Direct Observation of Multiple Photon Absorption by Free Electrons in a Wide Band-Gap Insulator under Strong Laser Irradiation

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We measure the kinetic energy of photoelectrons emitted from an α-quartz surface irradiated by short (100 fs) and intense laser pulses. In the high intensity regime (above 100 GW/cm^2), we observe a high-energy tail in the photoemission spectra at 620 and 560 nm. This effect disappears for the doubled frequencies. These observations give direct evidence of free-electron multiple photon absorption in the conduction band, in keeping with recent Monte Carlo simulation results.

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Intense laser sources have allowed the observation of photoemission of materials with a work function larger than the photon energy. The so-called "multiphoton photoemission" can yield important information, especially in the case of insulators [1,2]. Studying the behavior of wide-gap optical materials under strong laser irradiation is also of fundamental importance for many mechanisms such as defect creation and optical breakdown [3–5]. In these processes, the key point is the energy transfer between the laser field, the free electrons, and the lattice. Numerous investigations have been performed with pulse durations in the nanosecond and the picosecond domains, and Shen *et al.* [6] showed that the interaction between free electrons and near infrared photons (1064 nm) in SiO_2 and NaCl leads to a progressive lattice heating, up to temperatures close to the melting point, the conduction electrons gaining energy from the field they give up to the lattice via collisions with phonons. Monte Carlo simulations confirmed this approach [7]. This experiment gave an indirect indication that electrons promoted in the conduction band can absorb supplementary photons. Photoelectron spectroscopy seems a natural method to directly demonstrate this effect. To our knowledge, no such measurements have been performed yet in a laser wide band-gap solid interaction experiment, probably because of experimental difficulties related to the space-charge effects and the charging of the insulating sample. In this Letter, the use of subpicosecond laser pulses enables us to measure, for the first time, the kinetic-energy distribution of emitted photoelectrons from a laser irradiated surface of α quartz. The experimental results directly reveal multiple photon absorption by free electrons in the conduction band.

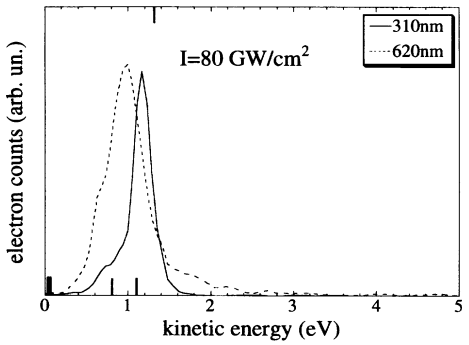
Our laser system is based on a CPM dye laser, amplified up to 2 mJ/pulse in five YAG-pumped rhodamine 6G dye cells, yielding 70 fs pulses at 620 nm. Continuum generation is used to obtain pulses at 560 nm, which are amplified in a similar way. Second-harmonic generation (SHG) in a KDP crystal yields pulses at 310 and 280 nm, with a typical duration of about 150 fs. The laser beam is focused onto a Y-cut single crystal of α quartz ($10 \times 10 \times 0.5$ mm^3) kept under UHV conditions (10^{-10} Torr) to preserve surface cleanliness. The sample is biased to a low negative voltage and heated to around 350 °C in order to avoid a positive charge buildup due to electron emission [8]. A time-of-flight spectrometer [9] is placed in front of the sample. If the spectrometer potential is low (typically 5 V), only the electrons emitted into a small solid angle around the normal to the surface are detected, so collection efficiency is low, but an energy resolution of 0.1 eV can be obtained for electrons with a few electron volts of initial kinetic energy. However, it is necessary to take into account "contact potentials" which are difficult to measure in the absence of a reference line. Our energy scale is thus labeled, assuming that the lowest energy measured in any of our low intensity spectra was close to zero, which corresponds to a contact potential of -1.25 eV. This value may seem high, but one has to remember that the origin of contact potentials is the alignment of Fermi levels that, in our case, implies at least one metal/insulator interface, which may explain this high value. However, we certainly cannot exclude that this energy scale is off by a few tenths of an eV.

Measuring the actual intensity on the sample is not easy because the pulse energy is extremely small, and also because the focal section of the beam is not measured *in situ*. It is assumed to be diffraction limited, which is probably optimistic. In the case of the second-harmonic beam, where calorimetric measurements of the pulse energy are very difficult, an absolute uncertainty of $\pm 25\%$ is not unrealistic. Relative intensities for each wavelength are precise within $\pm 5\%$. Practically, the data are sorted according to the pulse energy as measured for each laser shot with a photodiode.

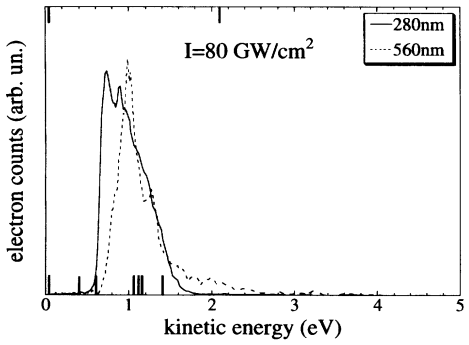
Photoemission spectra, corresponding to four different wavelengths, are presented in Fig. 1 [310 and 620 nm

in Fig. 1(a) and 280 and 560 nm in Fig. 1(b)]. In all spectra, a narrow peak centered around 1 eV is observed. The 620 and 560 nm spectra both present a high-energy tail, absent in both uv spectra, which extends far beyond one photon energy: High-energy electrons result from an intense visible irradiation, which is not observed in the near-uv case. Figure 2 shows electron spectra obtained for different intensities at 310 and 620 nm: The spectrum at 310 nm is practically intensity independent, while the high-energy tail at 620 nm strongly increases with laser intensity.

One has to rule out the possible artifacts and, in this case, space-charge effects: Coulombic explosion of a high-density electron cloud leaving the sample can result in a symmetrical energy broadening of the spectrum [10], producing both fast and slow electrons. Therefore, the flight tube was set to a higher potential (15 V) in order to detect even very slow electrons. The spectrum kept its form and no symmetrical broadening was observed. In addition, we performed an experiment at 310 and 620 nm under identical space-charge conditions and did not obtain a high-energy tail at 310 nm. So space-charge effects are not responsible for the high-energy tail observed for both



(a)



(b)

FIG. 1. Experimental photoemission spectra corresponding to four wavelengths: (a) 310 and 620 nm; (b) 280 and 560 nm, for a laser intensity of 80 GW/cm^2. The vertical bars on the energy axis show the positions of the expected lines obtained from the band structure in the ΓM direction. Initial states in the valence band (bottom) or oxygen vacancy states (top).

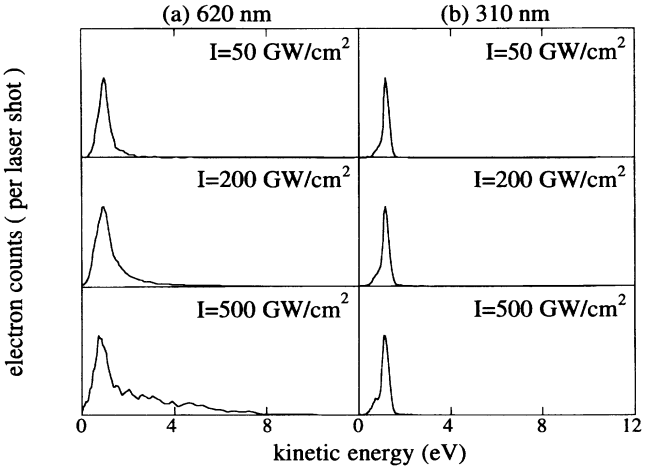


FIG. 2. Experimental photoemission spectra corresponding to two wavelengths [(a) 620 nm and (b) 310 nm] and three different intensities (50, 200, and 500 GW/cm^2).

visible wavelengths: It is only for the maximum intensity spectrum that a small broadening is observed on the low-energy side of the 1 eV peak which could signal the onset of space-charge phenomena.

Another possible cause for the strong difference of behavior between uv and visible wavelengths could be an error in the relative intensities. It is worth noting, however, that the uncertainty in the comparison between intensities at both wavelengths is not high enough to be responsible for the difference between the spectra: Even if the visible intensity was underestimated by 25% and the uv one overestimated by as much, comparison of the medium intensity spectrum at 620 nm with the maximum intensity spectrum at 310 nm would demonstrate the effect. Moreover, the relative uncertainty between the intensities at both wavelengths, though larger than the relative uncertainty at one wavelength, is certainly not that important because (i) $\pm 25\%$ is the absolute uncertainty in the uv only, where calorimetric measurements are unprecise because of the extremely small energy per pulse, and (ii) a number of causes of uncertainty are shared by both wavelengths and do not affect the comparison (e.g., diffraction limited beam assumption).

The uv spectra, not subject to additional laser intensity effects, should give information about the photoexcitation process, at least (because of the uncertainty on the contact potential) in their compared positions. We are not measuring a surface photoemission (such an emission should vanish for a laser polarization parallel to the surface, which was checked not to be the case). Bulk photoemission can then occur for initial states in the top of the valence band or for defect states, as shown in [11]: Heating the sample under vacuum results in an oxygen deficient surface, with two occupied defect states located at 7.35 and 5.2 eV below the conduction-band edge [12]. One would then expect that three- (two-) photon excitation of the valence (defect) states would yield an electron spectrum lo-

cated 1.2 (0.8) eV higher for a 4.4 eV photon than for a 4 eV one. This only holds in the case of the defect states. Indeed, energy conservation criteria only, and the band structure calculated in [13], leads to the conclusion that *the main effect of an increase of the photon energy is to make accessible many deeper states in the valence band to 4.4 eV excitation, which does not result in a higher final energy in the conduction band,* except of course for the topmost two bands, the only one accessible to three-photon transitions in the 4 eV case. This is particularly true along the ΓM direction (k_y direction, our detection direction), where a projected band gap of 2 eV starting 2 eV above the conduction-band edge forbids three-photon absorption from the topmost states of the valence band at 4.4 eV. Of course, energy conservation is not the only criterion, but the three-photon cross sections involved cannot be calculated at present. Possible indirect transitions should also be considered, but it would not significantly change the conclusion: Even in this case, the above mentioned effect of an increased photon energy would persist, that is a broadening rather than an upward shift of the spectrum, which is what we observe. The positions of the expected final energies for the different transitions have been indicated on the figures (using the band structure along the ΓM direction) and are consistent with the spectra observed, assuming that the almost zero energy electrons are lost (given the uncertainties in both the precision of the calculation and the graphical method used to extract these energies, they could even fall below the vacuum level). Indeed, the almost exact coincidence is a matter of sheer luck (neither the calculations of [13] nor our experimental precision allow us to expect such a result). Finally, about the projected band gap in the ΓM direction, let us recall that such gaps are filled in the surface region by the exponential tails of electron waves outside the solid, into which electrons coming from the bulk can be scattered, which would explain why this gap is not apparent in our high intensity visible spectra. This leads us to suspect that transport in the presence of the laser field is important in the shaping of our high-intensity spectra.

The high-energy tail observed at high intensities for visible wavelengths shows evidence of energy absorption from the laser field in addition to that necessary to overcome the band gap, since electrons with an energy larger than the photon energy are detected. This could occur directly, simultaneously with the interband transition [by a process similar to atomic above-threshold ionization (ATI) [14]], or subsequently, during the transport of the electron to the surface in the presence of the laser field. It is difficult to completely discard the ATI hypothesis, but the orders of magnitude for this process are such that it is extremely unlikely to explain our observations. Moreover, a preliminary experiment using 30 ps pulses also showed the effects observed here in the subpicosecond regime, but for intensities in the GW cm^{-2} range, where ATI should be negligible. This effect of the pulse duration, on the contrary, supports the assumption of an effect occurring during transport, since the laser field can act upon the electron throughout the pulse duration. According to this assumption [6], free electrons in the conduction band can absorb one photon if they simultaneously absorb or emit one phonon, in order to conserve energy and momentum. This free-carrier absorption has been studied in semiconductors and the cross sections for these different processes have been calculated [15]. Applying a second-order perturbation theory, expressions for photon absorption rates of an electron of initial momentum $\mathbf{k}$ and energy $E_{\mathbf{k}}$ can be derived [16]:

$$W_{\pm}(\mathbf{k}) = \frac{I}{(\hbar\omega_{\nu})^4} F_{\alpha}(\omega_{\pm}, E_{\mathbf{k}}, \beta), \tag{1}$$

where ω_{ν} is the laser frequency, β the angle between the electron momentum and the laser polarization, $\hbar\omega_{\pm}$ the total electron energy change due to the photon and the phonon, and F_{α} a complex function of these quantities and material parameters. α stands for the different kinds of electron-phonon collisions (optical and acoustical phonons), and I is the laser intensity. The main implication of this expression is that, when the frequency is doubled, the corresponding photon absorption probability is drastically reduced (by a factor of 16). Furthermore, the high-energy tail must spread out when the laser intensity increases. Therefore, this model can qualitatively explain the observed spectra.

A quantitative check can be obtained using Monte Carlo simulations. Our approach is similar to that of Refs. [7,17–19]. The simulation takes into account the different scattering processes described above: Electron LO phonon interactions are treated with a Fröhlich Hamiltonian, and a deformation potential is used to describe electron-acoustical phonon coupling. Electron-photon-phonon collision rates are calculated with Eq. (1). Many simplifications are made: The LO phonons dispersion is ignored and that of acoustical phonons is taken as linear; the conduction band is supposed spherical and parabolic. Photoemission is modeled, assuming that an electron can escape from the sample when its energy is larger than the electronic affinity, and detected only if emitted into a small solid angle around the normal to the surface equal to our experimental collection cone, taking into account the electron refraction at the surface. The initial energy of the electrons is taken as 3 eV and the electronic affinity as 1.5 eV. Electrons are distributed homogeneously in the sample, and a Gaussian time envelope (100 fs at $1/e$) is used to represent the laser pulse. The results of the simulation are presented in Fig. 3. The spectra are composed of two main features: a peak centered around 1.5 eV, mainly corresponding to the electrons that leave the sample without absorbing a supplementary photon, and a shoulder, corresponding to the electrons that have gained more energy from the field. This shoulder grows when laser intensity increases and, in the 310 nm case, this effect is very reduced. For the high intensity case, free electrons can absorb up to four photons

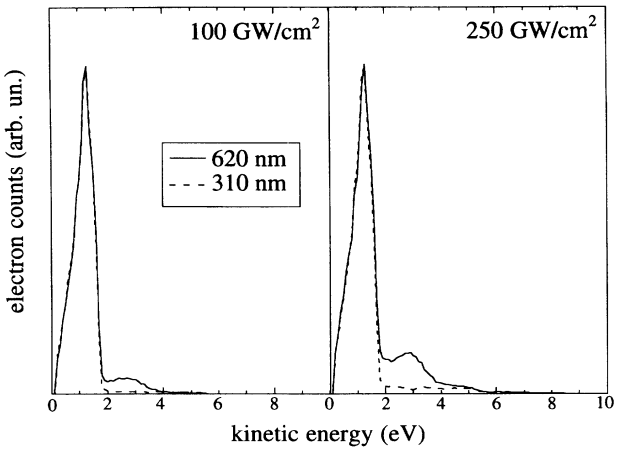


FIG. 3. Monte Carlo simulation of photoemission spectra, corresponding to 620 and 310 nm and two different intensities (100 and 250 GW/cm^2).

from the 620 nm laser field. The simulation reproduces the difference experimentally observed between the two wavelengths and quantitatively agrees with the result at 620 nm. A small effect is still visible at 310 nm, which we do not observe in the experiment but, as discussed earlier, our experimental intensity may be overestimated in this case. The results of our simulation are consistent with the work of Arnold and Cartier [7]. A feature that is not included in our simulations, which could also explain the remaining differences with the experimental results, is the possibility for the electrons to be trapped or recombine. Indeed, as we demonstrated recently [20], this is, in quartz, an extremely fast process, leading to an average lifetime of 150 fs for free electrons.

Simulations also shed some light on the uv/low intensity case: There, the electrons are not "kept alive" by laser heating and lose their energy very rapidly. As a result, the only electrons able to escape in the vacuum are those excited very close to the surface (within a few nanometers) which experience very few collisions and whose energy remains reminiscent of their initial excitation energy. Other electrons are rapidly scattered down to the conduction-band edge where they can be reexcited in an electron-photon-phonon collision, which provides an additional contribution to the electron spectrum. The probability of such reabsorption is weak for uv light, but the number of electrons concerned is large. Such processes are taken into account in our Monte Carlo simulation since all the electrons are followed at least until the laser is turned off. They do not seem to play a key role in the photoelectron spectrum, and taking into account trapping and recombination should still reduce their effect.

In conclusion, we have directly demonstrated, using photoelectron spectroscopy, that the photogenerated carriers can gain energy from the laser field during their transport in the conduction band of α quartz. Although a number of remaining questions concerning the initial excitation process clearly deserves more attention, this observation is an unequivocal demonstration of the accuracy of the assumption formulated by Shen *et al.* [6]. This effect, a key point in the understanding of the damage of optical material, can be interpreted as a kind of inverse bremsstrahlung in which the third body needed to conserve simultaneously energy and momentum is the phonon. Because of the extremely high collision rate in α quartz, this process is particularly likely, and laser heating of free electrons is found to be efficient even in the subpicosecond regime at high intensities. Monte Carlo simulations based on the work of Fischetti and his followers [7,17–19] are found to predict, with reasonable accuracy, the result of this experiment and thus can be safely used to anticipate the effect of strong laser irradiation of optical material.

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