Strong Oscillations in Molecular Valence Photoemission Intensities

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Photoemission from the two outermost ionizations [highest occupied molecular orbitals (HOMO and HOMO-1)] of $Mg(\eta^5\text{-}C_5H_5)_2$ has been studied with synchrotron radiation in the gas phase. Strong oscillations in the HOMO-1/HOMO ratio, qualitatively similar to those well-known for fullerenes, are found. Excellent agreement with the experimental ratio is provided by accurate cross section calculations both at the density-functional theory and time-dependent density-functional theory level, indicating that a many electron response has a minor role for this effect. A comparison with the calculated values for other metal sandwich compounds indicate that the presence of oscillations is a widespread phenomenon, and a potential source of interesting information on the structural and electronic properties of the target molecule.

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The first photoemission experiments on C_{60} [1] showed surprisingly strong oscillations in the cross sections of the outermost ionizations [conventionally highest occupied molecular orbital (HOMO and HOMO-1) bands]. The phenomenon was hitherto unknown and generated significant interest. The oscillations are regular and persist almost undamped to the highest energies investigated, around 300 eV, by which photon energy the cross sections have decreased by over 3 orders of magnitude. The original interpretation suggested band structure effects, but this was quickly dismissed when it appeared that the same phenomenon persists unaltered in the gas phase [2], demonstrating that it is purely a molecular effect, and that solid state effects on the photoemission spectrum of C_{60} are of minor importance. The effect was deemed to be unique in the molecular case, associated with the closed cage of C_{60} (and higher fullerenes, e.g., C_{70} [3]), and several theoretical models have been put forward to explain its origin. These range from pure spherical well models [4,5] to multiple scattering extended x-ray absorption fine structure type models [6], to accurate local-density approximation (LDA) calculations [7]. It seems intuitively obvious to associate the observed oscillations with the formation of standing waves inside the cavity, with out of phase oscillations of different angular momentum components. It may be recalled that the HOMO, $6h_u$, may be characterized rather well by an angular momentum $l = 5$, while HOMO-1, $6g_g + 10h_g$, by $l = 4$, so that dipole selection rules give rise to photoelectron waves of different angular momenta and different parity. With a judicious parameter choice a fair computational reproduction of the experimental cross sections is achieved [8]. On the other hand, accurate numerical calculations at the density-functional theory (DFT) level allow an excellent reproduction of the experimental pattern [7], but do not lend themselves to an easy interpretation of the results in terms of a simple model. Ultimately, however, the validity of the various descriptions should be tested against their predictive power and the range of application. Of particular interest would be the presence, and interpretation, of such phenomena in globular clusters, since they could be an important signature of their spatial arrangement. For instance, oscillations have been predicted in the cross sections of alkali metal clusters, although their filled sphere structure gives rise to a different pattern [5,9].

In the course of an investigation of the photoionization of transition metal sandwich molecules, such as ferrocene and bis-benzenechromium, we noticed a wide oscillation in the branching ratio of outermost ionizations [10,11], but the cross sections seemed to eventually diverge, and were not followed to high energy either experimentally or theoretically. It was only in a study of the main group metallocene $Mg(\eta^5\text{-}C_5H_5)_2$ [bis(cyclopentadienyl)magnesium, $MgCp_2$], that a more pronounced oscillation was obtained, and we decided to follow it at higher energy. Oscillations that bear a strong similarity to those found in C_{60} were apparent. Since our model, which accurately solves the Kohn-Sham (KS) equations both in the discrete and continuous spectrum, has shown to be quite dependable, we have undertaken an experimental investigation of outermost photoemission in $MgCp_2$. It is still a matter of debate whether multielectron effects, notably first order response effects, are important in photoionization, in particular in the C_{60} case [12–15]. To assess the importance of such effects in the present case we have performed cross section calculations at the time-dependent density-functional theory (TDDFT) level, which includes first order response, with our newly implemented code [16], which allows accurate treatment of systems of this size.

MgCp$_2$ was synthesized according to the literature procedure [17] and sublimed prior to use. The photoelectron (PE) spectral measurements were carried out on the undulator based Gas Phase Photoemission beamline at the Elettra synchrotron light source (Trieste, Italy), using a 50 mm mean radius electron energy analyzer (VSW Ltd.) mounted at the magic angle [18]. The overall resolution was better than 300 meV along all the studied photon energy region. MgCp$_2$ is an air sensitive solid and therefore particular care was taken in handling it to minimize exposure to air or moisture. Samples of MgCp$_2$ were warmed in a resistively heated oven just few degrees above room temperature.

The computational approach employed has already been described [16,19]. It utilizes a discretization of both bound and continuum functions in a multicenter basis of B-spline functions times spherical harmonics. Bound state orbitals are obtained by conventional diagonalization, while the full set of open channel continuum orbitals are obtained by a least squares approach. The initial ground state density is obtained using a conventional LCAO calculation, employing the Amsterdam density functional program [20], and a double zeta plus polarization basis. In addition to the LB94 exchange correlation (XC) potential, which we currently utilize because of the correct coulombic tail, the more recent statistical average of different orbital model potential [21] has also been tested.

The bonding in MgCp$_2$ is largely ionic although there is a significant covalent bonding interaction involving the Mg $3p$ ($3s$) orbitals. The two lowest ionizations arise from the e_1' (e_{1u}) HOMO-1 and e_1'' (e_{1g}) HOMO orbitals in D_{5h} (D_{5d}) notation. These are the antisymmetric and symmetric combinations of the outermost orbital, e_1' (π), of the $(C_5H_5)^-$ ring. Photoelectron spectra at 42 and 58 eV are reported in Fig. 1. Both ionizations show some vibronic structure, but they are well separated (vertical IP's are 8.1 and 9.0 eV [22]) and can be easily resolved, so that their relative areas can be accurately evaluated. Figure 2 reports the calculated HOMO and HOMO-1 cross sections, evaluated at the LDA and TDDFT levels. LDA cross sections for C$_{60}$ are also reported for comparison. Characteristic oscillations, analogous to those obtained in C$_{60}$ (lower panel) are displayed in MgCp$_2$, both in the KS and TDDFT results. Apart from narrow resonances just below 60 eV (Mg $2p^{-1}$ threshold), the latter are consistently higher, but the profile is very well conserved. Also convergence of the cross sections towards a common value is apparent at high energy. In Fig. 3 experimental values for the HOMO/HOMO-1 ratio are reported together with KS and TDDFT calculated values with the LB94 potential, and additional points evaluated at the KS level with the SAOP potential. We have chosen to plot the HOMO-1/HOMO ratio to keep the odd/even correspondence with C$_{60}$ regarding the parity for ease of comparison. The experimental and theoretical KS ratio for the latter is reported in the lower panel. A rigid shift of all calculated values by 6 eV to higher energy is employed, to agree with the experimental minimum at 42 eV.

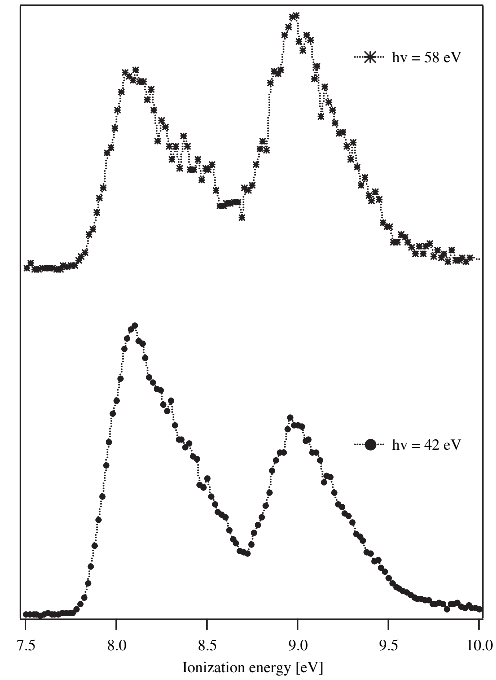

FIG. 1. PE spectra of MgCp$_2$ recorded at $h\nu = 42$ and 58 eV of photon energy, that is, respectively, near the minimum and the maximum of the HOMO-1/HOMO curve.

Several considerations are readily apparent. (i) Concerning the theoretical approach, it is clear that the agreement between KS and TDDFT results employing the same LB94 XC potential is rather close, so that response effects have a rather limited influence on the ratio, which therefore accurately reflects the single particle potential. This is an important simplifying feature for the purpose of interpretation, and possible correlation with the geometrical structure of the cluster. Even adoption of the SAOP potential has a negligible effect, apart from close to threshold, where the calculated values are somewhat larger, but do not change the qualitative picture. Again this is a good sign indicating that the cross section oscillations are in a sense robust, that is, not very sensitive to fine details of the potential, and therefore a potential source of structural information. (ii) The quality of the agreement between the experimental and calculated values is very satisfactory, showing that the KS Hamiltonian, when accurately solved, is capable of an excellent reproduction of the experimental pattern. This gives, therefore, a handle for the interpretation of such data, and the extraction of structural information, by least squares adjustment between the experimental and com-

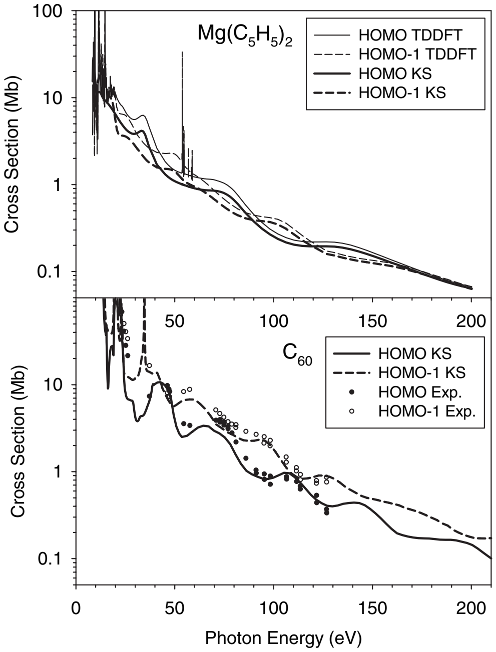

FIG. 2. Upper: cross sections of HOMO and HOMO-1 ionizations of $MgCp_2$ computed at KS and TDDFT levels. Lower: HOMO and HOMO-1 cross sections of C_{60} evaluated at the KS level, and experimental results [6,8].

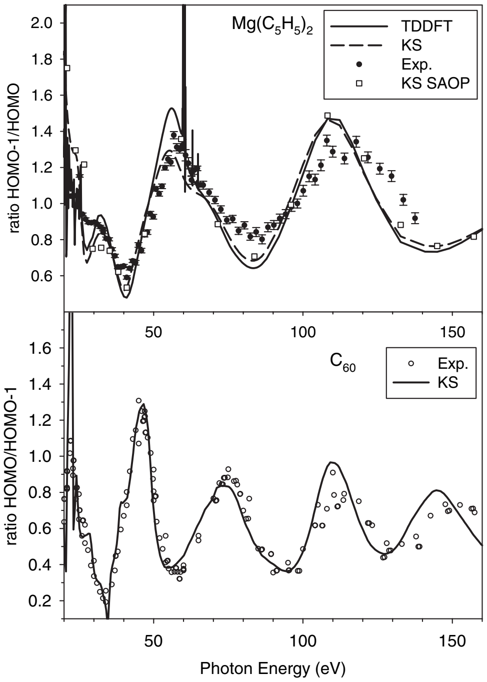

FIG. 3. Upper: Experimental HOMO-1/HOMO cross section ratio in $MgCp_2$ and computed value at KS and TDDFT levels. Calculated values are shifted by 6 eV to higher energy. Lower: HOMO/HOMO-1 cross sections ratio of C_{60} evaluated at the KS level, and experimental results [6,8].

puted spectra, in a similar way to which structural information is extracted from near edge x-ray absorption data. (iii) It is immediately apparent that, while qualitatively very similar, oscillations in $MgCp_2$ are very different from those observed in C_{60}. First of all, the period in $MgCp_2$ is much larger. This can be attributed to the smaller size of the Cp_2 cage: the Mg-C distance is 2.339 Å compared to the radius of 3.562 Å of C_{60}. While the inverse relationship is obvious from box quantization, or Fourier transform [23], a precise quantitative relationship, which is very interesting, is still to be determined. Also the difference in shape may be important. The second quantitative aspect is the size of the oscillations. If we quantify it as the deviation of the first oscillations (excluding the threshold region) from the statistical ratio, which is 1.0 for $MgCp_2$, but 0.6 for C_{60}, we obtain a value around 0.4 for $MgCp_2$, and 0.3 for C_{60} (0.6 for the first peak). So, perhaps surprisingly, oscillations in $MgCp_2$ are as strong as in C_{60}. The third aspect is the much quicker damping of the oscillations at higher energy. Unfortunately we have not been able to follow the spectra beyond 140 eV but the calculation clearly predicts a flattening out towards the statistical ratio at 200 eV. On the contrary, oscillations in C_{60} apparently persist up to at least 300 eV, without any clear sign of damping. C_{70}, where oscillations are rather similar to those in C_{60}, shows however a significant damping [3], although not as sharp as in $MgCp_2$. Here the most obvious candidate is the different shape. It appears that deviations from the spherical symmetry are principally apparent in the damping of the oscillations. Already the reduced symmetry in C_{70} gives rise to a significant damping, and it becomes rather abrupt in the $MgCp_2$ case, probably also because of its open cage in comparison with C_{60} and C_{70}. Comparison with other sandwich molecules is reported in Fig. 4. It is apparent that important oscillations are quite widespread at least in such compounds, although not as pronounced as in $MgCp_2$. These differences are a clear reflection of the different electronic structure. The most interesting signature is the lack of convergence of the ratio to the statistical value. We interpret it as a neat indication of the metal d orbital participation, in the Fe and Cr compounds, to one of the two π ring orbitals, the symmetric combination e_1'' in $FeCp_2$ and e_{1g} in $Cr(C_6H_6)_2$, which are strongly $d \rightarrow p$ bonding ($3d_{xz}$, d_{yz} components). Since at higher energies the metal $3d$ cross section is significantly larger than the C $2p$ one, and is probably non oscillating, its contribution causes both a decrease of the ratio with increasing energy and a smoothing of the oscillations. Conversely, when properly interpreted, such features give a clear cut indication of the amount of metal d orbital participation, and, in general, of orbital composition.

We would like to conclude with a comment on the model interpretation of the oscillations. Appealing as a spherical well can be, even with model shape parameters, it will hardly be possible to capture the variety of features already revealed. Moreover, different semiempirical model parameters are often employed by various calculations to describe different aspects of the same system (see, e.g.,

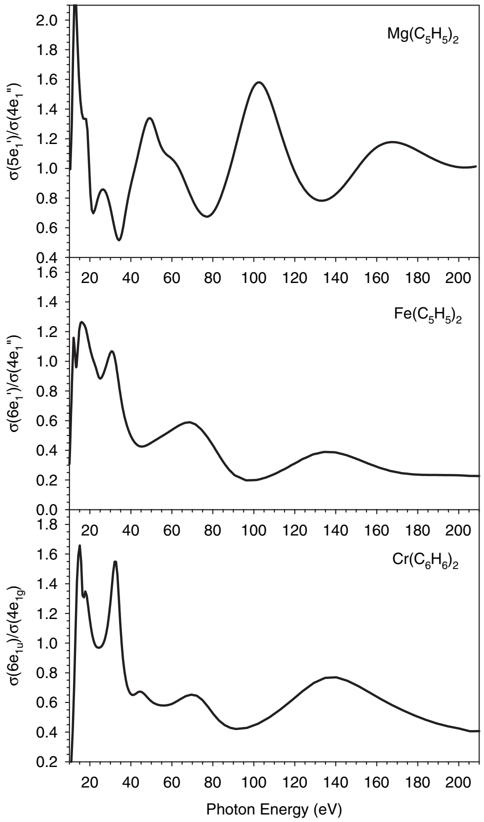

FIG. 4. HOMO-1/HOMO cross section ratio for metallocenes evaluated at the KS level. Upper: $MgCp_2$. Central: $FeCp_2$. Lower: $Cr(C_6H_6)_2$.

Ref. [24]). While present results indicate that the observed oscillations can be well described by a single particle potential, the observed features appear to depend strongly on the full three dimensional potential, and the underlying atomic geometrical pattern. In fact, very poor results are obtained by taking only the spherical part of the molecular DFT potential, which appears much too weakly bonding, so that spherical wells have to simulate the anisotropic part as well.

From the results obtained in $MgCp_2$, and an analysis of theoretical results on other sandwich compounds, it appears that the well-known HOMO/HOMO-1 oscillations observed in fullerenes are a much more widespread phenomenon, which has up to now escaped observation just because of the usually limited range of photon energies considered in molecular photoemission experiments, and in general the paucity of a wide range of experimental data on large molecules. The phenomenon can be well described as a potential scattering, and is quantitatively reproduced by accurate LDA calculations. On the contrary, many electron effects appear to be of minor importance. Large quantitative differences have been observed between C_{60} and $MgCp_2$, and further qualitative differences are predicted with other sandwich molecules. The significant information content of such oscillations both for structural and electronic properties is underlined.

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