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EXPRESSION OF CONCERN

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Expression of Concern: Direct observation of the THz Kerr effect (TKE) in deionized, distilled and buffered (PBS) water

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Expression of concern for 'Direct observation of the THz Kerr effect (TKE) in deionized, distilled and buffered (PBS) water' by Andrzej Dobek *et al.*, *Phys. Chem. Chem. Phys.*, 2017, **19**, 26749–26757, https://doi.org/10.1039/c7cp04061j.

A reader highlighted a number of concerns in relation to this *Physical Chemistry Chemical Physics* publication. Two independent experts agreed that these aspects of the work were unclear and that further information was required. The authors of the *Physical Chemistry Chemical Physics* publication were invited to respond to these concerns. After the corresponding author replied to each of these points, the two independent experts were invited to give their opinion on the authors' response. Each of the initial concerns is listed below, along with the corresponding author's response and the experts' views on the response.

Comment 1

Reader: It is stated in the abstract that the THz field used is 13.5 kV cm^{-1}. These fields should not be enough to trigger any nonlinear response in liquid water. For such a response, higher THz fields are needed. See for example ref. 1 and 2.

Author: The measurements were performed in the laboratory of Prof. Robert H. Giles at the Department of Physics and Applied Physics, University of Massachusetts Lowell. The group of Prof. Giles has been engaged in the construction of THz lasers and in applications of the THz technique for about 30 years. The THz-TDS system has been rebuilt and further experiments can not be performed. The corresponding author no longer has access to the lab notes of the lead researcher, so we are unable to provide more details of the instrument that the measurements were recorded on at this time. We analyzed the results with a measured energy of 6 μJ THz^{-1} pulse and with the minimal electric field it amounted to 13.5 × 10^3 V cm^{-1}. We did not know at the time about strong nonlinearities of water in a THz field.

Considering the THz Kerr effect results for water published since 2017, the THz electric field used in our measurements was one order (or more) of magnitude lower than that used by other researchers. One can estimate that for α = 50 cm^{-1} (THz absorption coefficient) the mean maximal value of the electric field is $E_{\mathrm{THz}} = 3.07 \times 10^6$ V m^{-1} instead of a minimal value $E_{\mathrm{THz}} = 1.35 \times 10^6$ V m^{-1}. For this value and different arbitrarily chosen E_{THz} values, Kerr constants and nonlinear refractive index intensity coefficients are given in Table 1. For comparison, data published in Tcypkin *et al.*[1] are shown. To get $n^I_{p2} = 7 \times 10^{-16}$ m^2 W^{-1} published in the same paper, we should obtain birefringence $\Delta n = -2.52 \times 10^{-6}$ in deionized water at an electric field one order of magnitude lower than we did.

Expert 1: The authors stated that the energy of the THz pulse is 6 μJ. This value is very large. It is not consistent with the electric field of 13.5 kV cm^{-1}. If one focuses the 6 μJ (or 1.5 μJ) THz pulse properly by using a parabolic mirror, we expect to obtain much higher strength of the electric field. I think that electric field strength is at least one order of magnitude higher than is enough to induce the nonlinear response in liquid water. Something is wrong either in the measurement of the THz pulse energy or the field strength. Therefore, I strongly support the reader's and expert's comments. Again, a field strength of 13.5 kV is too small to observe any nonlinear response in liquid water. The authors should resolve this inconsistency.

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Table 1 Kerr constant value and nonlinear index intensity coefficient n_{p2}^{I} estimated for different THz electric field values inducing birefringence $\Delta n = -2.52 \times 10^{-6}$ in deionized water

Electric field $E_{THz} \times 10^{-6}$ V m^{-1}	Kerr constant – $K \times 10^{12}$ m V^{-2}	Nonlinear refractive index intensity coefficient – $n_{p2}^{I} \times 10^{16}$ m^2 W^{-1}
0.1	310	840
1.35	1.73	7.84
3.07	0.33	2.01
20.00	7.88×10^{-3}	2.09×10^{-2}
30.00	3.5×10^{-3}	9.3×10^{-3}
88.60 (5 mJ per pulse)	4.01×10^{-4}	2.4×10^{-3}
19.40 (Tcypkin *et al.*)[1]	—	−700

Expert 2: I do not quite understand the reply to this Comment 1 (and implicitly Comment 5) as it seems to be mixing up the energy of the 800 nm pulse and that of the THz pulse. The text also talks about conversion in a lithium niobate crystal but Fig. 1 shows a ZnTe crystal. Furthermore, Fig. 1 gives 6 mJ per visible pulse instead of 6 μJ. So, I have a gut feeling that the THz pulse energy is correct: conversion from 6 mJ visible to 1.5 μJ THz (less than 0.03% conversion) would be what you might expect for ZnTe. Judging the THz electric field strength is difficult without knowing the focal length of the off-axis parabola *etc.* Table 1 in the reply would need much more explanation. Overall, I think this is an unsatisfactory response.

Comment 2

Reader: The shape of the THz Kerr signal has two lobes and is explained as a reflection. It is unclear to me what reflection, of which beam reflected by which surface, could give such an effect.

Author: No signal was detected when one of the beams, probed at 800 nm or THz, respectively, was blocked.

The simplest explanation of the Kerr signal shape was assuming the reflection of the THz pulse by cell walls. Considering the thickness of the cell (120 μm), the reflectivity of the windows and the absorption of water for THz frequency the birefringence signal could be fitted.

Expert 1: The same statements are repeated as in the publication. There is no additional information to support this claim. It is still unclear for me to understand the origin of the two lobes in the THz Kerr signal.

Expert 2: The response that no signal was detected when either the 800 nm or terahertz beam was blocked would also be consistent with a THz Kerr signal from quartz. The second part of the response is incorrect: a reflection off the cell walls that are separated by 120 μm should have a delay of 20 ps and not 1 ps as was observed, while the reflected terahertz pulse should be strongly attenuated by absorption from water. Therefore, this response is unsatisfactory.

Comment 3

Reader: It is not clear what is the energy per pulse of the source (6 μJ per pulse in the abstract or 6 mJ per pulse in Fig. 1?) and of the THz (1.5 μJ per pulse would imply a THz peak field of *ca.* 200 kV cm^{-1}, but 1.35 × 6 V m^{-1} = 13.5 kV cm^{-1} is given in the abstract).

Author: Fig. 1 shows that the energy is 6 mJ for the laser source, which corresponds to the total energy per second, measured using an energy meter for the laser beam working at the repetition rate of 1 Hz. The laser working at the repetition rate of 1 kHz delivered 6 μJ per pulse.

Expert 1: Now I understand that the output power of their laser system is 6 W. However, a 6 μJ output from the femtosecond regenerative amplifier at the repetition rate of 1 kHz is very small for commercially available systems. The authors should give more information on the laser system, such as the model and company names and so on.

Expert 2: If the 800 nm pulses are 6 μJ, that means that the conversion to terahertz is 25%, which is impossible (at present).

Comment 4

Reader: The data could possibly be explained by a large nonlinearity of the quartz windows of the sample holder, which are known to display these effects.[3]

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Author: The birefringence was not observed in an empty cell (p. 26750, Samples and experimental setup). In addition, if the birefringence would come from the quartz walls of the cell, it should be the same from the cell filled with water. However, we detected signals different in amplitudes and shape for three different samples.

Expert 1: I still do not understand why the authors cannot observe any nonlinear response from the quartz even though they do observe the response from water. The authors should do supporting experiments to show the signals from the empty quartz cell.

Expert 2: The reply is ''birefringence was not observed in an empty cell'' but we don't get to see that data. The fact that the signal changes with different aqueous samples does indeed support that the signal is due to a THz Kerr effect in water: if the signal was caused by quartz, the signal would travel on the 800 nm probe pulse, which would not be affected by the different aqueous samples. On the other hand, a THz pulse would be affected by the different aqueous samples (due to a change in the THz refractive-index spectra causing changes in reflectivity) but that then implies that the signal originates somewhere in the water sample.

Comment 5

Reader: It is not realistic that the fundamental laser source emits 6 μJ per pulse and the THz emitted by lithium niobate is 1.5 μJ per pulse. The highest conversion efficiency reported to date is *ca.* 1%, if lithium niobate is cooled and another laser frequency is used (not 800 nm). See for example the works by the group of Kärtner *et al.*[4]

Author: See my response to Comment 1.

Expert 1: Again, there is inconsistency between the pulse energy and the electric field strength of the THz pulse. The authors should answer this question properly. In this sense, I agree with both the comments from the reader and the expert.

Expert 2: 25% conversion is still impossible.

Comment 6

Reader: In order to prove this is a Kerr signal, it should scale with pump intensity (THz) and with the probe field amplitude (800 nm). This should be demonstrated with experimental data.

Author: The intensity dependence of the Kerr response in water was not studied by us. The setup used in our measurements was a copy of the system applied by Hoffmann *et al.*[5] The authors have shown that the magnitude of the signal scales square with the applied THz field in the studied polar and nonpolar liquids. In the measurement geometry only, induced birefringence could be detected.

Birefringence Δn described by eqn (7) and (8) in our publication relates to the square of the THz inducing electric field with the amplitude Δn. All the fits obtained with the THz intensity used in the experiments prove such a dependence.

The THz Kerr effect signal, even when induced by THz pulses of maximum intensity, was very low and the accumulation of 50–100 passes was necessary to get the proper accuracy. Therefore, no study was done with a lower inducing energy.

Expert 1: Based on the statements above, there is no new and additional information to support the claims that the observed signal originates from the THz Kerr effect. I agree with the comments both from the reader and the expert. Intensity and field dependence are really important data that convince us of the origin of the signals.

Expert 2: The data in the paper are consistent with the Kerr effect, so I think this is satisfactory. The authors' 2020 publication[6] has much nicer data that is certainly consistent with a THz Kerr effect, so I'm happy with this aspect.

Summary

In summary, the independent experts were not satisfied with the response from the corresponding author. After receiving this feedback the corresponding author of the *Physical Chemistry Chemical Physics* publication was unable to provide any further clarification.

In line with Committee on Publication Ethics guidelines, *Physical Chemistry Chemical Physics* is publishing this expression of concern in order to alert readers that we are presently unable to confirm the accuracy of the data reported in this paper.

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