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Anisotropic hot electron emission from fullerenes

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Photoelectron spectra for fullerenes C_{60} and C_{70} ionized using 800 nm laser pulses with pulse durations from 120 to 1000 fs show thermal electron kinetic energy distributions but they also exhibit angular anisotropy with respect to the laser light polarization. The effective temperature of electrons, measured along the laser polarization direction, is significantly higher than in the perpendicular direction. We explain this observation by considering that the emission of the thermal electrons is uncorrelated with the phase of the laser pulse, unlike directly ionized electrons, and, depending on the time of emission, they may experience an additional "kick" from the vector potential of the laser field when they are emitted from the molecule. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4704828]

The short pulse laser ionization dynamics of few electron systems has a rich structure where an important role is played by the laser intensity. Atoms and small molecules may ionize directly via multiphoton absorption, which can give rise to above-threshold ionization or, for higher laser intensities, field ionization.[1] For large molecules and clusters the ionization process may be more complicated and more complex interactions involving, e.g., non-adiabatic multielectron dynamics may have to be taken into account.[2,3]

Fullerenes serve as model systems for the latter class of molecules. It is now well established that an important factor in the photoionization of fullerenes is the rapid redistribution of the excitation energy. Early experiments with ns pulses[4] provided evidence for the occurrence of statistical, thermionic emission from the vibrationally hot molecules. For shorter pulses, the situation is dramatically different. Experiments with pulses in the sub-50 fs range have shown above-threshold ionization peaks from C_{60},[5] whereas pulses longer than ∼100 fs give photoelectron spectra with a significant contribution from thermal electrons with very high effective temperatures of above 1 eV (∼12 000 K).[5] This observation was explained by considering a rapid redistribution of energy among the electronic degrees of freedom while the vibrations remain cold, and the mechanism has later been found to explain the spectra of several other large molecules.[6] The electron-vibrational coupling time has been estimated to be 240 fs for C_{60}[7] and is similar for C_{70}.

This paper deals with pulse durations on the order of 100 fs, where electrons are believed to be thermally emitted from the transient hot electron gas. We report the observation of an angular anisotropy of the thermal electron energy distributions and propose an explanation based on the influence of the laser electric field on the statistical electron distributions. Electrons that are emitted from the molecule will receive an additional momentum "kick" from the vector potential of the laser electric field if they are not emitted in phase with the oscillating electric field. The results provide further strong evidence for the delayed, statistical emission of the hot electrons.

Experimentally, purified C_{60} or C_{70} powders were heated in an effusive oven to 450 °C and the fullerene vapor was crossed with a focused laser beam. A Ti:sapphire regenerative amplifier laser system with a fundamental wavelength of 800 nm (1.55 eV) or the second harmonic at 400 nm was used. The shortest possible pulse duration was 120 fs FWHM with pulse durations up to 3.8 ps achieved by detuning the compressor. The positive ion products were analyzed in a time-of-flight mass spectrometer. The photoelectrons were detected using a velocity-map imaging electron spectrometer similar to the one described in Ref. 8. The laser polarization direction and the detector plane were parallel, and the 3D cylindrically symmetric velocity distribution was reconstructed from the measured 2D distribution using BASEX.[9] The electron kinetic energy was calibrated using the well-known above-threshold ionization peaks from xenon.[10,11]

Figures 1(a) and 1(b) show raw velocity-map images for ionization of C_{60} and C_{70} following excitation with 180 fs pulses. The intensities (5.4 TW cm^{-2} and 6.1 TW cm^{-2}) lie well below the threshold for field ionization of fullerenes.[8,12] Photoelectron energy distributions can be obtained from a 2π angle integration of the inverted photoelectron images from Figure 1. However, the images obtained with 800 nm, 180 fs are clearly asymmetric (Figures 1(a) and 1(b)) when compared to the isotropic image obtained from excitation with ns (Figure 1(c)) or 400 nm, 120 fs (Figure 1(d)) pulses. Angle-resolved photoelectron spectra were extracted from the inverted images by dividing them into 10° wide angular segments.

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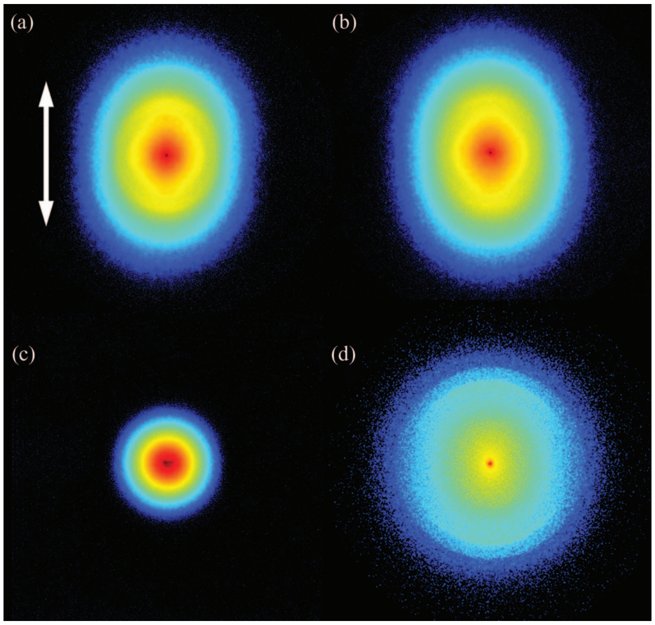

FIG. 1. Raw photoelectron images in logarithmic color scale. (a) C_{60}, 800 nm, 180 fs, 5.4 TW cm^{-2}, (b) C_{70}, 800 nm, 180 fs, 6.1 TW cm^{-2}, (c) C_{60} 532 nm, ns, (d) C_{60}, 400 nm, 120 fs, 0.26 TW cm^{-2}. The laser polarization direction was parallel to the white arrow shown in (a).

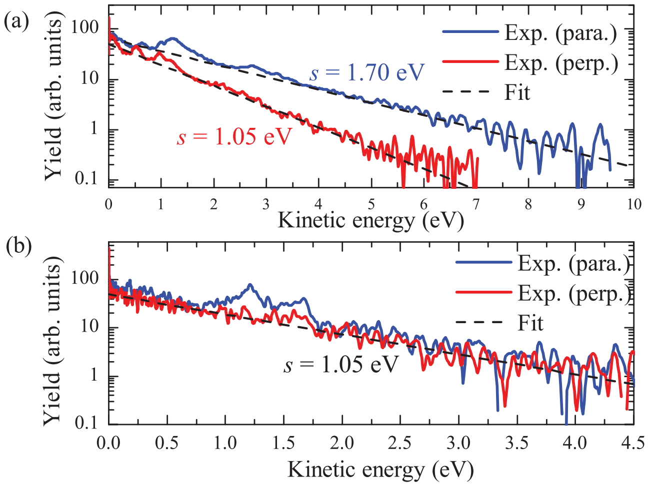

FIG. 2. (a) Angle-resolved photoelectron spectra for C_{60} obtained after (a) 180 fs, 800 nm, 5.4 TW cm^{-2} excitation and (b) 120 fs, 400 nm, 0.26 TW cm^{-2} excitation.

Figures 2(a) and 2(b) show C_{60} angle-resolved spectra for both 800 and 400 nm excitation. Only two segments are shown for clarity: parallel and perpendicular with respect to the laser polarization direction. The general features of the spectra agree with previous non-angular-resolved experiments for these pulse durations.[5,7,8] The thermal contribution can be well approximated by the exponential function $I(\varepsilon) \propto \exp(-\varepsilon/k_BT)$, with ε being the electron kinetic energy and T the effective electron temperature.[7] The observed effective electron temperature, $s = k_BT$, is very high, above 1 eV, and it increases with increasing laser fluence.[7,8] A series of peaks can be seen superimposed on the thermal electron signal below kinetic energies corresponding to the photon energy (predominantly along the laser polarization direction). The structure is due to single-photon ionization of excited electronic states.[13] The kinetic energy of the electrons produced from single-photon ionization of the excited states is not influenced by the laser polarization direction, in contrast to the thermal electrons.

The effective temperature of the thermal electron distribution, s, from the 800 nm data is clearly higher in the direction of the laser polarization. The ns data (Figure 1(c)) show a constant effective temperature with emission angle, as expected for a completely isotropic thermionic electron emission. Electrons emitted after excitation with the much lower light intensity of the 400 nm, fs light pulses (Figures 1(d) and 2(b)) also give isotropic thermal electron distributions, indicating that the strength of the electric field of the laser is an important parameter in determining the degree of anisotropy.

For isotropic, thermal emission, the rate constant for emission of electrons with kinetic energy ε_{em} from a cluster with an internal energy E is given by the Weisskopf formula,[14,15] applying the principles of detailed balance

$$k(\varepsilon_{em}, E) = \frac{2m_e}{\pi^2\hbar^3}\frac{\rho_d(E)}{\rho_p(E)}e^{-\Phi/k_BT}\sigma(\varepsilon_{em})\,\varepsilon_{em}e^{-\varepsilon_{em}/k_BT}. \quad (1)$$

Here, m_e is the electron mass, ρ_d and ρ_p are the level densities of the ionized and neutral fullerene, respectively, Φ is the ionization energy, $\sigma(\varepsilon_{em})$ is the cross section for the reverse process, the capture of an electron in the Coulomb potential of the ion and the temperature k_BT is connected to the internal energy via the heat capacity of the excited system (at fs time scales only the electrons are considered to be excited). A model based on the Weisskopf formula provided a very good description of the angular-unresolved thermal electron kinetic energy distributions produced on excitation with 180 fs, 800 nm laser pulses, as reported earlier.[7] The rate constant estimated with the Weisskopf formalism for such an ionization mechanism for C_{60} (Ref. 7) can be well approximated with the simple Arrhenius-type formula $k(T) = A\exp(-\Phi/k_BT)$, with $A \approx 2.7 \times 10^{15}$ s^{-1}, Φ the ionization potential of the molecule (7.6 eV), and T the emission temperature.

The dependence of the effective temperature on emission angle with respect to the laser polarization direction can be explained by considering the influence of the laser field on the statistical distribution of emitted electrons. Although we are assuming a thermal emission mechanism for the electrons, the rate constant for emission is expected to be very high due to the high electron energy within the molecule. This is in contrast to the thermionic emission observed from excitation with ns laser pulses where the energy is equilibrated between electronic and vibrational degrees of freedom and the electron emission takes place up to many microseconds after excitation.[4] The time-dependence of the electron yield can be calculated using the parameters determined earlier from fitting the photoelectron spectra.[7] The internal energy, E, is estimated from considering the balance between photon absorption (using an average absorption cross section, σ_p, of 0.12 Å^2) and the coupling to vibrational degrees of freedom

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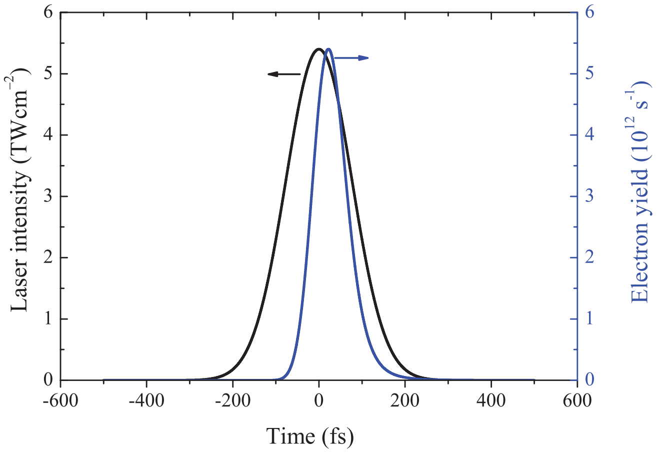

FIG. 3. Calculated electron yield obtained from Eq. (3) as a function of time for 180 fs, 800 nm, 5.4 TWcm^{-2} excitation. The laser intensity envelope is also shown for comparison.

(with a time constant $\tau = 240$ fs):

$$\frac{dE}{dt} = \sigma_p I(t) - \frac{E}{\tau}. \tag{2}$$

The time evolution of the mean electron temperature is then calculated by assuming a Fermi gas heat capacity, $C_V = \frac{\pi^2 N k_B^2 T}{2E_F}$ to give $k_B T(t) = \sqrt{\frac{4E(t)E_F}{\pi^2 N}}$, with N the number of valence electrons (240 for C_{60}) and the Fermi energy, $E_F = 30$ eV.[16] The time-dependent electron yield is then given by Hansen *et al.*[7] as

$$Y(t) = k(t)\exp\left(-\int_{-\infty}^{t}(k(t')dt')\right). \tag{3}$$

An example is shown in Fig. 3 for $\lambda = 800$ nm, a pulse duration of 180 fs and an intensity of 5.4×10^{12} Wcm^{-2} (corresponding to the excitation conditions for the results shown in Fig. 2(a)). Under these conditions the electron emission occurs while the laser pulse is still present, however, the majority of electrons are emitted after the maximum of the laser pulse is reached.

For direct photoionization, the "appearance" of the free electron is correlated with the maxima of the oscillating laser electric field. Short intrinsic delays may be expected but these are on the order of a few attoseconds. The free electrons are thus produced when the vector potential of the electric field, **A**, is close to zero and they do not experience any additional momentum increase in the laser field for the short laser pulses that are relevant here. This is the situation for the electrons produced from multiphoton ionization of Xe, used for calibration of the photoelectron spectrometer, and for the "Rydberg" electrons that are observed to be superimposed on the thermal electron distribution from the fullerenes. However, for the statistical, thermal electron emission one cannot expect any correlation between the time of electron emission and the phase of the laser field. It is therefore possible that electrons emitted out of phase with the laser field will experience a momentum increase, $-q\mathbf{A} = \mathbf{e}_z q\, E_0/\omega\, \sin(\omega t_0)$, where $-q$ is the electron's charge, E_0 is the electric field amplitude, ω is the laser angular frequency, t_0 is the time of emission, and $\mathbf{e}_z$ is the unit vector along the polarization direction. The maximum increase in electron kinetic energy that can be achieved in this way is $2U_p$, where $U_p(\text{eV}) = 9.34 \times 10^{-20}\, \lambda(\text{nm})^2\, I(\text{Wcm}^{-2})$, is the ponderomotive energy. We estimate the detected electron distributions by carrying out a Monte Carlo calculation that determines the distribution of thermally emitted electron momenta as a function of time, t, weighted with the calculated yield, $Y(t)$, and then adds the additional momentum gain from the vector potential to each electron, calculated at the time of emission, t. The effective temperature, s, is then determined from a log-lin plot of the electron yield versus electron kinetic energy, in the same was as for the experimental data shown in Fig. 2.

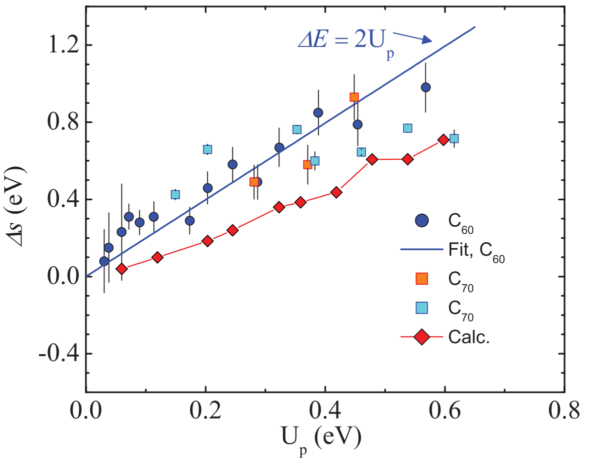

FIG. 4. The degree of anisotropy Δs (the difference between the parallel and perpendicular effective temperatures) in electron spectra as a function of the ponderomotive shift (U_p) for both C_{60} and C_{70} obtained for laser pulses ranging from 120 fs to 3.8 ps. The C_{70} data were obtained in two different experimental setups. A linear fit to the C_{60} data is also shown (blue line). The fitted slope was 2.0 ± 0.1. The results from the thermal emission calculations are shown as red diamonds.

A comparison of the effective temperature difference for directions parallel and perpendicular to the laser polarization direction, Δs, measured experimentally for C_{60} and C_{70} for different laser intensities and calculated for C_{60} using the procedure outlined above is shown in Fig. 4. The model somewhat underestimates the degree of anisotropy but shows the expected trend with increasing laser intensity. The agreement is very satisfactory considering that no parameters were varied in the model to obtain agreement with the experimental data and considering the inherent simplifications of the model (independence of the average photo-absorption cross section on internal energy, assumption of a Fermi gas heat capacity etc.). The model also reproduces the lack of anisotropy for the 400 nm experiments.

The calculations assume that the ionization potential of the molecule is not changing with time. In an unscreened field, the electron binding energy along the applied electric field direction will be lowered and raised in the presence of the oscillating electric field. However, a sufficiently polarizable molecule will screen the external field and consequently the activation energy for electron emission will be independent of direction, as assumed here. The polarizabilities of the fullerenes (79 Å^3 for C_{60} (Ref. 17)) are sufficiently large to justify this approximation. We have tested the

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consequences of allowing the ionization potential to oscillate with the electric field in our model. An oscillation in ionization potential leads to an increased total yield of electrons along the polarization direction but, since the electron emission is more strongly correlated with the maxima of the electric field strength, the anisotropy is actually decreased. An increase in the calculated anisotropy, in order to better fit the experimental data, can be achieved if the electron emission time occurs slightly earlier. This can be achieved by adjusting either the value of the average photo-absorption cross section used in the model or the pre-exponential factor in the simple Arrhenius expression for the electron emission. We have deliberately not adjusted the model parameters in this work to show the consistency with the earlier angle-integrated calculations.[7]

The angle-resolved photoelectron spectra obtained from fullerenes under fs laser excitation, with intensities well below the onset of field ionization, provide further convincing evidence for the thermal nature of electron emission from highly electronically excited molecules, prior to equilibration with vibrational degrees of freedom. The electron emission is not correlated with the laser electric field strength, as is expected to occur for direct photo-ionization. This leads to anisotropy in the apparent electron temperatures in directions parallel and perpendicular to the laser polarization direction. The relatively large degree of anisotropy observed in the experiments is also indicative of the effective screening of the electric field within the molecules due to the high polarizabilities.

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