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Hot electron production and diffuse excited states in C70, C82, and Sc3N@C80 characterized by angular-resolved photoelectron spectroscopy

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Angular-resolved photoelectron spectroscopy using wavelength-tuneable femtosecond laser pulses is presented for a series of fullerenes, namely, C70, C82, and Sc3N@C80. The photoelectron kinetic energy distributions for the three molecules show typical thermal electron spectra with a superimposed peak structure that is the result of one-photon ionization of diffuse low-angular momentum states with electron density close to the carbon cage and that are related to so-called super atom molecular orbitals. Photoelectron angular distributions confirm this assignment. The observed structure is less prominent compared to the thermal electron background than what was observed in C60. It can be concluded that hot electron emission is the main ionization channel for the larger and more complex molecules for these excitation conditions. © 2013 AIP Publishing LLC.

I. INTRODUCTION

A fundamental understanding of the electronic structure and photoinitiated electron dynamics in large organic molecules and carbon nanomaterials is important for optimizing their properties for use in molecular electronics and organic photovoltaics. C60 is an excellent model system for acceptor molecules, such as PC60BM, due to its high symmetry and simple chemical composition, which simplifies theoretical modelling.1 Photoelectron spectroscopy studies of gas-phase fullerenes after ca. 100 fs laser excitation have shown that an efficient energy redistribution produces hot electrons leading to the emission of thermal electrons with a characteristic Boltzmann-like photoelectron spectrum (PES).2 Superimposed on the thermal electron background, a series of clear peaks converging on the ionization energy can be observed that were initially assigned to one-photon ionization of Rydberg states with large orbital angular momenta (ℓ = 3, 5, and 7).3 Photoelectron angular distributions (PADs) have been shown to be a powerful tool to clearly identify the states giving rise to some of this peak structure in PES and could, in combination with a recent computational study by Mignolet et al., show that the peak structure seen in fs spectra is due to excitation of diffuse, excited states.4, 5 These diffuse states are Rydberg-like states with low orbital angular momenta (ℓ = 0, 1, and 2)4 and at least two radial nodes in the wavefunction (n = 3). The lowest-lying s-state predominantly consists of the excitation of the s “Super Atom Molecular Orbital” (s-SAMO) that was originally studied by Feng et al.5 using scanning tunnelling spectroscopy of fullerene supported on metal substrates. Higher-lying states, such as the p and d states, are further away from the core, in contrast to the s-SAMO, and therefore show a mixture of SAMO and more conventional Rydberg character, where the long range Coulomb force dominates the interaction.5 It is not clear how much of the SAMO-character is retained in larger and more complex fullerenes, although there have been a few studies, mainly theoretical, that have identified SAMOs in systems other than C60.7, 8

Recently, Grancini et al.9 found that in a solar cell composed of a polymer donor and PC60BM acceptor, above-gap excitation in the donor produces hot, delocalised interfacial charge transfer states that result in much more efficient charge dissociation. The diffuse SAMOs, giving rise to nearly free-electron bands in solids,7 could potentially play a key role in the diffuse charge transfer states mediating the efficient charge dissociation observed.9 A deeper understanding of the nature of the excited states and the hot electron dynamics in model acceptor materials may therefore lead to improved light-harvesting devices.

To probe the influence of molecular size and symmetry on both the thermal electron emission and diffuse excited states, we have carried out measurements on a series of fullerences with lower symmetry than C60, namely, C70, C82, and the endohedral fullerene Sc3N@C80. Experimentally, gas-phase studies are ideally suited for understanding the fundamental aspects of these states, since there are no solvents or surfaces present that perturb the electronic structure. The paper is organized as follows. In Sec. II, the experimental setup is briefly described and we show how binding energies and PADs are extracted from the measurements. We also briefly describe the computational methodology used.

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to compute the excited states and compare with the experimental binding energies. In Sec. III, PES with clear thermal electron signatures are presented for the molecules studied. Subsequently, the focus is shifted to assigning the peaks superimposed on the thermal background, which is possible by comparing to results for C60. PES and PADs are therefore first presented for C60 and then for C70, C82, and Sc3N@C80.

II. METHODS

A. Experimental setup

The experimental setup is similar to the one presented in Ref. 10. Neutral gas-phase fullerenes from purified powder of C60, C70, C82, and Sc3N@C80 were prepared from an effusive oven at a temperature of ca. 500 °C inside a vacuum chamber with pressure below 10⁻⁸ mbar. The output from a non-collinear optical parametric amplifier (NOPA), pumped by a regenerative titanium sapphire amplifier (producing 800 nm, 120 fs laser pulses of 3.8 mJ pulse energy), was passed into the vacuum chamber at right angles to the effusive molecular beam. The pulse duration after passing through a half-wave plate, Glan-laser polarizer, and a vacuum viewport was approximately 90 fs. The wavelength range used from the NOPA was 500–750 nm, but was complimented by the fundamental and second harmonic of the regenerative amplifier (800 and 400 nm, respectively). Mass spectra were collected with a time-of-flight mass spectrometer. For all spectra presented in this paper, the laser power was adjusted so that the lowest possible detectable signal was obtained, which typically meant that only singly charged molecular parents were observed. Typical mass spectra are shown in Figure 1. The intact molecular ion was the most abundant species in the mass spectra, although for C82 a small fraction of C84 was observed as well. The electrons were extracted onto a position sensitive detector consisting of a pair of microchannel plates and a phosphor screen using a standard velocity-map imaging (VMI) electrode configuration. The resulting VMI images were inverted using a modified version of Polar Onion-Peeling (POP) that included up to the tenth Legendre polynomial in the inversion procedure.

B. Data analysis

Data collected using 120 fs, 400 nm, and 1.1 TW cm⁻² intensity are presented in Figure 2 for C60. For this pulse duration and intensity, the PES typically show thermal electron emission, as characterized by an exponential kinetic energy distribution. A series of peaks can be seen superimposed on the thermal electron background, and in order to extract angular distributions for these peaks, it is first necessary to remove the thermal electron background. We do this by dividing the inverted VMI image into 10° angular segments, which is shown in Figure 2 for the segments corresponding to 0°–10° (parallel to the laser polarization direction), 40°–50°, and 80°–90° (perpendicular to the laser polarization direction). Clear peaks are observed along the laser polarization direction for this wavelength. Perpendicular to the laser polarization direction, an exponential distribution is observed (plotted in log-lin scale) due to thermal electron emission, although some residual peak structure is still visible. An exponential distribution is fitted to the 80°–90° angular segment and subsequently subtracted from all other angular segments. For longer wavelengths and higher intensities, the thermal electron background becomes asymmetric because of the laser field’s influence on the emitted electrons, which complicates the thermal background subtraction. Also, above-threshold ionization (ATI) peaks superimposed on the

FIG. 1. Mass spectra obtained for the different molecules (indicated in the figure) with typical laser excitation conditions where the intact molecular ion is the dominant species in the mass spectrum. The laser wavelengths and intensities were (a) 500 nm, 4.7 TW cm⁻²; (b) 520 nm, 2.9 TW cm⁻²; (c) 519 nm, 2.8 TW cm⁻²; and (d) 506 nm, 4.1 TW cm⁻². The pulse duration was approximately 90 fs.

FIG. 2. (a) Inverted VMI image obtained after ionizing C60 with 120 fs, 400 nm laser excitation of 1.1 TW cm⁻² (weighted by the radius for display purposes). ε is the electron kinetic energy. The yellow lines represent the angular segments that the image is divided into for producing the PES along the (b) 0°–10°, (c) 40°–50°, and (d) 80°–90° angular segments. Note that the perpendicular segment (80°–90°) is plotted in log-lin scale to emphasise the (exponential) thermal electron background.
ometries of C60, C70, and C84 were found to belong to the \( \theta \) symmetry imposed. All computations were carried out with a band of 500 excited states above the ground state, with the functional CAM-B3LYP used in Mignolet et al.,5 are better suited for describing highly excited states with a diffuse character. However, the computation of the correction term of CAM-B3LYP increases significantly the computation time and slows down the convergence, which precludes its use for the larger fullerenes C70 and C84 when a band of 500 excited states is needed. The use of a smaller basis set, compared to what was used previously5 for C60, is motivated by the same considerations. The present basis set is large enough to describe the lower-lying SAMOs of the three fullerenes computationally investigated in this study and therefore allows for a systematic comparison of their binding energies. For C60, we were able to compute the binding energies in B3LYP and CAM-B3LYP for two basis sets (see Table I). With the 6-31+G(d) basis set, the B3LYP binding energies are slightly higher than the CAM-B3LYP binding energies but the energy differences between the states remain similar (within 0.1 eV). The addition of diffuse functions increases the binding energies,5 but overall the energetic order of the lowest SAMO states is stable. In addition, the computed photoelectron angular distributions, which strongly depend on the symmetry properties of the SAMO states, do not change substantially when using the smaller basis set. The same is true of the anisotropy parameter, \( \beta \). The SAMOs of C70 do not exhibit a spherical symmetry but rather a cylindrical one. Therefore, the p and d manifolds of the SAMOs in C70 are not exactly degenerate. The \( p_z \)-SAMO orbital is lower in energy than the \( p_x \) and \( p_y \) ones, and the \( d_{z^2} \) SAMO is lower than \( d_{x^2-y^2} \) that are, in turn, lower than \( d_{xy} \) and \( d_{xz} \) and \( d_{yz} \).

A detailed description of the calculations of PADS was presented previously.5 The PADS for C60 and C70 were computed for a randomly oriented sample by rotating the molecular frame of the molecule to obtain a random orientation with respect to the laboratory frame. The computed PADS were subsequently analysed using Eq. (1) to obtain the \( \beta \)-parameters which were then compared to experiments.

### III. RESULTS AND DISCUSSION

#### A. Thermal electron emission

Thermal electron emission from fullerenes has previously only been studied in C60, C70, and, to a much lesser extent, La@C82 after 800 nm excitation.10,18 The resulting PES show an exponential background distribution \( I(\epsilon) \propto \exp(-\epsilon/k_B T_0) \), characterised by an apparent temperature

<table>
<thead>
<tr>
<th>Functional</th>
<th>Basis</th>
<th>s-state ( E_{\text{bind}} ) (eV)</th>
<th>p-state ( E_{\text{bind}} ) (eV)</th>
<th>d-state ( E_{\text{bind}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>6-31 + G(d)</td>
<td>2.14</td>
<td>1.26</td>
<td>0.77</td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td>6-31 + G(d)</td>
<td>2.10</td>
<td>1.14</td>
<td>0.62</td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td>6-31 + G(d) + diffuse functions (Mignolet et al.)5</td>
<td>2.35</td>
<td>1.46–1.72</td>
<td>1.14–1.35</td>
</tr>
</tbody>
</table>

C. Computational details

C60, C70, and C84 (D2 isomer) were optimized without imposing symmetry at the B3LYP/6-31+G(d) level. The geometries of C60, C70, and C84 were found to belong to the \( I_h \), \( D_{5h} \), and \( D_2 \) point groups, respectively. The excited states were computed by time-dependent density functional theory (TD-DFT) at the TD-DFT/B3LYP/6-31+G(d) level for a band of 500 excited states above the ground state, with symmetry imposed. All computations were carried out with GAUSSIAN 09.17
Angular-resolved PES, together with the corresponding mass spectra, obtained for C_{70}, C_{82}, and Sc_{3}N@C_{80} after 120 fs, 400 nm excitation are presented in Figure 3. The spectra can, just as shown previously in the case of C_{60} and C_{70}, be fitted to an exponential distribution for all wavelengths studied, indicating a thermal ionization mechanism. The fitted apparent temperatures perpendicular to the laser polarization direction (T_{a}^{⊥}) are similar for all molecules, verifying the thermal nature of the electron signal, since the temperature should only be weakly dependent on the excitation spectrum of each molecule. The C_{70} temperatures are higher than for the other molecules studied here but that can be expected, since fewer electrons result in a lower heat capacity, which in turn results in higher apparent temperatures for similar excitation intensities, as is the case for C_{60}/C_{70}. The results provide further evidence that efficient redistribution of excitation energy leading to thermal electron emission is a dominant ionization mechanism in fullerenes after fs laser excitation. Interestingly, this has also been shown to be the case for polycyclic aromatic hydrocarbons (PAHs), which demonstrates that rapid electron thermalization occurs in a large range of organic molecules and carbon nanomaterials.

B. Identification of SAMOs

To assign the peaks observed superimposed on the thermal background in Figure 3, it is useful to compare to C_{60}, since angular-resolved photoelectron spectroscopy has been successful in identifying excited states due to the high symmetry of this molecule, leading to an almost atomic-like behavior of the PADs with clear signatures of s- and p-states. Therefore, an inverted VMI image and the corresponding angular-resolved PES parallel and perpendicular to the laser polarization direction are shown in Figures 4(a) and 4(b) for C_{60} after 500 nm, 4.7 TW cm^{-2} laser excitation. Three peaks clearly stand out and are labelled according to the assignment made in Refs. 4 and 5, namely, s-, p-, and d-states. The rich peak structure converging on the ionization energy, corresponding to higher-lying states, is not resolved in this particular spectrum as the peaks become more densely spaced and the spectrometer resolution decreases with increasing kinetic energy (corresponding to decreasing binding energy in Figure 4). The Rydberg/SAMO states have orders of magnitude higher photoionization rates (of the order of 10^{14} s^{-1}) than those of the more localized valence states (with ionization rates of the order of 10^{10} s^{-1}), and will therefore ionize much more efficiently during the ca. 100 fs laser pulse, which is the reason why these particular states are observed in the fs PES. The large overlap between the neutral and ionic states implies that the vibrational energy is conserved upon ionization, in analogy with Rydberg fingerprint spectroscopy, which produces clear peak structure despite the high vibrational temperature at which the molecules are typically prepared experimentally. The peak structure is independent of wavelength and intensity, as is the case for the "fingerprint spectra" presented in this work. In Rydberg fingerprint spectroscopy, a highly excited state is initially populated and through internal conversion (IC), a large range of states is subsequently populated. As soon as a SAMO/Rydberg state...
is populated through various IC processes, it will ionize due to the high ionization rate. For fullerenes in the laser interaction zone where SAMO/Rydberg states are not populated on the timescale of the laser pulse, the excited valence states do not photoionize due to the vanishingly small ionization rate, and will therefore contribute to the rapid heating of the molecules which eventually leads to hot electron production and subsequent thermal electron emission.

The PADs for the three peaks, extracted from the angular dependent peak intensities, can be fitted according to Eq. (1) allowing the \( \beta \)-values to be extracted. The kinetic-energy dependent \( \beta \)-values, measured for a range of different wavelengths, are plotted in Figure 5 for the s, p, and d states. The s-state is clearly identified since \( \beta \approx 2 \) for all kinetic energies. The \( \beta \)-values for the p-state show a characteristic behaviour similar to what is calculated for the p-SAMO state.

In Ref. 4, results for \( C_7 \) were presented for one wavelength (400 nm). Here, we have repeated these measurements and also extended the wavelength range. The measured VMI and PES for \( C_7 \) are very similar to \( C_6 \) for all wavelengths measured, as shown in Figures 4(c) and 4(d) for 520 nm excitation. We have therefore assigned the three prominent peaks as s-, p-, and d-states in \( C_7 \) as well. The binding energies are slightly lower for \( C_7 \), as shown in Table II. The TD-DFT computations show SAMO states in \( C_7 \) with binding energies close to what was found for \( C_6 \) in agreement with experiments (see Sec. II). Due to the lower symmetry of \( C_7 \), the calculated p-state is split into a \( p_x \) state and two degenerate \( p_y \) states. The PADs extracted from the angle-resolved PES are also similar to those of \( C_6 \), as seen in Figure 5. In particular, the s-state shows \( \beta \approx 2 \) independent of kinetic energy, which provides further support for this assignment. However, \( \beta \)-values for the p-state are slightly larger than for \( C_6 \). The calculated PADs are in reasonable agreement with the experimental values (Figure 5).

A similar set of peaks for \( C_{82} \) is observed at the same binding energies as for \( C_6 \), although less pronounced compared to the thermal electron background (Figures 4(e) and 4(f)). Based on the binding energies and PADs, in particular for the s-state (Figure 5), it is reasonable to assign the same set of peaks to s, p, and d states of \( C_{82} \). Zhao et al. reported that the s-SAMO binding energy in \( C_{82} \) is 0.2 eV higher than in \( C_6 \). By contrast, computations performed by us have identified SAMO-like electronic states in \( C_{82} \) at very similar energies to \( C_6 \) and it is therefore natural to assume that the same is true for \( C_{82} \) since electronic states (TD-DFT) are more relevant than molecular orbitals (DFT) in laser spectroscopy experiments. Similarly to the difference between \( C_6 \) and \( C_{70} \), we observe that the PAD for the p-state of \( C_{82} \) is slightly different from that of \( C_6 \) and \( C_{70} \).

In our experiments on \( Sc_3N@C_{80} \), bands with maxima corresponding to the peak positions observed for the other fullerenes are just discernible, as shown in Figures 4(g) and 4(h). The \( \beta \)-values, in particular for the s-band, are consistent with those for the other fullerenes. We have therefore assigned the peaks/bands in the spectra to the same states that are observed in the other fullerenes studied. DFT computations of \( Sc_3N@C_{80} \) indicate the presence of SAMO-like orbitals with an approximate binding energy of 0.5 eV in contrast to what we present here. Similarly to \( C_7 \) and \( C_{82} \), the \( \beta \)-values for the p-band are different from \( C_6 \) and appear to be higher and peak at a lower kinetic energy for the larger, less symmetric molecules. The difference in molecular structure is obviously not large enough to significantly influence the binding energy (Table II), however, PADs are very sensitive to small changes to the molecular potential, which could explain the difference in the PADs. Also, electron-electron correlations between the

| TABLE II. Summary of experimental and computed (see Sec. II) binding energies of the lowest-lying Rydberg states of the fullerenes studied. |
|-----------------|----------------|----------------|
|                  | s-state E\(_{\text{bind}}\) (eV) | p-state E\(_{\text{bind}}\) (eV) | d-state E\(_{\text{bind}}\) (eV) |
| \( C_6 \)       | 1.90(1)       | 1.47(2)       | 1.02(1)       |
|                 | 2.14          | 1.26          | 0.77          |
| \( C_7 \)       | 1.86(2)       | 1.42(2)       | 0.99(3)       |
|                 | 2.20          | 1.19–1.24     | 0.73–0.79     |
| \( C_{82} \)    | 1.90(4)       | 1.42(5)       | 1.03(3)       |
| \( C_{84} \)    | 2.12          | 1.22–1.28     | 0.72–0.83     |
| \( Sc_3N@C_{80} \) | 1.94(5)     | 1.50(4)       | 1.04(2)       |
outgoing electron and the residual electrons can influence the $\beta$-values, however, $\beta \approx 2$ for the s-states indicates that this is not a significant contribution for these states.

C. Angle-integrated PES

More insights are gained by comparing the angle-integrated PES, since angle-resolved spectra along a certain direction can either show a large or small contribution from a given peak depending on the $\beta$-value. Angle-integrated spectra for three typical wavelength regions are shown in Figure 6. There is a slight spread in the wavelength due to experimental conditions, however, the spectra in each region are typically very similar. As previously mentioned, the peak structure becomes less pronounced with decreasing molecular symmetry and increasing size. The underlying thermal background signal is more dominant for the larger molecules, as expected for larger particles, which will show more bulk-like properties. The binding energy does not change considerably (Table II) and it can be concluded that the binding energies of the states are not largely influenced by details of the molecular structure. This is in agreement with Rydberg Fingerprint spectroscopy that does not show a large change in binding energy of similar molecular species. This is also supported by the TD-DFT computations that do not predict a larger energy of similar molecular species. This is also supported by the underlying thermal background signal.

IV. CONCLUSIONS

In conclusion, we have presented results obtained using a combination of velocity-map imaging and Rydberg fingerprint spectroscopy to study diffuse, excited electronic states of C_{70}, C_{82}, and Sc_{3}N@C_{80}. Due to the similarity to C_{60} spectra and, in particular, PADs characterised by $\beta \approx 2$, we have been able to assign peaks in the spectra to s-, p- and d-states. We observe an increasing thermal-to-Rydberg ratio in the spectra for increasing molecular size and complexity (but lower symmetry).

We have shown that the Rydberg fingerprint experimental technique combined with PADs has the possibility to identify potentially important diffuse states in carbon nanomaterials and complex organic molecules. The technique can also be used for probing the interplay between direct and thermal ionization and may provide important insights to help understand the electron dynamics of molecules of relevance to applications such as acceptor molecules in organic solar cells.

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