to be extremely low since the intensity of the primary $1\pi^{-1}$ hole state is low (see Fig. 3) compared to the σ^{-1} hole states.

The second very strong line appearing in the DES is observed at about 27.6 eV. This line was also observed at the same energy in the autoionization spectrum given by Correia *et al* [10]. At this energy no line is observed in the X-ray excited photoelectron spectrum, which suggests that the transition involves a final state of $^2\Pi$ symmetry. This agrees with the calculations by Freund and Liegener [5], in which this line is associated with the $4\sigma^{-1}\,5\sigma^{-1}\,2\pi^1\;^2\Pi$ state. Between the strong lines at 22.7 eV and 27.5 eV still another transition is predicted corresponding to the $1\pi^{-2}\,2\pi^1\;^2\Pi$ final state. A weak shoulder observed in the DES on the high binding energy side of the 22.7 eV line at an energy of approximately 25 eV might correspond to this final state. In the autoionization spectrum presented by Correia *et al* [10] the line is very well resolved and has an energy of about 25.1 eV. A vibrational progression observed in the HeII excited spectrum with the intensity maximum centered at 25.3 eV probably corresponds to the same line. This state at about 25.1 eV corresponds in our notation to the E-state. The above interpretation of the 25.3 eV structure is in conflict with the earlier interpretations by Åsbrink *et al* [15] and Potts and Williams [14] who suggested a $^2\Sigma^+$ state. From the line profile of the autoionization band we conclude that the Franck-Condon region in this case is very different from the Franck-Condon region in the HeII experiment.

In the recent monochromatized UPS [4] the F state shows up as a structureless band centered at 27.4 eV. The G-state forms a vibrational progression centered around 28.2 eV. The corresponding line in the X-ray excited photoelectron spectrum appears as a weak and broad feature centered at approximately 28.5 eV. In the DES a strong line is seen at about 27.6 eV. Hence, by comparing the DES, XPS and UPS spectra we assign the F-state to a $^2\Pi$ final state and the G- state to a $^2\Sigma$ final state. This assignment is also supported by the calculations in ref. [5], suggesting that the line following next to the strong 27.6 eV DES line associated with a $4\sigma^{-1}5\sigma^{-1}2\pi^1\;^2\Pi$ final state should correspond to a transition to the $4\sigma^{-1}1\pi^{-1}2\pi^1\;^2\Sigma$ final state. Thus, this line corresponds to a monopole shake-up process associated with the $4\sigma^{-1}$ primary hole state. These arguments are parallel to the assignment for N_2 where the corresponding line is associated with the $2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1\;^2\Sigma$ final state. However, the ordering of the F and G-states is reversed. The ordering is also reversed with respect to the ordering obtained in the calculations of ref. [25].

Above 30 eV the lines in the photoelectron spectrum are getting stronger, indicating that configuration mixing with the $3\sigma^{-1}$ state must be considered. The first structure is observed at about 31.1 eV in the XPS spectrum and appears as a shoulder on the low binding energy side of the next structure, which is peaked at 32.0 eV. In the DES a weak feature is seen at ca 31 eV and at this energy a weak structure is seen also in the autoionization spectrum of ref [10]. By comparing with the interpretation of the N_2 photoelectron spectrum above we may suggest that, apart from the contribution from a $4\sigma^{-1}\,1\pi^{-1}\,2\pi^1\;^2\Sigma$ state, there is also a substantial contribution from the double shake-up state $5\sigma^{-1}\,1\pi^{-2}\,2\pi^2\;^2\Sigma$ in this energy region to the XPS. According to the calculations in ref. [25] the energy of the former state is 1.2 eV lower than of the latter which might suggest that the structure at 32 eV corresponds mainly to the double shake-up process. On the other hand the intensity of this state is predicted to be much lower than for the single shake-up process, so the detailed interpretation will have to await further investigations.

By comparison to the interpretation for N_2 the weak structure at about 33.7 eV may be associated with the K state. This state should thus have $^2\Sigma$ symmetry and it may be identified with the state 14 in ref. [25] having a dominant $4\sigma^{-1}\ 1\pi^{-1}\ 2\pi^1$ configuration.

Two strong lines are observed at 34.7 eV and 36.0 eV. It may be suggested these lines correspond to $^2\Sigma$ states. The first line probably corresponds to an ionic state with a dominating $4\sigma^{-1}\ 5\sigma^{-1}\ 7\sigma^1$ configuration. In the calculations of ref. [25] this transition was found to have a fairly high intensity and an energy which is about 1 eV higher than the energy of the transition to the K state. The only remaining transition at the low binding energy side of the $3\sigma^{-1}$ state manifold which is given a high intensity in the calculations is a double shake-up process with the leading final state configuration $5\sigma^{-1}\ 1\pi^{-2}\ 2\pi^2$. This state may thus be associated with the line at 36.0 eV.

The main $3\sigma^{-1}$ line in the photoelectron spectrum resembles rather closely the corresponding line of N_2. Two obvious differences may be noted. First, the low binding energy component of the strongest line is weaker in the CO case. Also, the fairly strong component at about 41.0 eV in N_2 has a much weaker countepart in the case of CO. In the calculations of ref. [25] four component states are predicted with a dominating $3\sigma^{-1}$ configuration. Three of these are expected to have appreciable intensity in XPS. The two states with the highest binding energy are close in energy while the third component is predicted to have ca 1.5 eV lower binding energy. The sum of the intensities of the high energy components is almost twice as large as the intensity of the low energy component. Thus it seems reasonable to associate the highest peak at 38.7 eV with the the high energy states and the weaker shoulder observed at 37.5 eV with the state at lower energy. According to the above discussion the weak feature observed at about 38 eV in the DES suggests that there are weak excitations to $^2\Pi$ states in the region of the main $3\sigma^{-1}$ line. These transitions are, however, not expected to contribute substantially to the X-ray photoelectron spectrum.

At 45 eV, 54 eV and 66 eV binding energy we observe three weak and broad structures in the XPS. The existence of these structures can be inferred also from Fig. 2 in ref. [24]. As can be seen from Fig. 4 the two first of these coincide with broad lines in the DES [20]. By comparison with Auger energies the DES lines at 45 and 54 eV were assigned to a $3\sigma^{-1}\ 5\sigma^{-1}\ 2\pi^1\ {}^2\Pi$ final state and a $3\sigma^{-1}\ 1\pi^{-1}\ 2\pi^1\ {}^2\Sigma$ final state, respectively. As stated above, only $^2\Sigma$ states are expected to have any appreciable intensity in the photoelectron spectrum. We therefore assign the structure at 54 eV to the $3\sigma^{-1}\ 1\pi^{-1}\ 2\pi^1\ {}^2\Sigma$ state. This is supported by the fact that this state can be considered as a monopole shake up state and if we assume a localized $3\sigma^{-1}$ state the energy should be similar to the $\pi - \pi^*$ O1s core electron shake up energy. The O1s shake up spectrum from CO is complex [26], but is dominated by a large structure containing the $\pi - \pi^*$

transition at about 16 eV above the O1s main line which is somewhat larger than the distance of the 54 eV structure to the $3\sigma^{-1}$ main component, as would be expected.

The line at 45 eV in the photoelectron spectrum is more difficult to explain. One possible explanation would be that it contains a triplet parent coupled component associated to the line at 54 eV. However, this can only explain the high binding energy part of the structure since the difference in energy of about 9 eV between the maxima of the lines at 45 and 54 eV is too large to be explained by multiplet splitting. Another possible explanation would be a σ–σ^* shake-up transition associated with the $4\sigma^{-1}$ main line. Such a transition lies in the shake-off continua and would form a broad band reflecting a shake-off resonance. However, the structure in the DES indicates that states of $^2\Pi$ symmetry are also present in this region. This parallels the findings for N_2. Since the line in the DES is very broad it may reflect the presence of Rydberg series e.g with configurations of $^2\Pi$ symmetry like $3\sigma^{-1}\ 5\sigma^{-1}\ n\pi^1$.

The line at 66 eV in the photoelectron spectrum of Fig.4 has no counterpart in the resonance Auger spectrum. The most likely explanation for this line would be a σ–σ^* shake-up transition associated with the $3\sigma^{-1}$ main line. The energy distance between this line and the $3\sigma^{-1}$ main line is approximately the same as the distance of the line at 45 eV to the $4\sigma^{-1}$ main line. From the experimentally based arguments above this line should not be observed in the resonance Auger spectrum.

It is interesting to note that Masuoka [27] has found structures in the branching ratios for C^+ ions at photoexcitation energies of ca 39 eV, 47 eV, 55 eV and 70 eV. These energies correspond well to the energies of the $3\sigma^{-1}$ main line and broad structures at 45, 54 and 66 eV in Fig.3. A $3\sigma^{-1}$ hole state would probably be dissociative and thus, all the states at 45, 54 and 66 eV probably contain a large admixture of the $3\sigma^{-1}$ configuration. In addition, strongly dissociative states give rise to broad bands in the photoelectron spectra. However, the high binding energy lines in Fig.3 are considerably broader than the $3\sigma^{-1}$ main line and therefore additional explanations of the bandwidths, as outlined above, must be considered.

CONCLUSIONS

The inner and outer valence high resolution X-ray photoelectron spectra of N_2 and CO molecules have been presented. An assignment of the correlation states has been presented by a comparison to resonance Auger data from the literature. Several new structures are reported and are assigned to shake-up processes and to shake-off resonances.

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TABLE 1.

Vertical binding energies (peak positions) and assignments of the XPS spectra of N_2 and CO.

	N_2		CO	
State [a]	Energy (eV)	Symmetry	Energy (eV)	Symmetry
X	15.58	$^2\Sigma_g^+$	14.01	$^2\Sigma^+$
A	17.0	$^2\Pi_u$	17.0	$^2\Pi$
B	18.8	$^2\Sigma_u^+$	19.7	$^2\Sigma^+$
C	25.0	$^2\Sigma_u^+$	23.7	$^2\Sigma^+$
D	24.5 [b]	$^2\Pi_g$	22.7 [b]	$^2\Pi$
E	-	$^2\Pi_g$	25.2	$^2\Pi$
F	28.8	$^2\Sigma_g^+$	28.0 [b]	$^2\Sigma^+$
G	≈30.0	$^2\Pi_u$	27.4 [b]	$^2\Pi$
H	–	$^2\Pi_u$	–	
I	31.9	$^2\Sigma_u^+$	31.1	$^2\Sigma^+$
J	33.1	$^2\Sigma_g^+$	32.0	$^2\Sigma^+$
K	34.7	$^2\Sigma_g^+$	33.7	$^2\Sigma^+$
	37.0	$^2\Sigma_g^+$	34.9	$^2\Sigma^+$
	37.9	$^2\Sigma_g^+$	36.2	$^2\Sigma^+$
	40.8		37.5	$^2\Sigma^+$
	42.5	$^2\Sigma_g^+$	38.7	$^2\Sigma^+$
	44.0	$^2\Sigma_g^+$	46.0	$^2\Sigma^+$
	46.3	$^2\Pi_u$	55.6	$^2\Sigma^+$
	48.1	$^2\Pi_u$	65.4	$^2\Sigma^+$
	50.5			
	60			
	63			
	68			

[a] This classification differs from the previous. See text.

[b] From vertical energy in UPS (HeII) [4] and DES [6,20] spectra

FIGURES

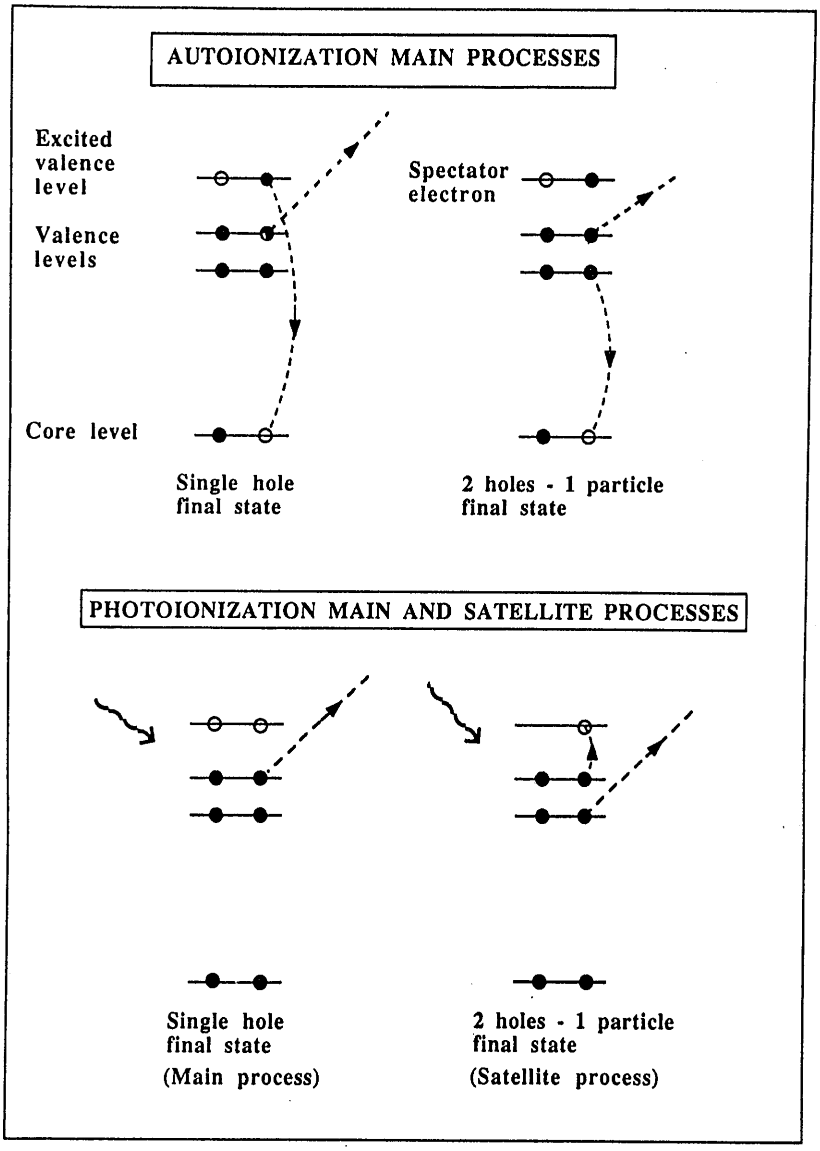

Fig. 1 *A schematic diagram illustrating the different main processes involved in the photoionization and resonance Auger (resonance autoionization) experiments. The same single hole and two holes - 1 particle final states can be reached in the two different experiments; the intensities of the corresponding spectral lines are, however, quite different.*

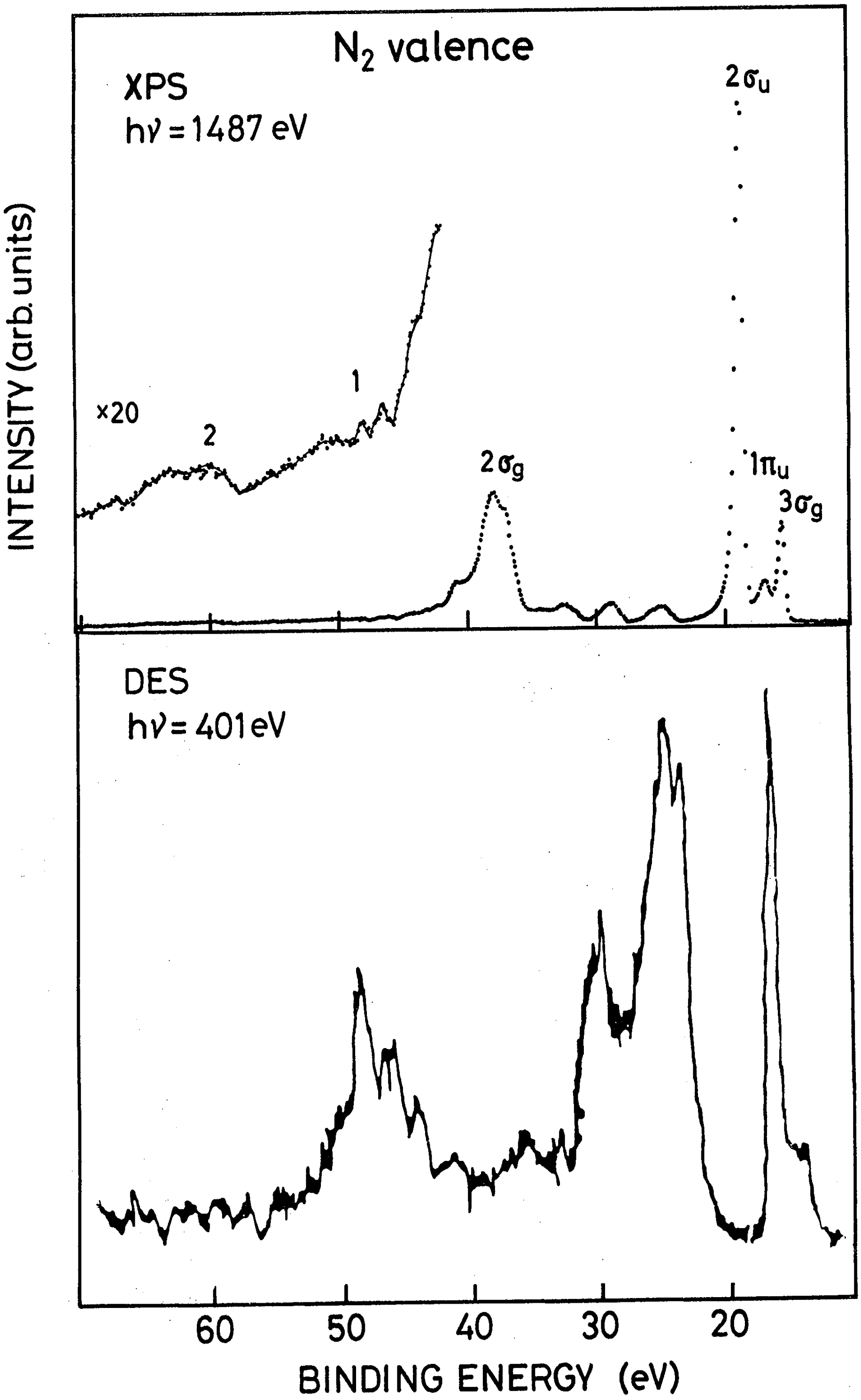

Fig.2 *Top:* *The X-ray excited valence photoelectron spectrum of* N_2.
Several new lines are recorded.
Bottom: *The resonance Auger spectrum (DES spectrum) of ref. [6].*

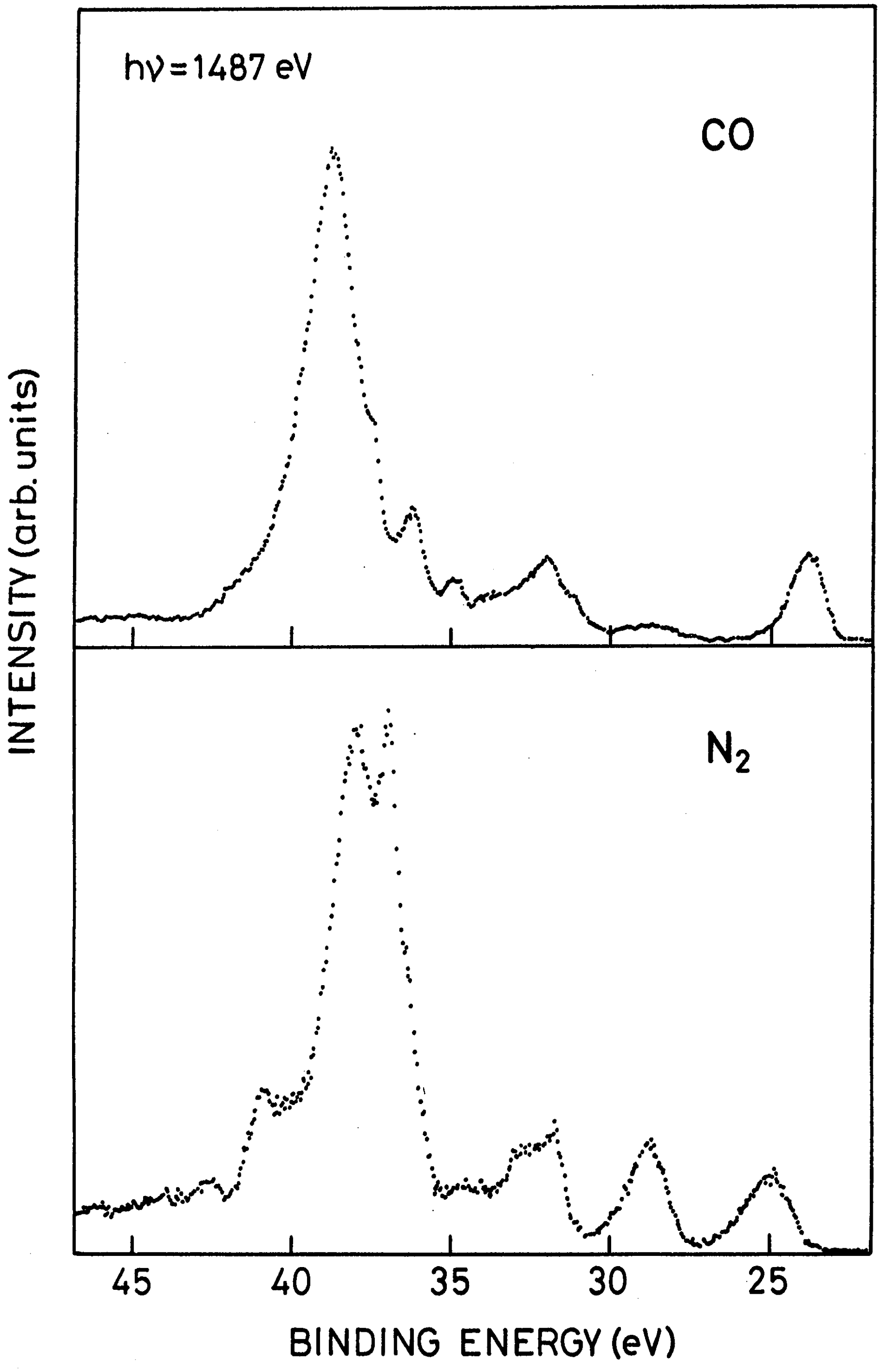

Fig. 3 *The X-ray excited inner valence photoelectron spectra of* N_2 *and CO.*

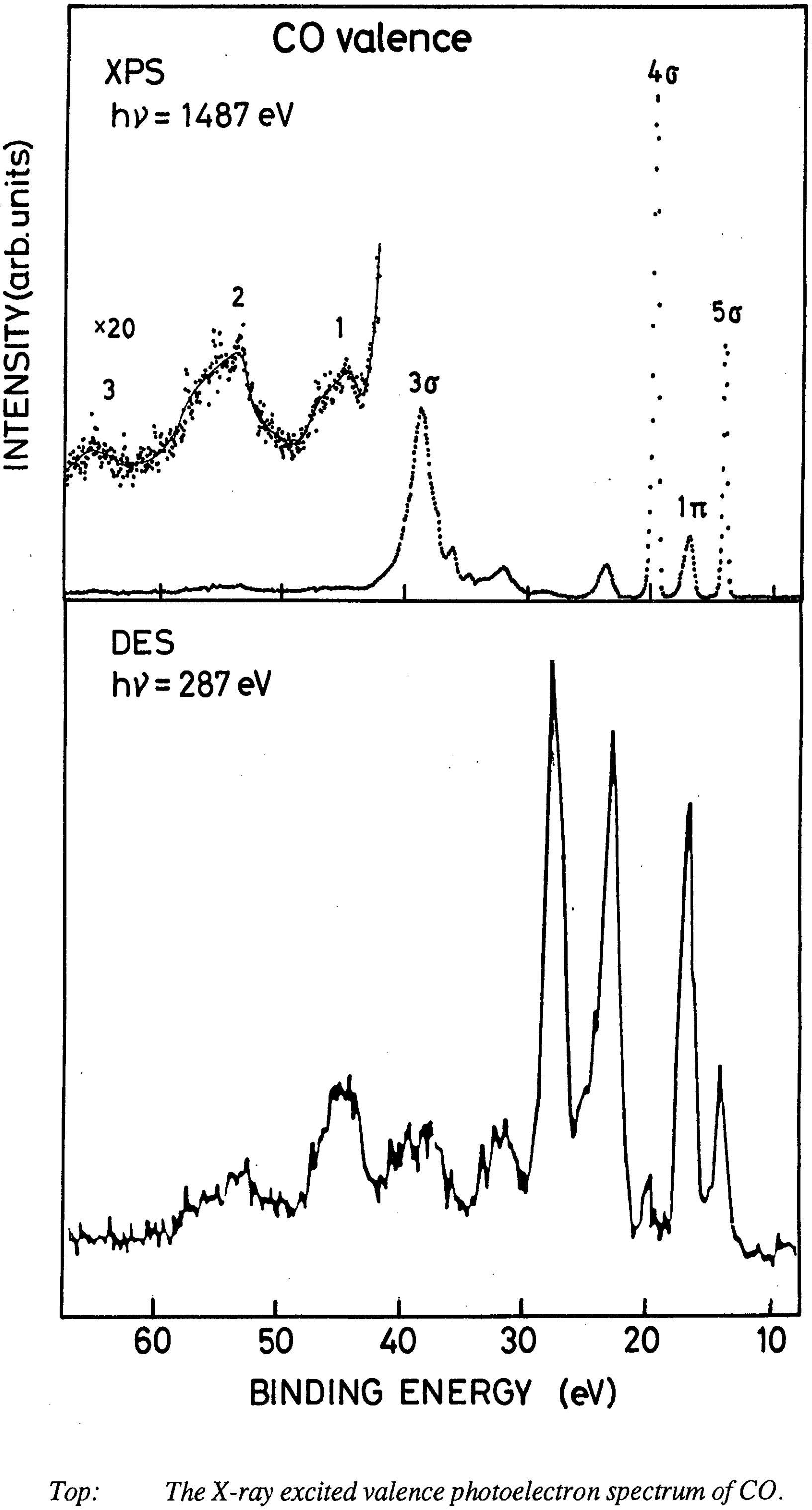

Fig.4 *Top:* *The X-ray excited valence photoelectron spectrum of CO. Notice the large similarity to the valence* N_2 *spectrum.*

Bottom: *The resonance Auger spectrum of ref. [20] (also called DES-spectrum) is inserted.*