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# Excitation energy dependence in the photoemission satellite structures in solid CO and N<sub>2</sub>

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We use the relative intensity of photoemission satellites in the outer core, inner valence region measured as a function of photon energy in order to identify the spectroscopic assignment for each individual satellite. The outer valence satellites show a decrease in intensity relative to the outer valence single particle emission over the excitation energy range from 40 to 140 eV. The  $3\sigma(2\sigma_g)$  derived structures, on the other hand, increase in intensity, measured relative to the outer valence emission as expected from the general behavior of the  $3\sigma(2\sigma_g)$  single particle cross section.

## INTRODUCTION

The photoemission of small molecules is well known to exhibit structures that cannot be explained in the single particle picture. These shakeup peaks are observed as satellites in deep core level photoemission or even more prominent in the inner valence or shallow core level region.<sup>1</sup> The nature of these peaks is well established; the ion created in the photoemission process is not necessarily in the ionic ground state but could end up in various excited state configurations. The energy difference between the various ionic final states is reflected by the difference in kinetic energy of the photoelectron ejected in the primary excitation process. The photoelectrons having the highest kinetic energy therefore correspond to a process where the ion is in its lowest energy state, the ground state. Usually, but by no means necessarily, this line carries the highest intensity and is therefore referred to as "main line." In a single particle picture it is described by the removal of just one electron or a single hole state. Higher lying states are, if an assignment in terms of single particle excitations is at all possible, given by two-hole, one-particle states. Often, however, due to strong configuration interaction, only a major contribution to a specific peak can be assigned.

In this paper we are dealing with the relative intensities of these two-hole, one particle satellites compared to the single hole state. To first approximation these intensities are given by the usual Golden Rule formula containing a matrix element where the dipole operator couples the total ionic wave function including the photoelectron with the neutral ground state.<sup>2</sup> At this place we only want to note that in a strongly correlated system this is not easily evaluated and also the Golden Rule formulation is not strictly correct because the Hamiltonian of the ionic and the neutral molecule are not identical.

Even though the physics of the process seems well established, the details are far from being completely understood. Often only the lowest lying molecular excitation is reasonably well identified in the experimental

spectra. In CO or N<sub>2</sub>, the molecules we are dealing with in this article, the lowest excited ionic state corresponds to an excitation of an electron from the  $1\pi'$  level to the  $2\pi'$  level; the prime denotes that these are levels of the ion. For example, we will discuss the branching ratios between optical excitation from the CO ground state  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$  into  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^1 + e^-$  and into  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^3 5\sigma^1 2\pi^1 + e^-$ . If we take the spin into account we will find the latter configuration to split into two doublet and one quartet state. Only the doublet states result from allowed optical transitions involving no spin flip so that we expect to see two shakeup peaks attributed to the  $1\pi' \rightarrow 2\pi'$  transition.<sup>3</sup> The shakeup structures at higher energies exhibit such a multitude of lines that it is almost impossible to assign the observed spectra to specific excited states of the molecule. This especially applies to the region where the energy is high enough to create a hole in the outermost  $3\sigma(2\sigma_g)$  core level, because the number of energetically almost degenerate configurations is very large.

In this paper we demonstrate an experimental procedure to establish the main configuration within each of the observed satellite peaks. Plotting the cross section of the satellite as a function of excitation energy clearly allows us to distinguish between a configuration with an outer valence hole  $5\sigma$ ,  $1\pi$ ,  $4\sigma(3\sigma_g, 1\pi_u, 2\sigma_u)$  or a hole in the  $3\sigma(2\sigma_g)$  shell of the molecule as the final state. We can establish some mixed behavior indicating the participation of both hole configurations in the same satellite peak. We also find that even for a "pure" final state configuration the satellite intensity measured relative to the main line is, in the range of our observations (40–140 eV), a monotonically dropping function with excitation energy. A comparison with XPS data leads to the conclusion that this function goes through a minimum and afterwards increases towards higher energies.

The experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin using a toroidal grating monochromator<sup>4</sup> and a commercial double pass cylindrical mirror electron analyzer (PHI-15-255G). The chosen geometry minimizes the possible influence of variations in the asymmetry parameter on the relative peak intensities as a function of photon energy. Integrating over the whole acceptance

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cone of the analyzer we find that the measured cross section  $\sigma_m$  is given by  $\sigma_m = \sigma(1 + 0.08\beta)$ , where  $\sigma$  is the total cross section and  $\beta$  the well-known asymmetry parameter. N<sub>2</sub> and CO were condensed onto a liquid He cooled Dewar. The copper body of the Dewar was coated with an *in situ* evaporated Au film of a few hundred Å thickness. The molecules were deposited until there was no substrate emission detectable in the photoemission spectra. On the other hand the films were sufficiently thin to avoid charging effects. The photon flux was measured using a W-wire diode in the unfocused beam between the output mirror of the TGM and the sample. In order to determine the relative photon flux we used the efficiency curve as calibrated by Saloman.<sup>5</sup> We also made sure that the electron analyzer did not distort the measured peak intensities. At a pass energy of 25 eV there seemed to be no unwanted source size effects present over the entire range of the experiment. Very much the same behavior was established before by Plummer and co-workers.<sup>6</sup>

## EXPERIMENTAL RESULTS

Figures 1 and 2 show a series of spectra taken at various photon energies for CO and N<sub>2</sub>. The curves are normalized to equal height for the emission of the  $1\pi(1\pi_u)$  orbital. In order to determine the intensity of the shakeup peaks we have subtracted a linear background of scattered electrons as indicated by the dashed line and integrated the counts between the various tic marks in the regions A through F for CO (A through E for N<sub>2</sub>). From these figures it clearly can be seen that the lower

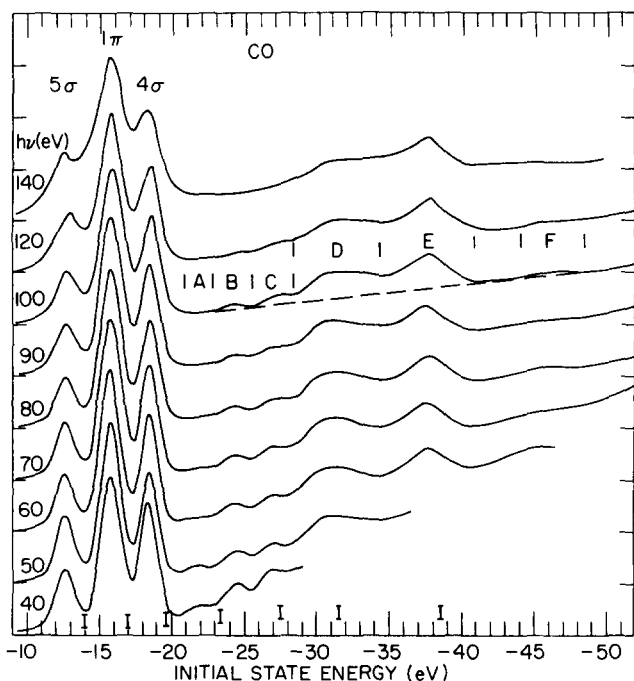


FIG. 1. Electron energy distribution curves (EDC's) of solid CO as a function of excitation energy. All curves are normalized to show the same intensity for the emission of the  $1\pi$  orbital. Integration regions for peaks A through F are indicated by tic marks. The background is subtracted as shown by the dashed line. The total accumulated counts for the  $1\pi$  level decrease from  $1.6 \times 10^6$  (40 eV) to  $6.6 \times 10^3$  (140 eV).

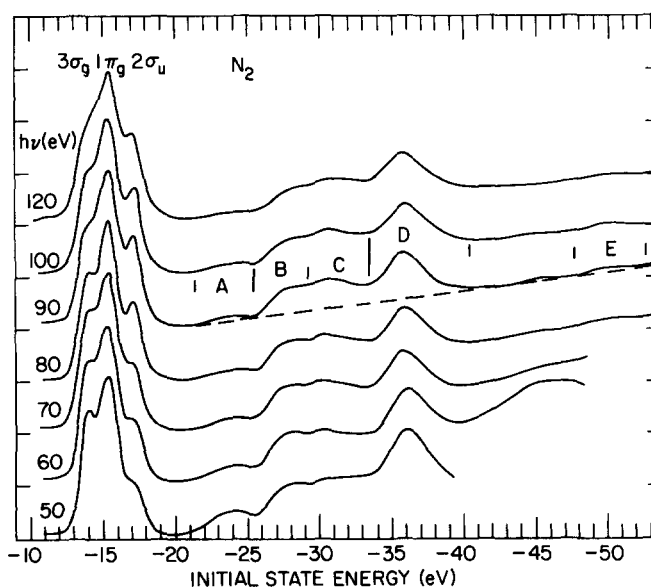


FIG. 2. EDC's of solid N<sub>2</sub> as a function of photon energy. All curves are normalized to show the same intensity for the emission on the  $1\pi_u$  orbital. Integration regions for peaks A through E are shown as well as the background correction (dashed curve) for inelastically scattered electrons. The total accumulated counts for the outer valence band vary from  $1.0 \times 10^6$  (50 eV) to  $3.2 \times 10^4$  (120 eV).

energy satellite intensities measured relative to the total outer valence electron emission in regions A, B, and C for CO (A for N<sub>2</sub>) are decreasing with increasing excitation energy. On the other hand, peaks D and E (B, C, and D for N<sub>2</sub>) increase in their relative intensity.

Figure 3 shows the absolute photoemission cross section for the total outer valence emission and separately the satellite region of CO. Our data points are normal-

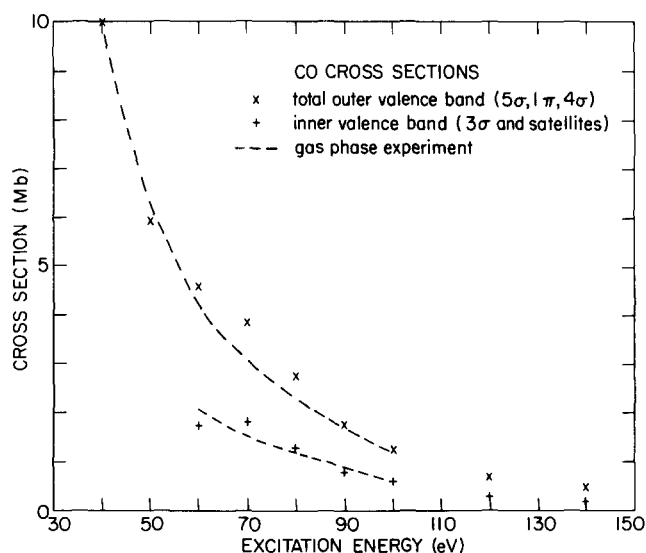


FIG. 3. Partial photolization cross section for the inner and outer valence states of CO. The data points are normalized at  $h\nu = 40$  eV to the gas phase outer valence results (Ref. 7). These independently determined data are also shown as the dashed curves.

ized at one point ( $h\nu = 40$  eV) to gas phase photoemission results<sup>7</sup> to give the absolute cross section, since we were only able to measure the relative incoming photon intensity but not absolute photon numbers and the analyzer efficiency was also only known on a relative basis. Our measured values agree very well with gas phase data<sup>7</sup> as indicated by the dashed lines. Over the photon energy range shown the cross section drops approximately by a factor of 20, for this reason we have shown normalized spectra in Figs. 1 and 2. The agreement between the two data sets also confirms that the analyzer corrections are done properly and no unwanted source size effects are present. The deviation around 70 eV photon energy might be due to solid state effects superimposed on the molecular photoabsorption cross section since we are comparing the spectra of solid CO to gas phase data. However, an error in the photon flux measurement cannot be excluded. The branching ratio for the outer valence emissions is almost constant over the entire energy range. More accurately it changes between 40 and 140 eV from 17%–18% for the  $5\sigma$ , 50%–55% for the  $1\pi$ , and 33%–27% for the  $4\sigma$ . Similar values have been reported for 40 eV,<sup>6</sup> and  $YM\xi$  (132 eV) gas phase spectra.<sup>8</sup>

Plotting the total cross section for N<sub>2</sub> photoemission in a similar fashion as done for CO in Fig. 3 we find not quite so good an agreement between our results and the optical absorption data of Cole and Dexter.<sup>9</sup> Our measured values show a drop in cross section between 50 and 120 eV by a factor of 12, whereas the optical cross section only drops by a factor of 8 over the same range.

Figures 4 and 5 now show the intensity of the satellite peaks as labeled in Figs. 1 and 2 measured, relative to the intensity of the total outer valence emission. Thus we eliminate all errors due to the photon flux measure-

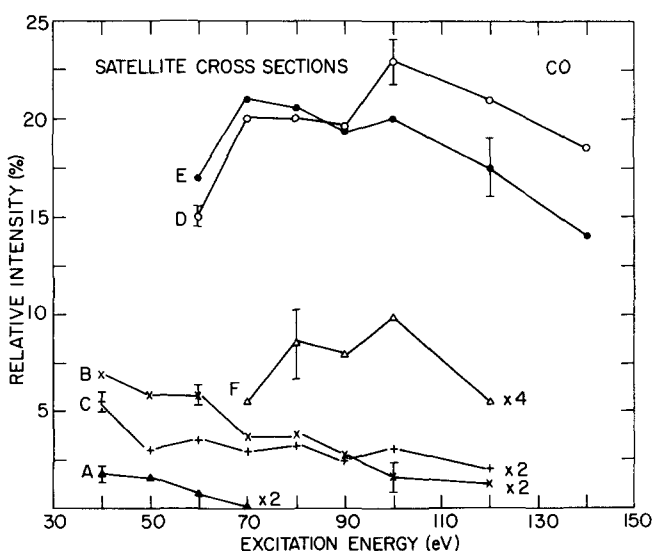


FIG. 4. CO satellite cross sections determined relative to the outer valence emission by integration over areas A through E as shown in Fig. 1 after background subtraction. Typical errors are indicated based on the uncertainty in background subtraction and counting statistics.

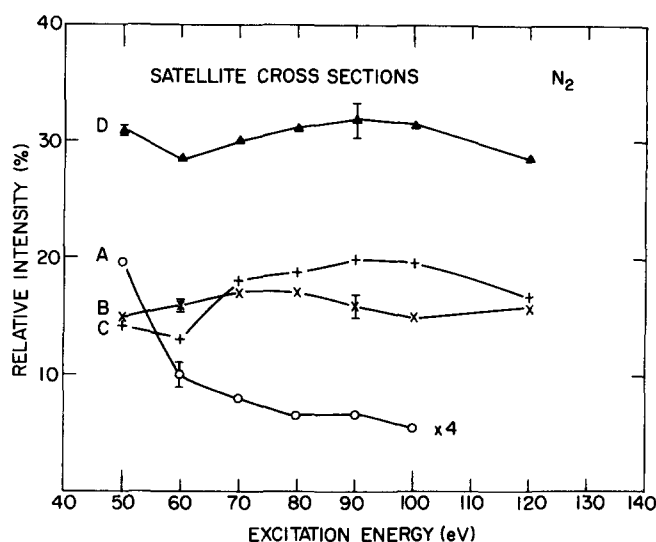


FIG. 5. N<sub>2</sub> satellite cross sections measured relative to the outer valence level emission. The integration is carried out for regions A through D after background subtraction as shown in Fig. 2. Typical errors based on the uncertainty in background subtraction and counting statistics are indicated.

ments. Also the satellite peaks seem to fall into either one of two categories as seen in Figs. 4 and 5. The lower lying satellites A, B, and C for CO (A for N<sub>2</sub>) which are shakeup peaks of the outer valence electrons drop in intensity relative to the single hole states, whereas the remaining satellite structure, which presumably is derived from the  $3\sigma$  ionization, shows a constant slightly rising relative cross section. This behavior is already obvious from an inspection of the raw data in Figs. 1 and 2 and not subject to any background subtraction or other data handling procedures. This empirical classification is especially helpful since state of the art calculations produce many more lines or different states than experimentally resolved peaks. Moreover even a convolution of the calculated spectra in general does not agree with experiment in both energetic position of the main lines and relative intensity.

Some of these satellite intensities have been measured previously by photoemission up to 40 eV excitation energy<sup>6</sup> and by  $e, 2e$  coincidence technique up to 50 eV excitation energy.<sup>10</sup> Also very recently some data were obtained at higher energies for N<sub>2</sub> ( $\leq 65$  eV) and CO ( $\leq 100$  eV) in the gas phase.<sup>7</sup> However, none of these authors noted the specifically different behavior between the cross sections of the outer valence satellites.

## DISCUSSION

Before we discuss the experimental results in detail, let us start with some qualitative theoretical considerations concerning satellite intensities and energies in diatomic molecules.

As mentioned in the Introduction the photoemission intensity into a final state with energy  $\epsilon$  is approximated by a Golden Rule formula

$$I(\epsilon) \sim \left| \sum_{j=1}^N \langle \psi_j(N-1, \epsilon) | \hat{p}_j | \phi_0(N) \rangle \right|^2, \quad (1)$$

where  $\phi_0(N)$  is the wave function of the neutral molecule in its ground state coupled by the dipole operator  $p_j$  to  $\psi_f$ , the wave function of the ion having  $(N-1)$  bound electrons and one in the continuum. Usually the time evolution of the wave functions during the photoabsorption process and the interaction with the outgoing photoelectron are neglected and one arrives at the following intensity equation in the sudden dipole approximation if one considers ionization out of a particular initial orbital  $i$ :

$$I_{i,\epsilon} \propto \left| \sum_f \langle \epsilon | p_i | i \rangle \langle \psi_f^{N-1} | \phi_i^{N-1} \rangle + \sum_f \langle \epsilon | i \rangle \langle \psi_f^{N-1} | \sum_{j \neq i} p_j | \phi_i^{N-1} \rangle \right|^2, \quad (2)$$

where  $\epsilon, i$  denote the one electron final and initial state,  $p_j$  the dipole operator,  $\psi_f^{N-1}$  the eigenstate of the ion, and  $\phi_i^{N-1}$  that part of the neutral  $N$ -electron wave function describing all  $N-1$  electrons of the molecule except the one to be ionized. In the first term the dipole operator connects the two one particle states involved in the direct ionization, so that the relative intensities for different ionic final states are governed by the multiplicative overlap integral. Consequently, for symmetry reasons in the first sum the two  $N-1$  particle wave functions must both have the same molecular symmetry and the ionized electron follows a dipole selection rule. This type of shakeup process is called "normal" shakeup. If normal shakeups are forbidden by symmetry the second term in Eq. (2) may still lead to a nonvanishing intensity. In this term the dipole operator connects the two  $N-1$  particle wave functions, which couple as in a normal dipole transition for a nonvanishing matrix element. The shakeup satellites generated by the second term in Eq. (2) are called "conjugate" satellites.

Usually the conjugate satellites are not included into calculations. Martin and Shirley<sup>11</sup> however pointed out that these contributions might be very important, especially at low photon energies. At high photon energies the first term in Eq. (2) dominates. Assuming a plane wave final state one gets a rough estimate of the excitation energy dependence of both terms in Eq. (2). Then the dipole operator single particle matrix element  $\langle \epsilon | p_i | i \rangle$  can be replaced by  $\hbar k_\epsilon \langle \epsilon | i \rangle$  since plane waves are eigenfunctions to the momentum operator. This results in

$$I_{i,\epsilon} \propto \left| \sum_f \hbar k_\epsilon \langle \epsilon | i \rangle \langle \psi_f^{N-1} | \phi_i^{N-1} \rangle + \sum_f \langle \epsilon | i \rangle \langle \psi_f^{N-1} | \sum_{j \neq i} p_j | \phi_i^{N-1} \rangle \right|^2. \quad (3)$$

For sufficiently high kinetic energy of the photoelectron, i. e., large  $k_\epsilon$ , the first term of Eq. (3) tends to dominate because of the multiplicative factor  $\hbar k_\epsilon$ . Moreover, it has been shown that the second term does not contribute for large  $k_\epsilon$ ,<sup>11</sup> so that we are left with the normal shakeups only as in Aberg's cross section formula in this limit.<sup>12</sup>

We are well aware of the deficiencies of the plane wave final state assumption especially in the energy range of the spectra we present here. Nevertheless, the important question remains whether conjugate shake-

ups contribute at low energies. This can be positively answered by referring to the work of Agren and co-workers,<sup>27</sup> who have assigned a transition in the soft x-ray emission spectrum of N<sub>2</sub>, which is directly equivalent to a conjugate shakeup process in photoemission.

Of course our discussion has to also include the shakeup energies. However, state of the art inner valence shakeup calculations<sup>23-27</sup> at present are still so much in disagreement with respect to energetics, that an assignment based solely upon these calculations seems somewhat arbitrary. On the other hand the spectrum of the low energy satellites correlated with core ionization ( $N1s$ ,  $C1s$ , or  $O1s$ ) seems to be largely understood.<sup>1,3,13-17</sup> Therefore we will try to transfer this interpretation to the valence region, assuming that the gross features of the ionic excitation spectrum do not radically change upon substitution of a valence hole for a core hole.<sup>15</sup>

We know that the low lying core hole satellites at 9.3 eV (8 eV) and 16 eV (15 eV) in N<sub>2</sub>(CO) are basically due to the two possible doublet states resulting from the singlet and triplet coupled  $1\pi_u \rightarrow 1\pi_g(1\pi \rightarrow 2\pi)$  excitation. The quartet two-hole, one-particle state (all three spins parallel) cannot be excited by optical excitation since it requires a spin flip. Analogous to the core satellite spectrum we expect the valence satellite spectrum to be dominated by the doublets given by the following single particle configurations:  $3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1$  and  $2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1$  for N<sub>2</sub> and  $5\sigma^{-1}1\pi^{-1}2\pi^1$  and  $4\sigma^{-1}1\pi^{-1}2\pi^1$  for CO. The energies will be similar but not equal to the core satellites. Roughly we expect the satellites to be 7 and 14 eV above the corresponding single hole state ( $3\sigma_g^{-1}, 2\sigma_u^{-1}$  and  $5\sigma^{-1}, 4\sigma^{-1}$ ). Additionally we want to note here that the  $1\pi_u^{-2}1\pi_g^1$  state of N<sub>2</sub> corresponds to a conjugate shakeup process the direct equivalent of which was found in soft x-ray emission.<sup>27</sup>

Also, the Coulomb interaction mixes all states of the same total symmetry such that a classification in single particle terms as done above is not exact.<sup>23-27</sup> This mixing makes it possible for all three  $\sigma$  single hole states in CO ( $3\sigma^{-1}, 4\sigma^{-1}, 5\sigma^{-1}$ ) to couple to the same two hole state. The strength of the coupling depends on a coupling matrix element and the energetic separation of the states. The mixing of the states also gives rise to interference effects in the satellite intensity as experimentally observed for acetylene.<sup>35</sup> For N<sub>2</sub>, because of the additional inversion symmetry, only the  $3\sigma_g^{-1}$  and  $2\sigma_u^{-1}$  single hole states couple to the same two-hole, one-particle states. On the other hand the excited state spectrum of the  $2\sigma_u^{-1}$  primary hole state should be pure.

Apart from the  $1\pi_u \rightarrow 1\pi_g(1\pi \rightarrow 2\pi)$  shakeup discussed above, the higher excited ion states known from core ionization will lead to a manifold of states in the range from 15 to 30 eV below the  $2\sigma_u^{-1}(4\sigma^{-1})$  hole state when transferred to the valence region. This is exactly the energy range where the  $2\sigma_g^{-1}(3\sigma^{-1})$  primary hole state energy is supposed to be. Therefore these excited ion states couple to the  $2\sigma_g(3\sigma)$  primary hole state, if allowed by symmetry, even though the shakeup configuration only contains outer valence holes. This intensity borrowing<sup>17</sup> will, as indicated above, depend on the coupling matrix

element and the energy separation between the primary hole state and the excited configuration. Consequently the  $2\sigma_g^{-1}(3\sigma^1)$  state, being situated energetically within a whole manifold of excited ion states, distributes its intensity over several lines with decreasing weight for larger energy separation from the single particle ionization energy. Due to the complexity of the excited ion eigenvalue spectrum these states cannot be definitely assigned without a very accurate configuration interaction calculation. Apart from these higher excited states, we also expect the  $1\pi_u \rightarrow 1\pi_g$  ( $1\pi \rightarrow 2\pi$ ) satellite to couple to the  $2\sigma_g^{-1}(3\sigma^1)$  single particle state. The strongest interaction should be found for the singlet  $2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1$  ( $4\sigma^{-1}1\pi^{-1}2\pi^1$ ) configuration. The other satellites are energetically farther separated from the  $2\sigma_g(3\sigma)$  hole by at least 3.2 eV (5.7 eV) for N<sub>2</sub>(CO). For the same reason we expect that in N<sub>2</sub> the  $2\sigma_g$  interaction with these excited states is larger than in CO( $3\sigma$ ). On the other hand, the farther these excited states are separated from the  $2\sigma_g(3\sigma)$  primary hole, the closer they are to the  $3\sigma_g(4\sigma)$  single particle ionization energy. This leads to the conclusion that the cross section of these satellites should be mainly determined by those two single particle states. Using this rather simple minded picture, we conclude, without having done any calculation, that the low binding energy satellites, including mainly the triplet coupled  $\pi \rightarrow \pi^*$  excitations, should show a different cross-section behavior than the higher energy satellites close to the  $2\sigma_g(3\sigma)$  primary hole state.

In summary we propose the following:

(1) We expect "normal" and "conjugate" shakeup satellites to behave different as a function of photon energy.

(2) We expect four "normal" excited ion configurations to dominate the low energy spectrum of the satellites whereby the higher energy states show a cross-section behavior in line with the  $2\sigma_g(3\sigma)$  hole state and the low energy region is dominated by the parenthood of the outer  $3\sigma_g$ ,  $2\sigma_u$  ( $5\sigma$ ,  $4\sigma$ ) valence levels.

In the following we want to discuss the satellite spectra in detail comparing them also to previous experimental results<sup>4,6-10,18-22</sup> and more detailed calculations taken from the literature.<sup>23-32</sup> We start with N<sub>2</sub>.

First of all, we have chosen the photon energy range such that we largely eliminate effects of final state shape resonances in our spectra. Gas phase N<sub>2</sub> (CO) has a shape resonance of  $\sigma_u(\sigma)$  symmetry about 15 eV (12 eV) above the vacuum level as found from the excitation cross section of the  $3\sigma_g(5\sigma,4\sigma)$  orbital(s). Higher binding energy orbitals, like the  $2\sigma_g(3\sigma)$ , should be able to couple to the same final state resonance at an appropriately larger photon energy. This is demonstrated for the case of N<sub>2</sub> in Fig. 6, where we have plotted the relative intensity at 36 eV binding energy, peak D, which supposedly derives most of its intensity from the  $2\sigma_g$  single particle state. Clearly the cross section shows a maximum at 52.5 eV photon energy, locating the final state resonance about 16.5 eV above the vacuum level of solid N<sub>2</sub>. This is an excellent agreement with the gas phase outer valence results because we have to take into account a 1.5 eV shift of the apparent binding energy in

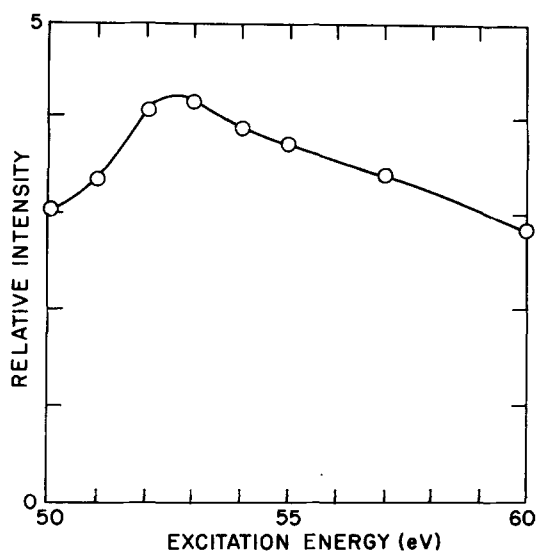


FIG. 6. Intensity of the N<sub>2</sub> photoemission signal at 36 eV binding energy measured relative to the  $1\pi_u$  emission as a function of photon energy showing the coupling to the  $\sigma_u$  final state shape resonance.

solid N<sub>2</sub> due to extra molecular screening.<sup>32</sup> This only affects the position of the final state resonance with respect to the vacuum level but not the photon energy at which the resonance is observed, because the transition energy between the two states should not change compared to gas phase results at least in first-order approximation as confirmed by our data. We note here that the peak in Fig. 6 seems to be considerably narrower than data published earlier.<sup>7</sup> We attribute this discrepancy to the fact that we have plotted the intensity at one particular binding energy (36 eV), disregarding changes in the shape of the spectrum as the final state resonance "moves through," whereas the earlier work shows the integrated cross section over a 10 eV wide range.

It is also remarkable that this peak D, even though it is clearly of a different nature than a single particle photoemission peak, in its intensity is determined by the final state kinetic energy of the photoelectron rather than by the excitation energy. Apart from the observation of the  $\sigma_u$  resonance associated with the  $2\sigma_g$  emission and the corresponding  $\sigma$  shape resonance in the  $3\sigma$  emission of CO we assume our spectra to be basically free of final state effects. In particular there are no other final state resonances known in the chosen energy range. Also, as mentioned above, the fact that we do the experiments on solids, not on gases is not considered an obvious drawback. We observe extramolecular screening, which results in a lowering of the ionization potential by about 1.5 eV compared to the isolated molecule; but, as said before, the transition energies between various molecular states should not be affected by this screening mechanism. Or, in other words, to first order, the extramolecular screening shifts all orbital energies by the same amount. The effects of the symmetry reduction in the solid, which might break the inversion symmetry of the N<sub>2</sub> molecule and therefore allow interac-

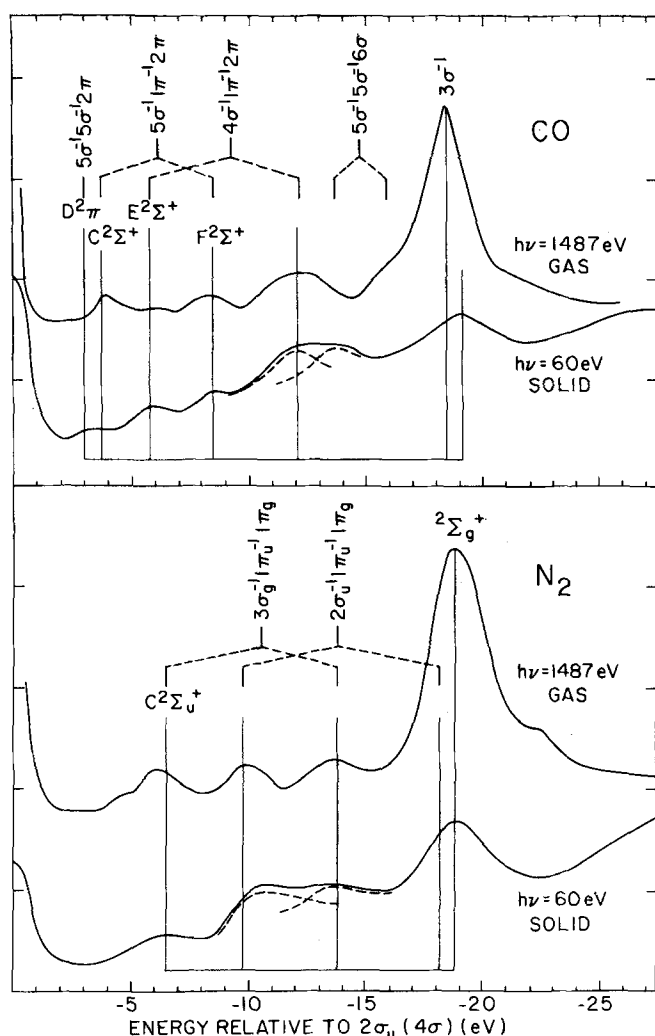


FIG. 7. Comparison between gas phase photoelectron spectra (Ref. 1) and our results. All spectra are aligned at the  $4\sigma$  ionization potential. The spectroscopic final state symmetry assignment is shown according to Refs. 18 and 19. For the assignment of the shakeup configurations see the discussion in the text.

tions forbidden in the gas phase, will be discussed later. Finally, characteristic electron energy loss features, which show up as pressure dependent peaks in gas phase spectroscopy,<sup>1</sup> do not seem to have a large contribution to the features in our spectra. The largest loss peak is observed at 12.9 eV (11.4 eV) for N<sub>2</sub> (CO).<sup>33</sup> This would result in additional peaks in our spectra, for example at 23.5 eV for CO which clearly are not observed for any photon energy.

Let us now turn to a detailed comparison of our data with theory<sup>24-32</sup> (see also Fig. 7). According to core level experiments, calculations and our qualitative discussion above peak A in the N<sub>2</sub> spectrum, which is also designated as the C state of N<sub>2</sub> clearly corresponds to the triplet coupled excited ionic state  $3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1$  at a calculated energy difference at 9.7–10.4 eV compared to the ground state of the ion. This is clearly the first excited ionic state. The next configuration is about 4 eV higher in energy. Therefore the assignment of peak A

seems straightforward. Nevertheless it is very remarkable that the relative intensity of this shakeup peak does not scale with any valence level excitation. In its relative intensity the peak approaches a minimum at about 100 eV excitation energy and is rather strong again at x-ray energies.<sup>1,8</sup> As discussed in detail above, the fact that the intensity declines measured relative to the outer valence emission is independent of our evaluation of the absolute cross section. It also is obvious from an inspection of the normalized curves in Fig. 2.

At first glance there is no obvious explanation for this behavior. We are too high in excitation energy to attribute the observed effect to a deviation from the sudden approximation regime. In general, post collision interaction or the transition into the adiabatic regime should occur very close to threshold. Also shakeup peaks would disappear for a strictly adiabatic ionization process because the ion would have time to relax into its ground state. This all would explain a rise of shakeup intensity, but not the decline we observe over the first 100 eV.

Another explanation would be the presence of interference effects due to the contribution of several configurations to the same time. Experimentally this has been observed for acetylene.<sup>35</sup> In the case of N<sub>2</sub> however the inversion symmetry creates a problem because the C state of N<sub>2</sub> has  $^2\Sigma_u^-$  symmetry. This leaves one possible shakeup channel open. Only the  $2\sigma_u^{-1}$  single hole state can couple to the  $3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1$  configuration. This makes the drop in cross section even more surprising since the  $2\sigma_u^{-1}$  single particle cross section increases relative to the total outer valence emission. No other ionization channel can contribute to this peak unless the symmetry of the molecule is broken by forming solid N<sub>2</sub>. This would allow the  $3\sigma_g^{-1}$  and  $2\sigma_g^{-1}$  single particle states to couple to the same excited state configuration  $3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1$ . However, comparing the few gas phase spectra available to us, we find the same cross-section behavior for this state. Therefore, the lower symmetry of the solid probably is not the dominant factor.

It is interesting to note that Agren and co-workers<sup>27</sup> calculate a  $^2\pi_g$  state with a single particle configuration  $1\pi_u^{-2}1\pi_g^1$  only 0.2 eV higher than the  $C^2\Sigma_u^+(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1)$  state. This  $^2\pi_g$  state turns out to be essential for the interpretation of the N<sub>2</sub> 1s soft x-ray emission spectrum. Usually it is not included into any calculations because it corresponds to a conjugate shakeup process. Clearly, the presence of this conjugate shakeup channel could explain the drop in cross section of peak A in our spectra.

Turning now to the higher satellite lines B, C, and D (Figs. 2, 5, and 7) we note that peak B has a slightly different cross section behavior than peaks C and D which seem to have about the same intensity ratio. Calculations<sup>19-28</sup> tell us that in this energy range the states borrow most of their intensity out of the  $2\sigma_g^{-1}$  single particle state. Only the leading peak B has substantial  $3\sigma_g^{-1}$  character. The ionic state of peak B has the dominant configuration triplet  $2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1$ . The energy of this configuration is about 14 eV above the ionic ground state<sup>24</sup> in very good agreement with our experiment and gas phase data.<sup>7</sup> The next higher ionic configurations are calculated between 18 and 23 eV with about five strong

and several more weak lines.<sup>26</sup> The strongest lines in this multiplet are at 19.7 and 21.5 eV above the ionic ground state<sup>24</sup> borrowing their intensity out of the  $2\sigma_g$  level. The center of peak D is at 22 eV in reasonable agreement with theory.

As indicated in Fig. 7, peak C also coincides with the singlet coupled  $3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1$  configuration which couples only to  $2\sigma_u^{-1}$  but not to  $2\sigma_g^{-1}$ . In general the cross section shown in Fig. 5 indicates coupling to the  $2\sigma_g$  or  $2\sigma_u$  ionization channel for the peaks B, C, and D, since relative to the outer valence ionizations the  $2\sigma_u$  and  $2\sigma_g$  single particle cross section is expected to increase in the photon energy range of our spectra. Especially the ratio between the  $2\sigma_g$  and the sum of the outer valence cross sections ( $3\sigma_g$ ,  $1\pi_u$ ,  $2\sigma_u$ ) peaks at about a photon energy of 70–80 eV.<sup>7,26</sup>

In principle we should be able to assign shakeup peaks at higher excitation energies too. Experimentally we do find additional structure in our curves, peak E and between peaks D and E. The assignment however is not straightforward. The so-called  $\pi \rightarrow \pi^*$  shakeup in connection with a  $2\sigma_g$  hole,  $2\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1$ , does only couple to the  $2\sigma_u$  single particle state, but the energy difference is very large and therefore the coupling extremely weak. Otherwise we have to involve either symmetry breaking or a conjugate shakeup excitation leading to intensity of this ionic state.

Usually higher excited state configurations are also assigned to the structures in this energy range, but these states are so closely spaced in energy that a unique assignment becomes impossible. Therefore in Fig. 7, we only indicate the assignment of the singlet and triplet coupled  $\pi \rightarrow \pi^*$  shakeup configurations.

Having laid the ground by interpreting the N<sub>2</sub> spectra, we now turn to CO. This molecule does not have the inversion symmetry about its center like N<sub>2</sub> and therefore the multitude of shakeup configurations is even larger. Intensity borrowing occurs between all three orbitals ( $3\sigma$ ,  $4\sigma$ ,  $5\sigma$ ) leaving almost no peak in the shakeup spectrum with a unique single particle assignment.

The first two excited states are calculated about 10 and 17 eV above the ionic ground state.<sup>23–32</sup> This agrees approximately with peaks A and C in our spectra. Both excited state configurations correspond to holes in both the  $5\sigma$  and  $1\pi$  shell and one electron promoted into  $2\pi$ . The spin configuration of the electrons in the  $\pi$  orbitals, causes an energy difference of about 7 eV depending on whether both electrons are in a singlet or triplet configuration.<sup>3</sup> Of course in either case the  $\pi$  electrons couple to the  $\sigma$  hole to form a doublet state. The triplet state is lower in energy and should also have a lower intensity<sup>3</sup> in agreement with our results.

From gas phase experiments we know that there are four ionic states between 20 and 30 eV binding energy. They have been identified by Codling and Potts<sup>22</sup> and Asbrink *et al.*<sup>18</sup> by recording their vibrational progressions. The results of these gas phase experiments are indicated in Fig. 7. The lowest energy state at 22.3 eV has been identified<sup>18</sup> to be of  ${}^2\pi$  symmetry. The excited state configuration is  $5\sigma^{-1}5\sigma^{-1}2\pi^1$ . Calculations that have

this state included<sup>26</sup> find negligible coupling to the  $1\pi^{-1}$  single hole state. On the other hand, this same final state configuration would, in a conjugate shakeup process, couple to the  $\sigma$  single hole states. Since the intensity of peak A drops very rapidly with photon energy, we prefer to interpret this  ${}^2\pi$  state to originate from a conjugate shakeup process. There is a second ionic state of  ${}^2\Sigma$  symmetry contributing to peak A. This state is, analogous to N<sub>2</sub>, the triplet coupled  $5\sigma^{-1}1\pi^{-1}2\pi^1$  state deriving its intensity from mostly the  $5\sigma^{-1}$  and  $4\sigma^{-1}$  single particle states contribute too, but with weaker intensity. At x-ray excitation energies only the  ${}^2\Sigma$  component of peak A shows up in the spectra as can be seen from the comparison in Fig. 7. Above, by comparison to the core ionizations, we deduced that the triplet coupled state is closer in energy to the  $4\sigma^{-1}$  in CO than the corresponding state of N<sub>2</sub> relative to the  $2\sigma_u$ . This can be accounted for by the lower binding energy of the  $5\sigma$  in CO and the lower triplet excitation energy.

The assignment of the peaks at higher energy is now straightforward. They are in sequence to be assigned as the triplet coupled  $4\sigma^{-1}1\pi^{-1}2\pi^1$  excitation (peak B), the triplet coupled  $5\sigma^{-1}1\pi^{-1}2\pi^1$  excitation (peak C), and the singlet coupled  $4\sigma^{-1}1\pi^{-1}2\pi^1$  excitation (peak D). For peak D the assignment is not as clear cut as for the peak at lower binding energy. All calculations predict a multiplicity of ten or more lines in the energy region from 19.5–33 eV above the  $4\sigma$  hole. All these states couple rather strongly to the  $3\sigma$  single hole state even though they are highly excited configurations of outer valence holes. There is some consensus in all calculations about the presence of a  $5\sigma^26\sigma^1$  configuration as indicated in Fig. 7. Nevertheless, because there are quite a few closely spaced states, the assignment cannot be made at present in a unique way. In view of this fact the strong intensity variation of this part of the spectra, as shown in Fig. 7, is not too surprising. Obviously as we go to x-ray excitation, peak E, which is closest to the  $3\sigma$  quasiparticle energy becomes stronger and it seems as if the x-ray spectrum has more single hole character. So far there are no calculations available that could follow up on the rather dramatic intensity redistributions in the  $3\sigma$  region (peaks D and E). A theoretical effort in this direction would be highly desirable.

As expected from our theoretical discussion above, the low energy satellites (peaks A, B, and C) approximately follow in cross section the outer valence single hole states. The general decrease of peaks B and C could partially be explained by the relative decrease of the  $4\sigma^{-1}$  single hole cross section or by interference. On the other hand, peaks D, E, and F follow exactly the  $3\sigma^{-1}$  single hole cross section which, relative to the sum of  $5\sigma^{-1}$ ,  $1\pi^{-1}$ , and  $4\sigma^{-1}$ , is expected to peak between 70–90 eV.

## CONCLUSIONS

We have demonstrated for the case of CO and N<sub>2</sub> that the cross section of satellite peaks if plotted vs excitation energy allows us to identify the main character of a



line. We clearly recognize whether a satellite has mostly outer valence level ( $4\sigma^{-1}$  as  $5\sigma^{-1}$ ) single particle character or derives its intensity from the  $3\sigma$  core level excitation. Using a rather qualitative picture about the excited ionic states we can nevertheless make a very detailed assignment of the shakeup configurations. We also find that the lowest energy satellite, which in general is interpreted as a normal shakeup, is energetically degenerate with a satellite resulting from a conjugate shakeup process. Therefore, measuring the satellite cross section vs photon energy might turn out to be a very powerful technique in the future when we are dealing with more complex molecules.

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