Conf-750344--2

MULTIPLE EXCITATION IN FREE MOLECULES*

Thomas A. Carlson

Oak Ridge National Laboratory

Oak Ridge, Tennessee 37830, USA

INTRODUCTION

This lecture will be the only one in the book that will deal specifically with free molecules. It thus faces the problem of covering in a relatively short space a subject that is more complex than the corresponding one on atomic systems, and whose literature, in the case of certain experimental investigations, is more extensive. However, by making a limited selection of material, and by covering some material superficially, we should be able to obtain an overview and flavor of multiple electron excitation in molecules.

The subject to be covered in this lecture is at the heart of the interest of the school: viz, multiple excitation in the photoionization process. We shall restrict ourselves mainly to studying satellite structure in the photoelectron spectra of core shells. In only a few cases has satellite structure been identified [1] in the photoelectron spectra of the valence shell. This is due in part to the fact that the large number of molecular orbitals closely spaced in energy makes difficult the separation of satellite lines from main lines; and in part to the fact that most studies on the valence shell have been done with low energy radiation, where there is often insufficient energy available to give rise to electron shakeup. Core shell photoelectron spectroscopy is usually carried out with Al or Mg Kα x rays, which usually have sufficient energies (1487 eV and 1254 eV) to produce photoelectrons with velocities far in excess of the bound valence electrons. Thus, our field of interest will be limited to the area of the sudden approximation.

For practical reasons we shall also primarily restrict the discussion to electron shakeup (transition to excited but bound states) rather than electron shakeoff (transition to the continuum). In photoelectron spectra the contribution of electron shakeoff is very hard to extract since the continuum spectrum is spread over a large energy range, whereas the discrete peaks due to electron shakeup are easy to detect. The study of electron shakeoff by means of measuring the ionic charge is hampered by fragmentation of the molecular ions. Study of satellite lines in x-ray fluorescence and Auger processes can, however, yield information about both electron shakeup and shakeoff, and will be mentioned briefly at the end of this lecture. Although the material to be discussed will be somewhat circumscribed, I believe that which is covered will give an idea of the added interest and complexity that molecules bring to the problem of many-electron excitation.

II. GENERAL ASPECTS OF ELECTRON SHAKEUP IN MOLECULES

As with atoms the photoelectric cross section for ejecting an electron from orbital, λ, of a neutral molecule, and ending up in the final state $\phi_{n,\lambda}$ of the ion is given by the expression

$$\sigma(E) = \overbrace{\frac{4\pi\alpha a_o^2}{3} E(h\nu)\,|\langle\nu_E|\underline{r}|u_\lambda\rangle|^2}^{\text{dipole}} \quad \overbrace{|\langle\phi_{n\lambda}|\phi_o\rangle|^2}^{\text{monopole}} \tag{1}$$

Equation (1) was derived [2] within the framework of both the dipole and sudden approximation. If we further assume that at higher kinetic energies of the photoelectron there will be little variation in the dipole contribution with changes in the photoelectron energy because of relatively small energy differences between the ground and excited states of $\phi_{n,\lambda}$, then the probability for monopole excitation is

$$P_{n\lambda} = |\langle\phi_{n\lambda}|\phi_o\rangle|^2 \tag{2}$$

where ϕ_o is the state of the neutral molecule in which one electron is missing from orbital, λ; or, in other words, is a collection of frozen orbitals of the singly-charged ion in which one electron has been removed from orbital λ. $\phi_{n\lambda}$ is one of a number of n configurations, for both the ground and excited states, in which electrons from all the other orbitals have relaxed to the hole created in λ. $P_{n\lambda}$ is thus the probability for going to a particular final state of the ion. Because of relaxation, the probability for going to the ground state is no longer unity and transitions to various excited states are also possible. For molecules the basic selection rule arising out of equation (2) is that $\phi_{n\lambda}$ has the same spin and space symmetry as ϕ_o. Within the framework of configuration interaction we may consider all possible configurations in the excited state that will properly mix. Single electron excitation, which we normally associate with electron shakeup, is one of the most important means of excitation but not necessarily the only one.

Table I contrasts the selection rules for monopole excitation between atoms and molecules. The capital letters representing the entire state illustrate the basic selection rules; the small letters representing the individual orbitals give the more restricted selection rules for single electron excitation. Γ for molecules are the irreducible representations or as sometimes called Mulliken symbols. Within the selection rule for single electron excitation the symmetry for an individual orbital is maintained: $\Delta\lambda = 0$. Angular momentum is not a good quantum number for molecules, except for linear molecules where the projection of the angular momentum onto the internuclear axis is quantized, and this projection quantum number, λ_p, follows the selection rule $\Delta\lambda_p = 0$ for monopole excitation. An interesting and important consequence of the localization of a core vacancy should also be mentioned. In the linear homonuclear molecule, e.g., N_2, gerade and ungerade symmetry exists. One would expect in this case that the following monopole selection rules pertain: $u \rightarrow u$; $g \rightarrow g$; $u \nrightarrow g$. However, when a hole is created in one of the 1s shells of N_2, the molecular orbital selection rules regarding u and g symmetry no longer apply.

It is highly instructive in studying molecules to compare the shakeup structure formed by creating core vacancies in each of the different atoms of a molecule. The core binding energies for various elements are sufficiently different that the photoelectron spectra are easily separated experimentally. If the excitation of the valence shell was identical regardless of the core vacancy formed, the shakeup spectra as represented by the satellite lines would be identical. This is rarely the case [3-5]. For example, figure 1 shows the photoelectron spectra of CO_2 with data for photoejecting electrons from either the C(1s) or O(1s) levels. The details of the shakeup structure are quite different. Since molecular orbitals are rarely equally distributed over the whole molecule, it is not surprising to find the shakeup probability for a given orbital strongly dependent on the location of the core hole. If an orbital

TABLE I. Selection rules for electron shakeup

Atoms	Molecules
$\Delta S = \Delta L = \Delta J = 0$	$\Delta S = \Delta\Gamma = 0$
$\Delta s = \Delta\ell = \Delta j = 0$	$\Delta s = \Delta\lambda = \Delta\lambda_p = 0$
	but $u \nrightarrow g$ not applicable to core hole

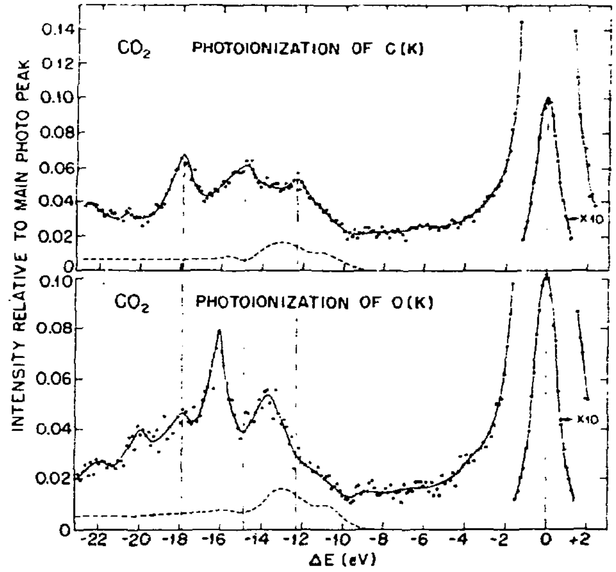

Figure 1. Comparison of satellite structure found in photoelectron spectrum of C(1s) and O(1s) of CO$_2$ using Al Kα x rays. Figure reproduced from Carlson et al., ref. [3].

has a high population density associated with a given atom, a localized hole in that atom will tend to preferentially excite the electron in that orbital.

The energy of excitation is dependent on the location of the core vacancy for two basic reasons. First, the extra atomic relaxation energy can be different according to which element has the core vacancy. This can cause changes in the total energies for both the ground and excited states, the shakeup energy being the difference between the two. Second, there will be a splitting of lines due to the possibility of more than one spin state. When photoionization occurs in a core orbital, an unpaired spin results. If electron shakeup occurs, both the valence shell and excited orbital will also contain unpaired spins. Within the monopole selection rules two states can arise which have the same configuration and state designation, but differ as to which pair of orbitals have parallel spins. The two states are commonly called lower and upper. See figure 2 for a pictorial description. In neon the upper and lower states have been clearly identified [5]. The intensities are roughly equal and the energy separations are about 4 eV. For the other rare gases the splitting between the upper and lower is smaller [5,7]. For molecules the extent of spin coupling is still open to question, but it may be more important than first realized.

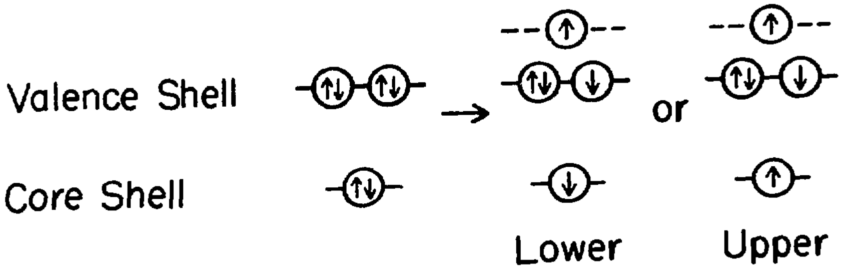

Figure 2. Schematic representation of formation of upper and lower spin states following electron shakeup.

III. COMPARISON OF THEORY AND EXPERIMENT FOR SPECIFIC MOLECULES

The first calculation of electron shakeup for molecules using equation (2) employed [8] semiempirical molecular orbital calculations, such as CNDO [9]. Since the semiempirical calculations do not involve the core electron specifically but treat the core as a fixed potential, it is necessary to use the equivalent charge approximation. That is, the effect of removing a shielding electron from the core is simulated by increasing the nuclear charge by one. This method of course neglects the effect of spin coupling between the partially filled shells. It gives only marginal agreement with experiment, but can be applied to complex systems that are not amenable to detailed calculations.

Recently, improved calculations of electron shakeup for molecules using Hartree-Fock wave functions and configuration interaction have been made [10-13]. The reader is warned tha rarely is a complete basis set used for molecular Hartree-Fock calculations, so the quality of the wave function may change considerably with the choice of the basis set. This uncertainty plus the wide possibilities for choices of configuration interaction result in a large variation in conclusions reached by different calculations.

In Table II are listed results of calculations made by Hillier and Kendrick [11] on nitrogen compared with experiment. The experimental data are from a spectrum reported by Gelius [5]. These data are taken with a monochromatic source of x rays and show a number of peaks that were not possible to resolve previously. Such an experiment requires the use of a powerful x-ray source employing a rotating anode, and a highly efficient spectrometer with a position sensitive detector in order to make up for the loss of intensity caused by the use of a monochromator. The availability of highly resolved spectra will make it possible in the future to test more closely, at least for simple molecules, the validity of theoretical calculations.

TABLE 11. Electron shakeup in photoionization of K shell of N_2 a)

Line	"Predominant" Orbital transition	Theory b) E	Theory b) I	Experiment c) E	Experiment c) I
1	$1\pi \rightarrow 2\pi$	7.7	0.2	9.3	2.1
2	$1\pi \rightarrow 2\pi$	18.3	5	16.0	24.6
3	$5\sigma \rightarrow 6\sigma$ $5\sigma \rightarrow 6\sigma$	21.5 22.3	1.6 0.2	19.6	0.9
4	$5\sigma \rightarrow 7\sigma$	23.0	0.3	20.8	0.3
5	$1\pi \rightarrow 3\pi$ $5\sigma \rightarrow 8\sigma$	23.7 24.6	1.6 0.1	∿ 22.1	∿ 0.7
6	$5\sigma \rightarrow 8\sigma$	25.1	1.2	23.0	1.9
7	$4\sigma \rightarrow 7\sigma$ $5\sigma \rightarrow 10\sigma$	27.8 28.0	0.5 0.1	24.6	3.1
remainder		31-35	4.9	27-29	∿ 4

a) Satellite position (E, eV) and intensity (I, %) are with respect to main peak.

b) Ref. [11].

c) Ref. [5].

Hillier and Kendrick [11] have employed configuration interaction in the final state wave function using single-electron excitations which yield configurations of $^2\Sigma^+$ symmetry (the same as the ground state for a hole in the 1s shell of N_2). Equation (2) was then used by substituting the wave functions for the various excited configurations which have been relaxed to the 1s vacancy. Configuration interaction was not used for the unrelaxed initial state. The agreement between theory and experiment is only marginal, particularly with regard to intensity. What is most striking is the prediction that the lower and upper states due to spin coupling (e.g., $1\pi \rightarrow 2\pi$) can be separated in energy by more than 10 eV and have intensity differences of more than an order of magnitude. If the assignment of the peaks are correct these conclusions are verified experimentally, but the assignment could of course be in error.

Of particular interest are the recent calculations of Martin et al. [13] on HF. They include configuration interaction in both the initial and final states and use a good basis set for the Hartree-Fock calculations. By so doing they have been able to obtain excellent agreement between theory and experiment. (See Table III). Note that inclusion of configuration interaction in the initial state raises the transition probability by about a factor

TABLE III. Electron shakeup in HF a)

Line	"Predominant" Orbital transition	Theory			Experiment	
		I(A)	I(B)	E	I	E
1	$3\sigma \rightarrow 4\sigma$	0	0.1	23.9	-	-
2	$3\sigma \rightarrow 4\sigma$	1.2	2.0	25.9	1.9	22.4
3	$1\pi \rightarrow 2\pi$	1.5	3.0	29.6	3.0	26.5
4	$3\sigma \rightarrow 5\sigma$	0	0	30.9	-	-
5	$1\pi \rightarrow 2\pi$	3.6	6.2	32.4	5.7	29.9
6	$3\sigma \rightarrow 5\sigma$	0.7	1.2	33.3	1.0	30.9
7	$1\pi \rightarrow 4\pi$	2.8	4.1	34.8	3.8	32.7

a) From ref. [13]. Satellite position (E, eV) and intensity (I, %) are with respect to main peak. Theory A has configuration interaction in the final state only, while theory B employs configuration interaction in both initial and final states.

of 1.4 to 2.0. Thus, configuration interaction in the initial state yields additional pathways to the final excited states. The correlated wave function in the initial state includes contributions of excited configurations that will effectively overlap with some excited configurations in the final state. The calculations suggest that the inclusion of configuration interaction in the initial state will nearly double the total shakeup probability, although the relative shakeup probabilities may not be strongly affected. On viewing Table III it is also interesting to note that the energy splitting for lower and upper states due to spin coupling ranges from 2.0 to 2.8 eV, while the intensity ratio is sometimes greater than a factor of 10.

Though the agreement in Table III between experiment and theory is excellent, the experimental data were not taken with a monochromatic x-ray source and the results of the higher states depend strongly on the goodness of the deconvolution. The authors had to assume a sizeable variation in the width of the different shake-up peaks (from 2.1 to 7.9 eV). In summary, although the agreement between theory and experiment for the sharper and more intense peaks (2, 3 and 5) can be taken seriously, the agreement of the remainder of the spectra should be taken as consistent with theory rather than proven.

To conclude this section, a few words ought to be said on the possible causes for broadening of the shakeup peaks in the photoelectron spectra of molecules. The natural line widths of the Al and Mg x rays are about 1 eV, while a slice of this line, as low as 0.2 eV, can be taken with a monochromator. The lifetime of the shakeup states ought not to be much different from that of the ground state, and depends primarily on the lifetime of the core hole. For a 1s vacancy in the first row elements this results in a natural width of only about 0.1 to 0.2 eV. Excited states which can lead to autoionization in the valence sheil might result in extra broadening. Large increased widths such as reported in Table III, may be accounted for by unresolved Rydberg states. With a monochromatic x-ray source this possibility might be checked. Finally, in molecules broadening can also occur through unresolved vibration states. One may often expect to find that the shakeup state has a substantially different molecular potential than the ground state, even to the point of having Franck-Condon transitions to a predisociated level. Not only broadening but a shift in the centroid of the photoelectron peaks of a few volts may occur. This incidentally means that calculations based on Koopmanns' frozen orbital approximation may be more realistic with regard to comparing vertical ionization potentials than calculations based on adiabatic binding energies.

IV. APPROXIMATE METHODS AND COMPLEX MOLECULES

For more complex molecules and even for simple molecules it is often desirable to use semi-empirical and other approximate methods for estimating the nature and extent of electron shakeup. The results of satellite structure for a number of gaseous molecules have been so rationalized [3,4,7]. One method has been to use energy separations measured in optical data on excited states of the neutral molecules to deduce shakeup energies. The argument for such a procedure follows from the assumption that the valence electrons are not strongly perturbed by a core vacancy. This assumption is rather poor, though data on neutral molecules may give some clues as to the relative spacing of the various excited states. A sounder procedure (based on the rationale of equivalent charge) is to use data on neutral molecules which are equivalent to the creation of a core vacancy. That is, NO is said to be equivalent to N_2^+ with a hole in one of the K shells. The limitations of this method are that the chance of finding data on a neutral molecule in which the equivalent charge approximation is applicable is rather poor and that the equivalent charge method neglects the effect of spin coupling.

Finally, a third approximate method for evaluating electron shakeup has been to make use of population analysis for a molecular orbital derived from a MO-LCAO model. That is

$$\phi_j = \sum_{A,\lambda} C_{A\lambda j} \, \phi_{A\lambda} \qquad (3)$$

where ϕ_j is the molecular orbital, $\phi_{A\lambda}$ the atomic orbital, and $C_{A\lambda j}$ are the relative atomic densities. When comparing the spectra made by forming core holes in the different atoms, one anticipates that the greatest chance for exciting a given molecular orbital will occur when the vacancy is made in the atom where the orbital is localized. The approximate methods are highly speculative, but as better calculations give us more insight into the nature of electron shakeup, it may be hoped that approximate methods will be made with more confidence.

Although it might seem that predictions of electron shakeup which can sometimes be so difficult, even for diatomic molecules, must be impossible for complex molecular systems. However, in cases where a special transition has an unusually high probability, the behavior of this transition can be understood for even very complex molecular species. For example, in organic compounds a distinctive satellite is found at low excitation energies (5 to 10 eV) which has been assigned to the π orbital associated with the carbon-carbon double bond. Clark and his co-workers [14] have studied this effect for a number of organic solids and polymers. The intensity of the shakeup peak is found to be dependent on the relative number of double bonds and the nature of substitutional groups attached to the carbon. Calculations based on CNDO molecular orbitals have also been used to help correlate the data. Recently, these studies have been extended to free molecules in the gas phase [15].

A large number of studies [16] have been made on the satellite structure found in the photoionization of the 2p shell of the first row transition metal compounds. The satellite structure is sometimes very intense, being as large as the main peak. Again the main satellite lines are found at lower excitation energies (from 4 to 12 eV). The satellite structure has been shown to arise primarily from electron shakeup [17] and to be due to transitions [18] from ligand orbitals to orbitals made up of the unfilled 3d shell of the transition metals. The nature of the shakeup structure is dependent upon both the nature of the metal ion and ligand, and can be rationalized on the basis of the energy separation between the ligand and metal orbitals.

V. USE OF AUGER AND X-RAY SATELLITES

The Auger process and x-ray fluorescence are essentially two step processes. First, a vacancy is created in the core shell by photoionization, electron impact, or some other method; and second, a radiative (x-ray emission) or nonradiative (Auger process) process fills the hole. In a molecule the hole is usually filled before molecular decomposition occurs, and the Auger or x-ray spectra will contain information about the initial ionization process by way of satellites corresponding to excited configurations in the initial state. If the most is to be learned about excitation in the molecular orbital, the x-ray or Auger transition should take place with the valence shell electrons.

Because x-ray emission involves a rearrangement with one electron while Auger processes involve two, the former spectrum ought to be simpler to analyze. However, since Auger transition rates to the valence shell are generally more intense, it is easier to obtain a high resolution Auger spectrum. Recently, high resolution x-ray spectra have been obtained [19], but as yet there have been relatively few attempts to analyze the data in terms of shakeup and shakeoff. I shall thus confine my remarks to Auger processes.

Figure 3 gives schematically the different Auger transitions as a function of initial excitation. When electron shakeup occurs, an Auger process, which involves the excited electron, will gain exactly the same energy that was lost to the photoelectrons, giving rise to the shakeup. For example [20], most of the high energy satellite structure in the KLL Auger of N_2, where the K hole is produced by photon irradiation, is about 16 eV higher than the main normal Auger lines, in good agreement with the excitation energy for the most intense shakeup peak in the photoionization of N_2.

When electron shakeoff occurs, the satellite structure is usually found at energies lower than the normal Auger peaks. For example, satellites observed about 15 eV lower than the main Auger peaks were assigned to electron shakeoff. Auger spectra from proton bombardment [21] were used to confirm this assignment, since at energies below 400 keV, protons give rise to extensive double ionization due to electron pickup and the peaks in the energy region of the Auger spectrum believed to be due to electron shakeoff were greatly enhanced relative to the normal Auger lines.

The use of satellite lines in Auger and x ray spectra for the study of shakeup and shakeoff in molecules has not yet received extensive attention, but the methods have substantial potential.

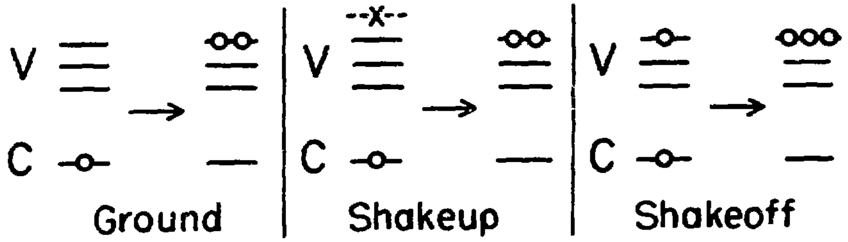

Figure 3. Schematic representation of Auger process as function of initial state excitation. V and C are valence and core shells, O represents a hole and X represents an excited electron.

SUMMARY

Multiple excitation in molecules offers a number of new challenging problems that are not found in atomic systems. In particular, there is the interesting question of the nature of electron shakeup as the result of producing a localized and non-central potential. In fact, are we correct in only assuming that monopole transitions occur? There is a strong need for extending fundamental studies in the general field of molecules, particularly in the area of theory. In addition, the investigation of strong shakeup satellites in complex molecules can be used to shed light on the nature of chemical bonding for these species.

REFERENCES

*Research sponsored by the U. S. Energy Research and Development Administration under contract with Union Carbide Corp.

[1]. A.W.Potts and T.A.Williams, J. Electron Spectrosc. 3, 3 (1974).
[2]. E.g., see H.Basch, Chem. Phys. 10, 157 (1975).
[3]. T.A.Carlson, M.O.Krause and W.E.Moddeman, J. de Phys. (Paris) 32, C4-76 (1971).
[4]. C.J.Allan et al., J. Electron Spectrosc. 1, 131 (1972/3).
[5]. U.Gelius, J. Electron Spectrosc. 5, 985 (1974).
[6]. D.P.Spears, H.J.Fischbeck and T.A.Carlson, J. Electron Spectrosc. 6, 411 (1975).
[7]. D.P.Spears, H.J.Fischbeck and T.A.Carlson, Phys. Rev. 9, 1603 (1974).
[8]. L.J.Aarons et al., Mol. Phys. 26, 1247 (1973).
[9]. J.A.Pople and D.L.Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York (1970).
[10]. I.H.Hillier and J.Kendrick, J.Electron Spectrosc. 6, 325 (1975).
[11]. I.H.Hillier and J.Kendrick, J.Electron Spectrosc. (in press).
[12]. H.Basch, J. Electron Spectrosc. 5, 463 (1974).
[13]. R.L.Martin, B.E.Mills and D.A.Shirley, (to be published).
[14]. D.T.Clark et al., J. Electron Spectrosc. (in press).
[15]. T.Ohta, T.Fujikawa and H.Kuroda, Chem. Phys. Lett. 32, 369 (1975).
[16]. For review, see M.A.Brisk and A.D.Baker, J. Electron Spectrosc. 7, 197 (1975).
[17]. T.A.Carlson, J.C.Carver and G.A.Vernon, J.Chem. Phys. 67, 932 (1975).
[18]. K.S.Kim, J. Electron Spectrosc. 3, 217 (1974).
[19]. L.O.Werme et al., Phys. Rev. Lett. 30. 525 (1973).
[20]. W.E.Moddeman et al., J. Chem. Phys. 55, 2317 (1971).
[21]. M.Stolterfoht, in Proceedings International Conference on Inner Shell Ionization (Atlanta, Georgia, 1972), ed. by R.Fink et al., USAEC Conf-720404 (Washington,D.C., 1973) p. 1043.