

Orientation-Dependent Multiphoton Ionization in Wide Band Gap Crystals

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Using different crystalline dielectrics and intense femtosecond laser pulses, we show that nonlinear absorption depends on sample orientation. This arises primarily because of the direction dependence of the effective mass of the electron. The multiphoton nature of the interaction creates a local probe that can be used anywhere in the material. We show that the structure of crystal quartz is not changed by repeated illumination of the focal region with 45 fs pulses.

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For intense laser pulses, multiphoton ionization (MPI) rates in molecules depend on the shape of the highest occupied molecular orbital and on its alignment with respect to the electric field [1,2]. Experiments in the gas phase with aligned N₂ and O₂ showed differences of more than 50% in the ionization yield depending on the angle between the linearly polarized laser electric field and the molecular axis [3,4]. Transparent dielectrics have band gaps comparable to the ionization potential of such molecules. This places them in a similar intense field ionization regime, leading us to expect that they should also show alignment effects. This would give us a structural probe of crystalline dielectrics that can follow local phase change with femtosecond precision and micrometer spatial resolution.

We realize multiphoton crystallography by measuring the dependence of the transmitted light on the alignment of the crystal to the laser polarization direction. We show that the alignment dependence of the MPI probability depends on crystal symmetry. Since MPI confines the interaction to a small region of the laser focus [5], this implies that we have a highly local probe of crystalline structure, anywhere in three-dimensional space. By using an optically contacted interface between fused and crystalline quartz, we confirm the local nature of the interaction.

Our calculations [6] show that the temperature rise induced by the probe is proportional to the pulse duration and is approximately 110 K for a 45 fs pulse at 10% absorption. The temperature increase would be only 12 K if a 5 fs pulse were used. Thus, probing crystal structure via multiphoton crystallography should not affect the crystal, especially if a few-cycle pulse is used. Using 45 fs pulses, we show that the crystal structure of α quartz is not changed by multiple laser shots at the same spot.

We have studied α quartz (α -SiO₂), sapphire (α -Al₂O₃), and lithium fluoride (LiF) and used amorphous fused silica as a control. The first two are birefringent and were z cut to reduce associated complications. The LiF was cut square to its cubic lattice. We used linearly polarized 45 fs, 800 nm laser pulses with a repetition rate of 40–400 Hz. A microscope objective with a numerical aperture of 0.25 focused

the laser beam. The focus was ~ 150 μm inside the sample unless otherwise noted. This tight focusing (spot size ~ 3.2 μm) allows us to reach high intensities without propagation being influenced by low-order effects such as self-focusing or self-phase modulation. In our experiment the pulse energies used were in the range of 20–300 nJ to give intensities between 0.5×10^{13} and 7×10^{13} W cm⁻² if the focus were in vacuum.

The crystals were placed on a translation stage to provide new material for every laser shot if required. The crystals were mounted with their z axes parallel to the laser k vector. A half wave plate (HWP) was placed in the incident laser beam to control its polarization alignment relative to the lattice. All transmitted light was collected by an integrating sphere, and the signal was acquired independently for every laser shot.

Figure 1 shows the transmission as a function of alignment angle for α quartz with zero degrees corresponding to alignment of the laser electric field vector and the crystal x axis. By eye, one can discern two dominant modulation periods, of $\sim 60^\circ$ and $\sim 180^\circ$, in the transmission. The

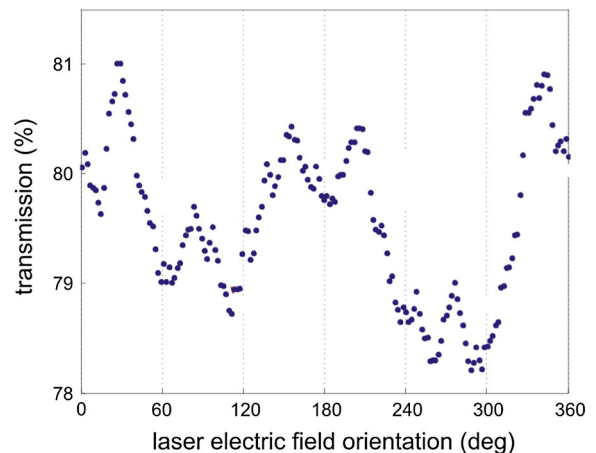


FIG. 1 (color online). Transmission measured in α quartz as a function of the alignment of the laser polarization to the crystal x axis. A 10-points moving average has been applied to the raw data.

modulation amplitude as seen in Fig. 1 is below 1%. The signal noise level before averaging is of the order of several percent. Therefore, we apply a Fourier analysis technique to improve the signal-to-noise ratio and examine the modulation in more detail. We measure the alignment dependence of the transmission while rotating the HWP at $6\frac{2}{3}$ rpm. Signal modulation frequencies are obtained by discrete Fourier transform (DFT). The results for the three crystals are shown in Fig. 2. The ordinate in the figure is the modulation amplitude as a percentage of the average transmission, which was set to 0.8 by choice of the laser pulse energy. The abscissa is the recurrence frequency of the alignment angle, where 2 corresponds to a rotation period of π (or twofold rotational symmetry), 4 to $\pi/2$, and 6 to $\pi/3$. Fused (amorphous) silica (not shown) has no modulation. All crystal samples show strong DFT features. α quartz and sapphire both show modulation with π and $\pi/3$ rotational periods. The latter corresponds to their trigonal lattice system. The π modulation is due to a residual birefringence and is discussed below. LiF has a cubic unit cell and shows strong $\pi/2$ periodicity. It is clear that the absorption of intense femtosecond pulses measures the symmetry of the lattice [Fig. 2 (bottom)]. We now confirm that the angle-dependent changes in the linear or low-order nonlinear [7] refractive index do not contribute to our measurements. By doing so, we also confirm the high spatial resolution in the z direction. We use an optically bonded sample of fused and crystal SiO_2 . With this sample we repeat the Fourier transmission experiments for different positions of the focus relative to the fused silica- α -quartz interface. Experimentally, we identify the surface

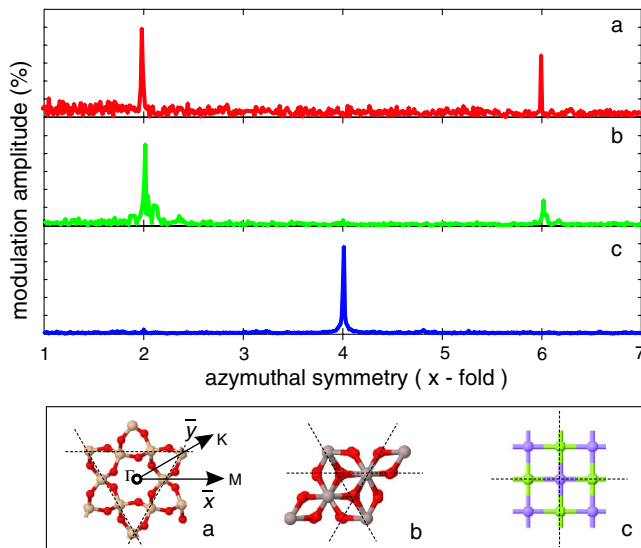


FIG. 2 (color online). Transmission modulation spectra for (a) α quartz, (b) sapphire, and (c) lithium fluoride. The vertical scale is 0–0.75% for (a),(b) and 0–1.5% for (c). Corresponding crystal structures (the bottom panel) [18,19] (z -cut view) are shown looking down the z axis with dashed lines as eye guides for the symmetry.

by the small reflection (0.4%). The surface position is established (zero in Fig. 3) by forcing the reflection to retrace the optical path.

The results for the two peaks in Fig. 2, corresponding to the twofold and sixfold symmetries, are presented in Fig. 3. The two peaks have different dependence on the focus position. The magnitudes of both peaks are zero before the interface when the absorption occurs in fused silica and is azimuthally symmetric. When the focus approaches the interface, the crystalline structure shapes the absorption, and the sixfold peak rises sharply. The sixfold peak maximizes when the focus meets the interface. There is almost no signal change after the focus is fully inside the crystal. The fact that the magnitude of the sixfold peak does not change with the propagation depth indicates that linear and low-order nonlinear effects do not contribute significantly to the angle-dependent absorption. A twofold peak also appears only inside the α quartz, but its magnitude grows more slowly with focus depth. This is typical for linear and Kerr-like propagation effects that increase with interaction length. However, in our experiment, the twofold peak is due to a combination of the birefringence experienced by peripheral laser beams (due to strong focusing) and residual, angle-dependent ellipticity that is due to imperfect alignment of the rotating HWP. This parasitic birefringence induces an angle- and depth-dependent ellipticity at the focus that modulates MPI via the effective intensity. Notably, the twofold peak is absent from amorphous fused silica and nonbirefringent LiF but is also present in birefringent sapphire.

All of the results presented so far were obtained using a fresh spot for every laser shot. We use a model developed in Ref. [6], which is based on the calculations of the electron density in the conduction band due to field ion-

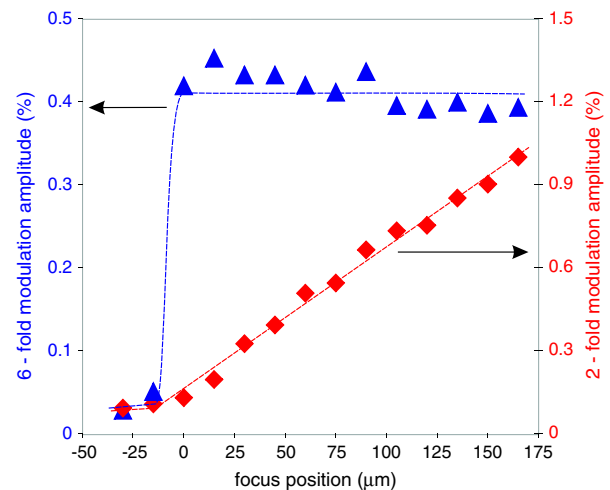


FIG. 3 (color online). The amplitude of the sixfold (\blacktriangle) and twofold (\blacklozenge) modulation in transmission as a function of focus position z in an optically bonded fused silica and α -quartz sample. The focus is in fused silica for negative z and in α quartz for positive z . The pulse energy was 90 nJ.

ization and avalanche. Using the modeled carrier density, we can estimate the associated temperature rise at the focus, assuming that all energy absorbed from the laser pulse is transferred to heat [6]. For α quartz, a 20% absorption of the 45 fs pulse causes 156 K heating with every laser shot. The heat dissipates completely between shots. To confirm that the crystal is not modified by the measurement, we apply the method to measure any changes in the crystal structure that may accumulate from laser shot to laser shot. We measure crystal structure at a given point as a function of the number of shots. Over our measurement range (1–1000 shots), we see no change.

The dependence of the adsorption on the alignment of the crystal lattice to the laser field implies that the multiphoton ionization rate $W(I)$ is dependent on the alignment angle ϕ . An analytical approach to high-order nonlinear adsorption in dielectrics is to approximate the interaction by an intensity threshold I_{TH} , below which light is not absorbed and above which all of the light is absorbed [$W(I) = 0, I < I_{\text{TH}}$; $W(I) = \infty, I > I_{\text{TH}}$]. This leads to the “lawn mower” description of nonlinear adsorption in dielectrics [6]. Under this model, a modulation of $W(I)$ with ϕ translates to a modulation in I_{TH} . A feature of the model is that the transmission T depends on the input intensity I_{IN} in a manner that includes I_{IN} only as the ratio $I_{\text{IN}}/I_{\text{TH}}$ or, in terms of pulse energy, $E_{\text{IN}}/E_{\text{TH}}$. The consequence is that we can write $\partial T/\partial E_{\text{TH}} = -E_{\text{IN}}\partial T/\partial E_{\text{IN}}$, implying that $\Delta T \propto -E_{\text{IN}}\partial T/\partial E_{\text{IN}}$, where ΔT is the modulation in the transmission.

Since any highly nonlinear absorption will behave in much the same way, in Fig. 4 we compare the measured amplitude of the sixfold modulation with the quantity $-E_{\text{IN}}\partial T/\partial E_{\text{IN}}$ as a function of E_{IN} . We obtain $\partial T/\partial E_{\text{IN}}$

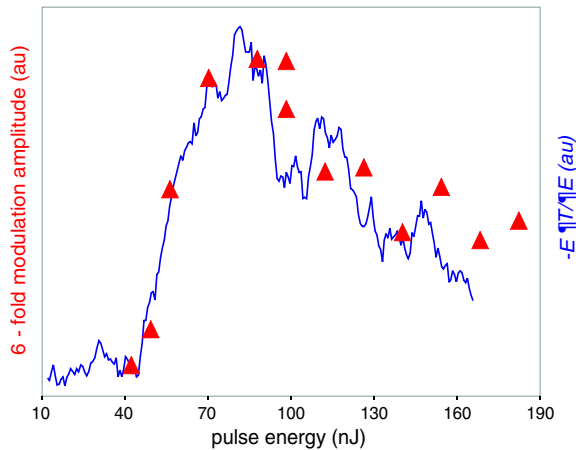


FIG. 4 (color online). Comparison of the energy dependence of the sixfold transmission modulation in α quartz with the expectation from an alignment dependence of multiphoton ionization. (\blacktriangle) Sixfold transmission amplitude; (line) the quantity $-E_{\text{IN}}\partial T/\partial E_{\text{IN}}$, with $\partial T/\partial E_{\text{IN}}$ obtained as the numerical derivative of the transmission measured as a function of E_{IN} . The two series of data have been normalized for comparison purposes.

by numerical differentiation of the measured T vs E_{IN} dependence at a fixed angle (the choice of angle is not crucial as the modulation in T is small). It is clear that the sixfold modulation shows the energy dependence expected, confirming that this modulation relates to an angle dependence of the rate of multiphoton ionization.

In small gas phase molecules, alignment effects relate to the symmetry of the ionizing molecular orbital. In crystals, the electronic structure is discussed in terms of band structure not orbitals. Theory on tunneling in solids that traces back to Zener [8,9] predicts that

$$W(I) \propto \exp\left\{-\frac{(2\Delta)^{3/2}\sqrt{m^*}}{3\hbar\mathcal{E}}\right\}, \quad (1)$$

where \mathcal{E} is the electric field. The expression is very similar to the equivalent one for an atom except that the band gap Δ replaces the ionization potential, the electron mass becomes the reduced mass m^* , and the exponent is reduced by a factor of 2. Thus we expect multiphoton tunnel ionization in solids to depend exponentially on the band gap, just as it depends on the ionization potential in atoms and molecules. In addition, in crystals, $W(I)$ also depends exponentially on the reduced mass of the electron, a quantity that is also related to the band structure.

The explicit treatment of the effective mass in crystals as a tensor quantity in the theory of tunneling ionization was first introduced by Keldysh in Ref. [10]. However, in his later widely used work [11], the spatial asymmetries of the effective mass were ignored.

Concentrating on α quartz, we have obtained the band structure from theory, using the pseudopotential plane-wave method with the ABINIT code [12–14]. Trouiller-Martins-type [15], generalized gradient approximation pseudopotentials were employed with a Perdew-Burke-Ernzerhof exchange-correlation functional [16]. Inspection of the band structure shows that the minimum vertical band gap occurs at the Γ symmetry point. It is, therefore, direction-independent and cannot be the cause of the transmission modulation.

The reduced mass, however, is dependent on the direction in the crystal. In reciprocal space, the α -quartz structure is characterized by two symmetry points M and K . The associated directions Γ - M and Γ - K in real space are depicted in Fig. 2. They lie at an angle of $\pi/3$ to each other and line up with the crystal x and y axes, respectively. Because the curvatures of the highest valence band and the lowest conduction band depend on direction, the reduced mass of the electron responding to an aligned field is effectively different.

The reduced mass of the electron is a concept that is easily defined only for a parabolic band structure. This is not the detailed case in α quartz, but we obtain representative values of the reduced mass along different directions in the crystal from the calculated electronic energy levels using parabolic fitting. The estimated reduced mass

changes from $0.93m_e$ along Γ - M to $2.15m_e$ along the Γ - K direction. Therefore, from Eq. (1), we expect the ionization to be the most probable along the Γ - M direction where the reduced mass is the smallest. In our transmission experiments, we found that absorption is at its maximum when the laser polarization is parallel to Γ - M or the x axis and at its minimum when the laser field is along Γ - K (at 30° to Γ - M), in agreement with the theory. Because of the exponential dependency of the tunneling rate on the band gap value, we consider only transitions between the top valence band and the bottom conduction band.

From Eq. (1), the differences estimated in m^* imply a much larger transmission modulation than is found in the experiment. Translated into a threshold model, they imply a threshold increase of about $\times 2$. One possible cause is the two-band approximation in our final tunneling calculation. The lower degree of modulation found experimentally may be partially due to ionization not being in the tunneling limit. At a laser wavelength of 800 nm with an intensity of $3 \times 10^{13} \text{ W cm}^{-2}$, the Keldysh parameter γ is ~ 1 . In this regime, tunneling still plays a role in atoms [17], but its contribution is limited. The role of tunneling decreases at shorter wavelengths with the increase in γ . We have repeated the crystallographic experiments with 400 nm laser radiation for α -quartz and LiF crystals. In the perturbative regime ($\gamma > 1$), we do not expect an exponential dependence on m^* [11]. We found that in α quartz the modulation in transmission was not observed at 400 nm where the band gap is only three photons wide. In LiF, where four photons are required for ionization, the modulation is present. These results are consistent with the Keldysh analysis and suggest that the modulation is connected with tunneling.

It is interesting to compare the origins of angle-dependent tunneling in molecules and crystals. In molecules, interference between components of the tunneling electron wave packet, arising from different components of the parent orbital, is responsible for the angle dependence of the ionization probability [1,2]. In crystals, similar mechanisms may be in play, but the ionization dependence is dominated by the direction-dependent reduced electron mass since it appears in the exponent [Eq. (1)].

In conclusion, tunneling plays a major role in solid state physics. Usually, tunneling is driven by dc fields. We have shown that optical fields can be effectively used, broadening the range of potential applications. This opens a route to measure the dynamics of femtosecond phase changes far away from any surface.

Looking to the future, multiphoton crystallography can be applied in the midinfrared extending access to important

semiconductor materials such as gallium nitride and silicon. It will be possible to map out crystal size, orientation, and position in polycrystalline material. The technique is nondestructive, especially if few-cycle pulses are used. Although we have concentrated on nonbirefringent z -cut material, this was only a convenience, not a necessity.

Multiphoton crystallography adds to the array of multiphoton microscopies available to science, providing a superior spatial resolution due to the higher nonlinear nature of the process. Its use of only one laser wavelength removes phase walk-off constraints for the in-the-bulk measurements, compared to the multicolor methods.

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