The Journal of Chemical Physics

RESEARCH ARTICLE | AUGUST 06 2025

Relaxation spectra of molecular glass formers probed by tandem Fabry–Perot interferometry and photon correlation spectroscopy: A critical re-assessment

Ernst A. Rössler ; Manuel Becher

J. Chem. Phys. 163, 054510 (2025)
https://doi.org/10.1063/5.0273910

AIP Publishing

The Journal
of Chemical Physics

ARTICLE

pubs.aip.org/aip/jcp

Relaxation spectra of molecular glass formers probed by tandem Fabry–Perot interferometry and photon correlation spectroscopy: A critical re-assessment

Cite as: J. Chem. Phys. **163**, 054510 (2025); doi: 10.1063/5.0273910
Submitted: 2 April 2025 • Accepted: 14 July 2025 •
Published Online: 6 August 2025

Ernst A. Rössler[a)] **and Manuel Becher**

AFFILIATIONS

Nordbayerisches NMR Zentrum, Universität Bayreuth, 95440 Bayreuth, Germany

[a)] **Author to whom correspondence should be addressed:** ernst.roessler@uni-bayreuth.de

ABSTRACT

Relaxation spectra of molecular glass formers measured by tandem Fabry–Perot interferometry (TFPI) and by photon correlation spectroscopy (PCS) are revisited from well above T_m down to T_g. We scrutinize the claim that a generic relaxation stretching is found close to T_g, while varying stretching is established at high temperatures. The TFPI spectra observed in this work reveal no change of the stretching over a large temperature range, and a Cole–Davidson susceptibility yields stretching parameters within $\beta_\mathrm{CD} = 0.39$–0.80. The spectra display a high-frequency excess wing contribution, which prohibits a single power law description of the high-frequency flank of the main relaxation. Corresponding PCS decays measured close to T_g display no change in the stretching either. Yet, the PCS spectra are overall broader than the TFPI spectra. They exhibit some variation and are superiorly described by a Kohlrausch function with $\beta_\mathrm{K} = 0.52$–0.73. Three of the eight systems significantly deviate from the previously reported generic relaxation function. We do not find indications that the spectral width changes within a narrow temperature interval to bridge the different stretching monitored by the two techniques. In addition to other possible explanations, we consider a sharp transition of the dynamics in the ns range not covered by the two techniques so far. Comparing PCS spectra of weakly polar liquids with their dielectric spectra, we find counterexamples of the claim that they become identical; the PCS spectra are narrower in these cases. Still, in this limit, the dielectric spectra display identical spectral shapes.

I. INTRODUCTION

The dynamics of supercooled molecular liquids was thoroughly investigated by many techniques. In particular, dielectric spectroscopy (DS),[1–6] depolarized light scattering (DLS),[5,7–9] optical Kerr effect (OKE),[10,11] and nuclear magnetic resonance (NMR) relaxometry[12–14] accessed the reorientational dynamics upon cooling. Along with a strong increase in the characteristic time constant, the main (α-) relaxation spectrum displays a pronounced non-Lorentzian shape manifested in a high-frequency broadening approximated by a power law $\nu^{-\beta}$ with $\beta \leq 1$. Focusing on the results from DS, the magnitude of β turned out to vary strongly; yet, there is a trend that the lower the polarity of the liquid, the lower the stretching parameter β.[15–17] Moreover, β appears to become lower upon cooling.[1,18–20] Except for occasional reports,[5,21–23] only recently has a systematic quantitative comparison of the relaxation spectra provided by the different techniques started.

A comparison of twenty liquids showed that the spectra measured by photon correlation spectroscopy (PCS) close to the glass transition temperature T_g display a "generic structural relaxation" with a high-frequency power law exhibiting an exponent $\beta \simeq 0.5$.[24] Furthermore, from a comparison of PCS and dielectric spectra, it was suggested that dipolar cross correlation effects are responsible for the broad variety of the dielectric relaxation stretching, whereas PCS appears to be free of such effects, thus probing only self-correlations.[25–28] The important role of dielectric cross correlation was confirmed by molecular dynamics simulations[29,30] and substantiated by theoretical considerations.[31,32] As the cross correlation contributions change with temperature, this could also explain the failure of frequency temperature superposition (FTS) in the dielectric case. Assuming that dielectric cross correlation effects disappear in weakly polar liquids, PCS and dielectric spectra are expected to agree in this case, and examples were given.[24,28]

The generic relaxation is assumed to hold deep in the supercooled state—and it has important consequences.[20,28] It is well established that at high temperatures, the stretching parameter measured by tandem Fabry–Perot interferometry (TFPI) significantly varies among the different liquids.[9] Consequently, a generic PCS relaxation close to T_g implies failure of FTS when reaching high temperatures. In other words, a qualitative change in the evolution of the α-relaxation is to be expected in the supercooled liquid. Measuring TFPI and NMR relaxation over a wide temperature range, no indications of such a change were reported.[14,20] Yet, there are studies that suggest a "jump" of the stretching parameter when probed by TFPI and PCS, respectively,[8,33–35] possibly indicating a transition within a narrow temperature interval covered neither by TFPI nor by PCS. To our knowledge, this phenomenon has not been noted in the literature. In addition, the conjecture that DS and PCS spectra become identical in the case of non-polar liquids deserves further substantiation. Regarding weakly polar *o*-terphenyl, it was found that the dielectric spectrum is broader compared to the TFPI spectrum.[20]

In the present contribution, we address all three points by revisiting the analysis of the spectra compiled previously by TFPI and PCS in our group.[5,9,21–23,33] Not all data presented here were reported before. Whereas TFPI (together with a double monochromator) typically covers a frequency range of 300 MHz to 10 THz, PCS covers a time window of 100 s–10^{-8} s. Interferometry probes the α-relaxation peak at high temperatures, whereas PCS does at low temperatures; a direct comparison of the α-peak at the same temperature is not

TABLE I. Molecular liquids investigated and parameters of the DLS spectral analyses: glass transition temperature T_g, stretching parameters β_{CD} and β_{K} as obtained from TFPI (or OKE) and PCS, and the difference $\Delta\beta_{\mathrm{CD}}$ in the stretching parameter β_{CD} obtained from TFPI and PCS; bold numbers: present work, non-bold numbers: results from the literature; values in parentheses: converted along Ref. 44. Some entries differ from those in Ref. 9.

Name of liquid[a]	T_g (K)	Stretching parameter β determined from TFPI or OKE[b]	Stretching parameter β determined from PCS[c]	$\Delta\beta_{\mathrm{CD}}$
Benzophenone (benzph)[23]	207	$\boldsymbol{\beta_{\mathrm{CD}} = 0.71}$	⋯	
Decahydroisoquinoline (DHIQ)[9]	179	$\boldsymbol{\beta_{\mathrm{CD}} = 0.56}$	⋯	
Dimethyl phthalate (DMP)[45]	191	$\boldsymbol{\beta_{\mathrm{CD}} = 0.73, \beta_{\mathrm{K}} = 0.81}$	$\boldsymbol{\beta_{\mathrm{K}} = 0.72, \beta_{\mathrm{CD}} \simeq 0.64}$ $\boldsymbol{\beta_{\mathrm{K}} = 0.69, \beta_{\mathrm{CD}} \simeq 0.56}$[21]	0.09
Ethyl benzene (ethylB)[46]	115	$\boldsymbol{\beta_{\mathrm{CD}} = 0.54}$	⋯	
Glycerol[39]	188	$\boldsymbol{\beta_{\mathrm{CD}} = 0.48, \beta_{\mathrm{K}} = 0.61}$ $\beta_{\mathrm{CD}} \simeq b_{\mathrm{MCT}} = 0.43$[47,d]	$\boldsymbol{\beta_{\mathrm{K}} = 0.52, \beta_{\mathrm{CD}} = 0.39}$[26,e]	0.09
m-Tricresyl phosphate (*m*-TCP)[5]	205	$\boldsymbol{\beta_{\mathrm{K}} = 0.63, \beta_{\mathrm{CD}} = 0.49}$	$\boldsymbol{\beta_{\mathrm{K}} = 0.60, \beta_{\mathrm{CD}} = 0.46}$	0.03
2-Methyl tetrahydrofuran (MTHF)[45]	92	$\boldsymbol{\beta_{\mathrm{CD}} = 0.48, \beta_{\mathrm{K}} = 0.61}$	$\boldsymbol{\beta_{\mathrm{K}} = 0.59; \beta_{\mathrm{CD}} = 0.45}$	0.03
o-Terphenyl (OTP)[33]	245	$\boldsymbol{\beta_{\mathrm{CD}} = 0.65; \beta_{\mathrm{K}} = 0.77}$ $\beta_{\mathrm{K}} = 0.78$[48] ($\beta_{\mathrm{CD}} = 0.68$) $\beta_{\mathrm{K}} = 0.80–0.85$[8,f] ($\beta_{\mathrm{CD}} \simeq 0.75$) $\beta_{\mathrm{CD}} = 0.62$ ($\beta_{\mathrm{K}} = 0.75$) OKE[49]	$\boldsymbol{\beta_{\mathrm{K}} = 0.64, \beta_{\mathrm{CD}} = 0.51}$ $\beta_{\mathrm{K}} = 0.59$[30] $\beta_{\mathrm{K}} = 0.55–0.62$[8] $\beta_{\mathrm{K}} = 0.57–0.61$[50,g] $\beta_{\mathrm{K}} = 0.57–0.62$[34,h]	0.14
α-Picolin[51]	129	$\boldsymbol{\beta_{\mathrm{CD}} = 0.50\ (\beta_{\mathrm{K}} = 0.63)}$	$\boldsymbol{\beta_{\mathrm{K}} = 0.56, \beta_{\mathrm{CD}} = 0.43}$[21]	0.07
Propylene carbonate[22]	157	$\boldsymbol{\beta_{\mathrm{CD}} = 0.68\ (\beta_{\mathrm{K}} = 0.78)}$ $\beta_{\mathrm{K}} = 0.77 \pm 0.05$[52]	$\boldsymbol{\beta_{\mathrm{K}} = 0.57, \beta_{\mathrm{CD}} = 0.44}$[24,e]	0.24
Salol[9,21]	218	$\boldsymbol{\beta_{\mathrm{CD}} = 0.80\ (\beta_{\mathrm{K}} = 0.86)}$ $\beta_{\mathrm{K}} = 0.80–0.87$[53] ($\beta_{\mathrm{CD}} \simeq 0.75$) $\beta_{\mathrm{K}} = 0.70–0.90$ OKE[55,i]	$\boldsymbol{\beta_{\mathrm{K}} = 0.64, \beta_{\mathrm{CD}} = 0.51}$[21] $\beta_{\mathrm{K}} = 0.68 \pm 0.02$[54]	0.29
4-Tert-butyl pyridine (4-TBP)	164	$\boldsymbol{\beta_{\mathrm{CD}} = 0.56}$	⋯	
Toluene[37]	117	$\boldsymbol{\beta_{\mathrm{CD}} = 0.66}$	⋯	
Trimethyl phosphate (TMP)	136	$\boldsymbol{\beta_{\mathrm{CD}} = 0.39}$	⋯	

[a] Reference number indicates the source of the original data.

[b] Error of β_{CD}: ±0.01 (present work); β_{CD} values refer to an analysis of the TFPI data in the frequency domain, and β_{K} values refer to an analysis in time.

[c] Error of β_{K}: ±0.02 (present work); β_{K} and β_{CD} values refer to an analysis of the PCS data in the time domain.

[d] Within the MCT, the critical exponent b_{MCT} is not necessarily identical with β_{CD},[56] yet the identity was experimentally confirmed.[9,33,39]

[e] Own analysis.

[f] Two values at the lowest temperature taken.

[g] Value at the lowest temperature excluded.

[h] Two values at the highest temperatures omitted.

[i] A continuous increase with temperature is observed.

possible. For an effective experimental gap of about two to three decades, α-relaxation is not accessible by either DLS technique, and there are only a few liquids for which both TFPI and PCS data are available. We extend our previous spectral analyses of the TFPI data to temperatures close to T_g, where the slow dynamics spectrum is characterized by the appearance of the "excess wing," i.e., a high-frequency contribution of the α-relaxation, which is approximately described by a second power law with an exponent smaller than β, a phenomenon well known from dielectric spectra.[1,19,23,36]

We demonstrate that a TFPI master curve construction including α-peak and excess wing is possible for all temperatures for which "glassy dynamics" in terms of a two-step correlation function with a long-time stretched decay sets in, i.e., from temperatures well above the melting point T_m down to T_g. The corresponding PCS spectra are overall broader, and we do not find indications from either technique that the different spectral widths merge within a narrow temperature range. Some of the PCS decays depart from the generic spectral shape. In addition, we find counterexamples to the claim that dielectric spectra become identical with PCS spectra in the limit of weakly polar liquids. Yet, in this limit, the dielectric α-relaxation indeed shows an identical spectral shape.

II. EXPERIMENTAL SECTION

The measurements applying TFPI and PCS were described in detail before.[7,8,21,37–39] Experiments with a TFPI (JRS Scientific) and double grating monochromator (DM; Jobin Yvon, U1000) were performed in parallel. As a light source, we used a horizontally polarized Coherent Verdi-V2 laser at 532 nm. The TFPI was operating at vertical polarization in almost backscattering geometry (HV-depolarization geometry), and light scattered at 90° was directed, without polarization selection, into the DM, thus utilizing a 90° HT (horizontal-total, depolarized) scattering configuration. The spectral density $S(\nu)$ received after splicing together the spectral pieces from the different free spectral ranges of TFPI and DM measurements was converted to the susceptibility representation via

$$\chi''(\nu) = (1 + n(\nu))^{-1} S(\nu),$$

with $n(\nu)$ being the Bose factor. The spectra of each molecular liquid were normalized to an equal integrated intensity of Raman bands.

For the PCS measurements, the sample was mounted in a cold-finger (Advanced Research Systems). The incident light was vertically polarized. Scattered intensity was gathered in vertical–horizontal geometry using a single mode fiber. The fiber was then connected via a 50/50-splitter with two avalanche photodiodes (Perkin Elmer). Both signals were cross-correlated with an ALV 6010 correlator with a shortest lag time of about 6 ns. The measured intensity correlation function $g2(t)$ was transformed into the field correlation function $g_1(t)$ utilizing the Siegert relation,

$$g_1(t) = ((g_2(t) - 1)/\mathrm{a})^{1/2},$$

with the coherence factor a.[40] In the following, we denote $g_1(t) = C(t)$.

For performing a Fourier transformation, an algorithm based on the Filon algorithm was used because the arbitrarily spaced data points are incompatible with the fast Fourier algorithm.[41] In the time domain, we interpolated the α-relaxation by a Kohlrausch function or by an incomplete gamma function Γ_{inc}, which is the time domain representation of the CD susceptibility; explicitly, the normalized function reads[42,43]

$$\Phi_{CD}(t) = 1 - \Gamma_{inc}(t/\tau_\alpha, \beta).$$

The names of the systems investigated, together with their relaxation parameters, are listed in Table I.

III. RESULTS

A. Comparison of TFPI and PCS relaxation spectra

As mentioned, not many glass formers have been investigated so far by both TFPI and PCS. In our previous studies, we reported results on four liquids, namely, *o*-terphenyl (OTP),[33] m-tricresyl phosphate (*m*-TCP),[5] dimethyl phthalate (DMP),[45] and methyl tetrahydrofuran (MTHF).[45] In a different context, we investigated DMP, picoline, and salol.[21] Except for OTP, the PCS datasets were considered in the context of review articles or papers that focus on determining the time constant of the α-relaxation. Generally, FTS was found to hold within each dataset, TFPI and PCS. Regarding OTP, our paper concludes, "the decay observed by PCS appears to be somewhat more stretched compared to the result from DM/TFPI but is not showing any temperature dependence. Whether there is some change of stretching in a small interval around 300 K cannot be said."[33] Such a "jump" of the stretching parameter reported by the respective technique was observed for OTP by other studies[8,34] and also for salol.[35] In a recent paper, we stressed the high similarity among TFPI, PCS, and NMR at high-frequency and attributed an observed low-frequency broadening of some PCS spectra to possible instrumental artifacts.[19] However, the necessity of such a change

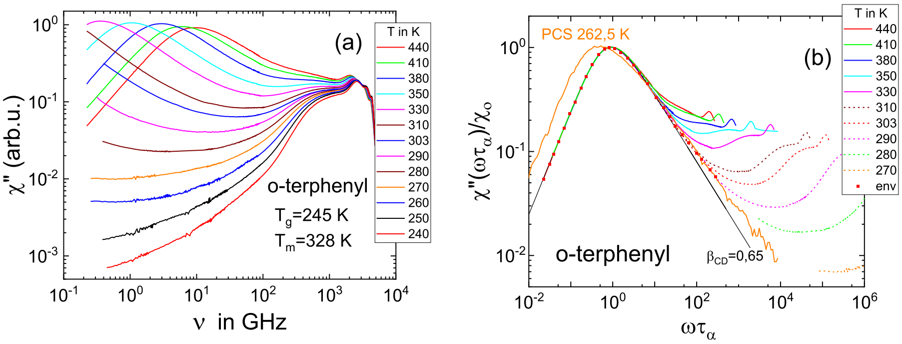

FIG. 1. (a) TFPI spectra of *o*-terphenyl at different temperatures.[33] (b) α-peak scaling of the data in (a). Solid lines: spectra that cover the α-peak; dashed lines: only its high-frequency flank is covered. Added: PCS spectrum shifted such to agree on the high-frequency flank of the TFPI data. Red squares: envelope of α-relaxation including onset of excess wing (env).

of the spectral width is a consequence of the claim that a generic relaxation stretching holds close to T_g, whereas diverse stretching is found at high temperatures.

In Fig. 1(a), we display the TFPI results of OTP.[33] In a range of 440–330 K, the evolution of the α-relaxation peak is observed upon cooling. At high frequencies, a crossover to fast relaxations, boson peak, and Einstein ("microscopic") peak is recognized, manifested by a susceptibility minimum. Below 330 K, the α-peak leaves the frequency window, but its high-frequency wing is still observable. In Fig. 1(b), we test the possibility of constructing a master curve in terms of plotting $\chi''(\omega\tau_\alpha)/\chi_o$ ("α-peak scaling"), where $\chi_o = \chi_{\max}$ is a weakly and monotonously changing temperature factor chosen such to achieve best spectral overlap [see also Fig. 6(a)]. The time constant $\tau_\alpha(T)$ needed for rescaling the spectra at temperatures when the α-peak is beyond the TFPI frequency window is taken from an independent source.[33,45] From 440 to 290 K at least, an envelope reproducing the high-frequency flank of the main relaxation can be constructed. The α-peak itself is well reproduced by a CD function with $\beta_{CD} = 0.65$. At the highest frequencies, the fit fails, probably due to the onset of an excess wing. For the purpose of a direct comparison with the results of the other liquids investigated, we constructed an envelope of α-peak and excess wing [red points in Fig. 1(b)]. We added our PCS result[33] [after Fourier transformation (FT)]; we display only a single spectrum as FTS applies. The spectrum is scaled such to provide overlap with the TFPI data at high frequencies. Clearly, the PCS spectrum is overall broader. Note that the PCS spectrum is measured at a temperature close to that of the TFPI spectrum at 270 K (orange dashed line) and appears to fit in well.

In Fig. 2, the reorientational function $C(t)$ derived from the TFPI spectra (via FT) is shown together with the PCS decays. Clearly, FTS holds for the TFPI data over an interval of about 130 K. Similarly, FTS holds for the PCS decays. The TFPI decays are reproduced by the time domain expression of the CD function with $\beta_{CD} \simeq 0.65$ [red dashed-dotted line as in the frequency domain—Fig. 1(b)]. Even at 440 K, well above T_m, the extent of stretching can easily be determined in contrast to the frequency domain, where the interference of the fast relaxation may hamper a clear-cut fit. All in all, 90% of the correlation is lost due to the α-relaxation virtually not changing its stretched shape. Yet, a direct comparison of the PCS decays with the TFPI decay (colored dots shifted to agree with the TFPI decay at 310 K) indicates that the PCS decays are more stretched at long

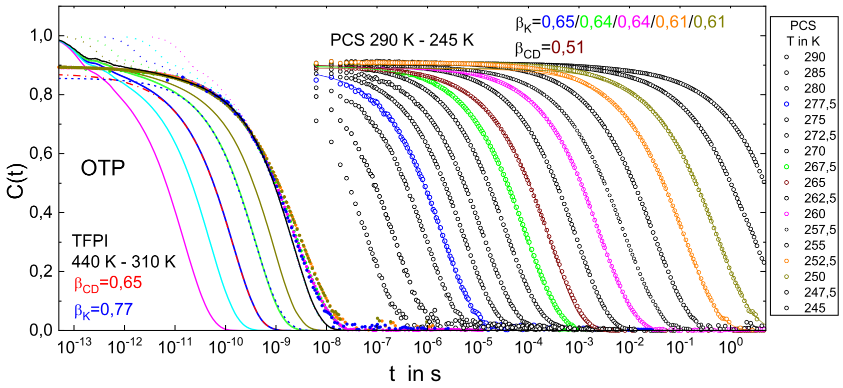

FIG. 2. Time domain representation of TFPI (colored lines, at 310, 320, 330, 350, 380, and 440 in K) and PCS data (open circles) of *o*-terphenyl (OTP). TFPI decays can be collapsed onto that at 310 K by horizontal shifting (dotted colored lines); a fit by a CD function yields $\beta_{CD} = 0.65$ (red dashed-dotted line at T = 350 K, blue data line), and a fit by a Kohlrausch function yields $\beta_K = 0.77$ (blue dashed line at T = 330 K, green data line) but overestimates the long-time decay. Colored circles indicate the PCS data for which Kohlrausch fits are performed with indicated values β_K; a CD fit underestimates the decay (see 265 K). For a direct comparison, PCS decays are shifted to provide the best overlap with the TFPI decay at 310 K (colored dots).

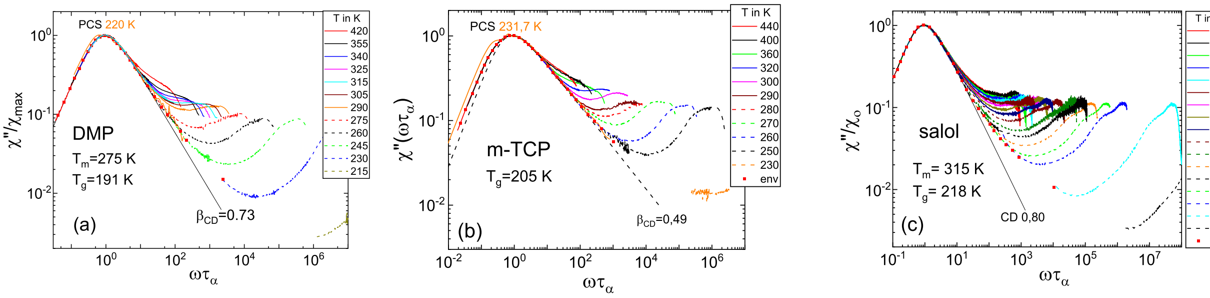

FIG. 3. (a) α-peak scaling of the TFPI spectra of dimethyl phthalate (DMP). (b) Corresponding scaling of the spectra of m-tricresyl phosphate (m-TCP). Added in (a) and (b): PCS spectra at indicated temperature. (c) Corresponding scaling of the salol spectra. Solid lines: α-peak covered; dashed lines: only its high-frequency flank covered. Red dots/env in [(a)–(c)]: envelope of α-relaxation including onset of excess wing.

times, while they virtually agree at short times—corresponding to the observation in the frequency domain [Fig. 1(b)]. A Kohlrausch fit of the PCS decays is superior to a CD function; one finds $\beta_K \simeq 0.64$, while a CD fit underestimates the long-time behavior. Vice versa, a Kohlrausch fit of the TFPI data overestimates it (cf. Fig. 2). At temperatures close to T_g, a weak trend appears in the PCS data to become even more stretched. At such temperatures, one expects traces of the excess wing,[21,57] and determining β_K depends on the fitting interval. In addition, possible instrumental artifacts due to problems stabilizing the PCS setup at the longest times may occur.

It seems that TFPI and PCS measure qualitatively different relaxation spectra, although the corresponding high-frequency flanks appear quite similar over the entire temperature range. Importantly, there is no indication from either technique that the different widths of TFPI and PCS spectra, respectively, approach each other; the corresponding β values display a step $\Delta\beta$ confirming our previous result (see Table I).[33]

In Fig. 3, we consider the α-peak scaling for the TFPI spectra of DMP (a),[45] m-TCP (b),[5] and salol (c).[21] Master curves can be constructed covering a wide temperature interval. Comparing with the PCS spectrum, the high-frequency flank, including the excess wing of the TFPI data, is well reproduced, but the PCS spectra of DMP and m-TCP are again broadened on the low-frequency flank. Some artifacts (slow oscillations) show up in the case of m-TCP, possibly indicating again instrumental problems. In the case of m-TCP, the TFPI spectra cannot be described by a CD function; a Kohlrausch function works well. In the case of salol, one clearly recognizes the emergence of an excess wing.

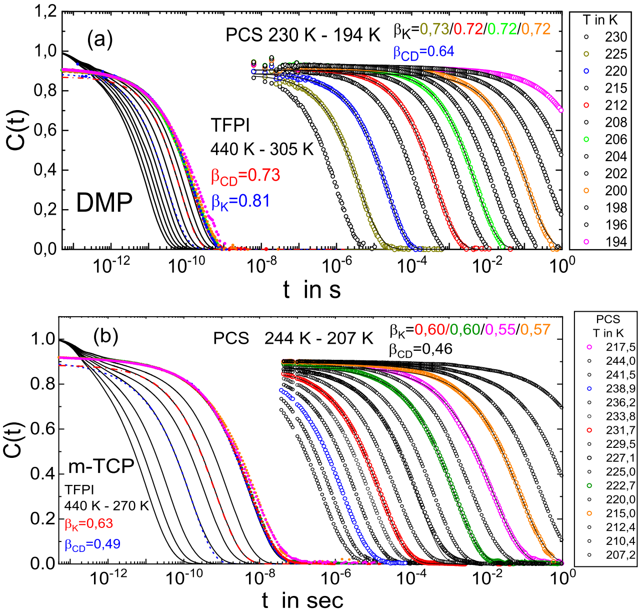

FIG. 4. (a) Time domain representation of TFPI (lines, at 440, 420, 400, 385, 370, 355, 340, 325, 315, and 305 in K) and PCS data (open circles) of dimethylphthalate (DMP). A CD function reproduces the TFPI decays (red dashed-dotted line), a Kohlrausch overestimates the long-time decay (blue dashed line). (b) Corresponding data of m-TCP, TFPI data at 440, 400, 360, 320, 300, 290, 280, and 270 in K. A CD function fails for the TFPI decays (blue dashed line), but a Kohlrausch fit works (red dashed-dotted). PCS colored circles indicate the data for which a Kohlrausch fit is performed; a CD fit underestimates the m-TCP decay (see 227.5 K). Stretching parameters are indicated (color refers to corresponding data). In panels [(a) and (b)], PCS decays are shifted (colored dots) to provide the best overlap with the TFPI decay at 305 K (DMP) and 270 K (m-TCP), respectively.

The corresponding time domain data are collected in Fig. 4. The TFPI decays follow FTS and are well described by a CD function (DMP) or a Kohlrausch function (m-TCP) with the same stretching parameter as in the frequency domain. Similarly, the PCS decays follow FTS, but again they are more stretched at long times while agreeing at short times; a systematic jump of the stretching is observed, which, yet, in the case of m-TCP, is quite marginal (Table I), and one clearly notices that a CD fit fails for the PCS data (see T = 227.5 K).

We also mention the data of methyl tetrahydrofuran (MTHF) (see Fig. 8, Appendix A). It is a low-T_g system, and the crossover from a single-step correlation function close to the boiling point to a two-step function at lower temperatures is well observable (Fig. 8).[45] The difference among the TFPI and PCS decays is marginal. In Fig. 9(a) (Appendix B), we show TFPI decays of decahydro isoquinoline, which display a particular spectral feature worth showing.[9]

Finally, we discuss the case of glycerol and propylene carbonate (PC), for which we published only TFPI data,[22,39] but PCS data were recently reported.[24,26] In the case of glycerol, the measurements densely cover all temperatures down to T_g [as for salol, Fig. 3(c)].[39] As shown in Fig. 5(a), the α-peak scaling encompasses the α-peak and a widely covered excess wing. A temperature-independent envelope is suggested down to the lowest temperatures (red dots). The inset of Fig. 5(a) shows the temperature dependence of χ_o. At low temperatures, χ_o becomes temperature independent, which corresponds to a temperature independent amplitude of the microscopic peak. Such behavior is found for all liquids studied. The high-frequency dependency of the PCS spectrum follows the respective TFPI spectrum, including the onset of the excess wing; however, the spectrum is overall broader. Referring to Fig. 6(b), we find $\beta_K = 0.52$, while the TFPI data can be fitted with $\beta_{CD} = 0.48$ ($\beta_K = 0.61$). In Fig. 5(b), we display the TFPI decays of PC compared to the (shifted) PCS decay taken from Ref. 24. In this case, a strong difference between PCS and TFPI decays is observed, while TFPI and PCS data each follow FTS.

In Fig. 6(a), we compare the envelope spectra extracted from the different TFPI master curves $\chi''(\omega\tau_\alpha)/\chi_o$ investigated. Clearly, the spectral shape varies strongly; CD parameters in the range $\beta_{CD} = 0.48$–0.80 are found (see Table I). Depending on the temperature range covered, the emergence of an excess wing is more or less recognized. The temperature for which master curves can be constructed is indicated; in some cases, up to 220 K is covered. In Fig. 6(b), we show the corresponding PCS time domain data. Decays in the middle of each investigated temperature range are chosen in order to consider decays fully covered and not spoiled by artifacts at the lowest temperatures. We added the results for salol and picoline, which were investigated in a different laboratory, and literature data of glycerol and PC.[24,28] Independent of the fact that the PCS decays follow FTS in each case, their stretching exhibits some variations. While five systems virtually follow the generic relaxation recently published by Blochowicz and coworkers (red crosses),[24,28] three systems, namely, DMP, *o*-terphenyl, and salol, show significant

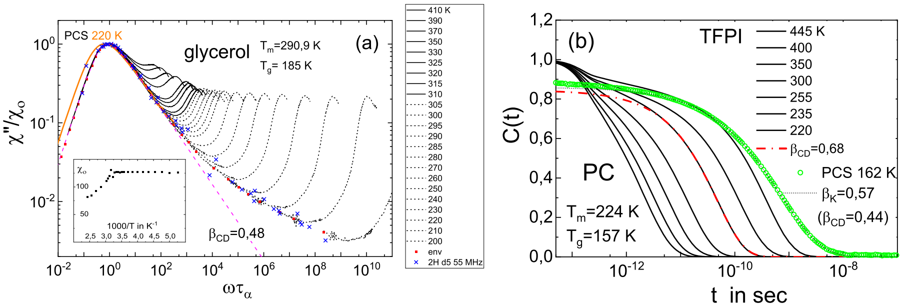

FIG. 5. (a) α-peak scaling for the TFPI data of glycerol. Solid lines: α-peak covered; dashed lines: only its high-frequency flank covered; added: PCS spectrum at 220 K,[26] ^{2}H relaxation rate of glycerol-d$_5$ at 55.2 MHz (blue crosses),[58] and TFPI envelope (red points). Inset: temperature dependence of χ_o. (b) Comparing TFPI data of propylene carbonate (PC, solid lines) in the time domain with a PCS decay (shifted, green).[24] Stretching parameters are indicated.

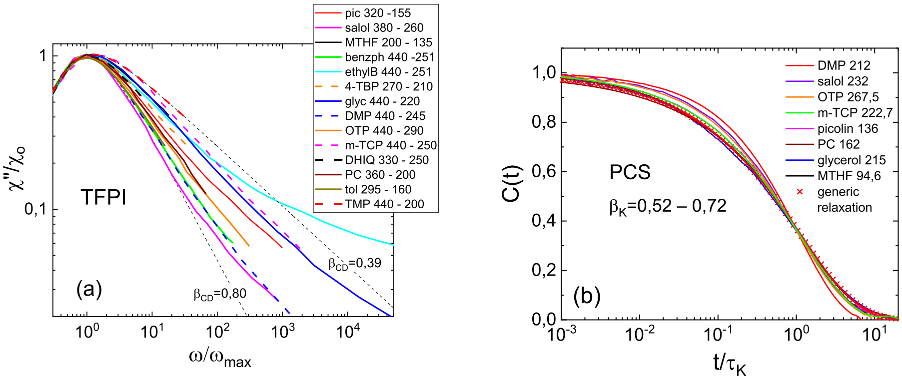

FIG. 6. (a) The spectral envelope of the α-relaxation obtained from the master curve construction $\chi''(\omega\tau_\alpha)/\chi_o$ (α-peak scaling) of the TFPI data for the molecular glass formers: α-picolin, salol, methyl tetrahydrofuran (MTHF), benzophenone (benzoph), ethyl benzene (ethylB), 4-tert-butyl pyridine (4-TBP), glycerol, dimethyl phthalate (DMP), *o*-terphenyl (OTP), m-tricresyl phosphate (m-TCP), decahydro isoquinoline (DHIQ), propylene carbonate (PC), toluene, and trimethyl phosphate (TMP); black dashed lines: limiting CD interpolations. (b) Corresponding reorientational correlation functions provided by PCS data of glycerol and PC from Refs. 26 and 24; red crosses indicate the generic spectrum.[24] Numbers in [(a) and (b)] indicate the temperature in K.

departures. A Kohlrausch function interpolates the decay curves; the stretching parameter varies in the range β_K = 0.52–0.72 (Table I). As demonstrated, these parameters correspond to a significantly stronger relaxation stretching compared to the TFPI decays.

B. Comparison of depolarized light scattering and dielectric spectra of weakly polar glass formers

Following the hypothesis suggested by the Blochowicz group, the dielectric spectra of low-polar molecular liquids are not expected to be obscured by contributions from cross correlation effects and, thus, should reflect the self-part of the reorientational correlations with its generic stretching close to T_g.[26,28] We show a collection of type-A glass formers [Fig. 7(a)], systems that do not exhibit a discernible β-relaxation, as well as type-B glass formers, glass formers with a more or less strong β-relaxation[59] measured in our group over time [Fig. 7(b)]. We included a broadband (BB) spectrum of *o*-terphenyl (unpublished; see also Appendix C). All spectra exhibit a relaxation maximum $\varepsilon_{max}'' < 1$. As shown in parts before,[17,28] within the scatter of the data, the spectra of type-A systems close to T_g show indeed a very similar spectral shape, encompassing both the α-peak *and* excess wing. The α-peak itself can be interpolated by a Kohlrausch susceptibility with β_K = 0.56. A comparison with the PCS spectrum of OTP at a similar temperature, however, reveals differences. It is significantly narrower. We included the generic PCS spectrum.[24] It reproduces the relaxation peak over a somewhat larger frequency range compared to the Kohlrausch function. This is not surprising, as the generalized gamma distribution applied for fitting the PCS data in Refs. 26 and 24 contains two spectral width parameters.[57] However, it does not cover the excess wing, the latter being universally shared by all systems displayed in Fig. 7(a).

In the case of weakly polar type-B systems [Fig. 7(b]; systems with $\varepsilon''_{max} < 2$), the spectral shape of the α-relaxation can only be safely accessed if the relaxation strength of the β-relaxation is relatively small and/or both relaxations are well separated, as is the case for DMP, isopropyl benzene, 3-toluidine, and TPP. A quite similar α-relaxation is observed. In the case of the other systems, the limit of an unperturbed α-relaxation is more clearly disclosed the lower the temperature is. For the systems presented, no excess wing is observed. Spectra closest to T_g are displayed. The α-peak can be approximated again by a Kohlrausch function with β_K = 0.56; deviations from the fit occur at high frequencies.

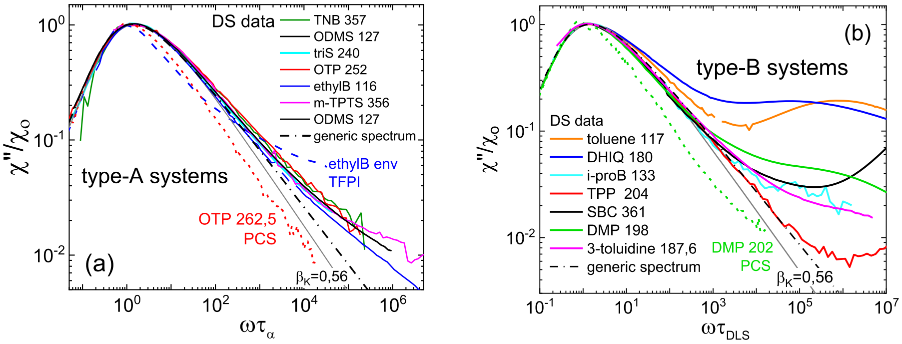

FIG. 7. (a) Dielectric spectra of low-polar type-A glass formers (systems marked by colored solid lines): trinaphthyl benzene (TNB),[60] o-terphenyl (OTP; unpublished), tristyrene (triS),[17] ethyl benzene (ethylB; unpublished), m-TPTS (a high-T_g glass former),[61] and oligo-dimethyl siloxane (ODMS; M = 311 g/mol).[62] Added the PCS spectrum of OTP (PCS: short dashes) and TFPI envelope of ethyl benzene (long-dashed line). (b) Dielectric spectra of type-B glass formers (colored solid lines): toluene,[59] decahydro isoquinoline (DHIQ),[60] isopropyl benzene (i-proB, unpublished), SBC (a spirochromane component),[63] triphenyl phosphite (TPP, unpublished), and added PCS spectra of DMP (dashed line).[5] The gray line in both figures denotes the Kohlrausch fit, the dashed-dotted line denotes the generic spectrum,[24] and the numbers denote the temperature in K.

Actually, the full high-frequency flank of the α-relaxation represented by that of TPP, for example, is reproduced by a power law with an exponent quite close to 0.50, as also reported in Ref. 64 (we find 0.48). Importantly, the α-relaxation is fully reproduced by the generic PCS spectrum included in Fig. 7(b).[24] The PCS spectrum of DMP measured at a similar temperature as the displayed dielectric spectra is narrower, yet with a rather similar high-frequency flank. In addition, it appears that the pronounced dielectric β-relaxation of DMP is not discernible in either the TFPI or PCS spectrum. We mention that the TFPI spectra of DHIQ [cf. Fig. 9(a) (Appendix A)] and toluene (Table I) are much narrower compared to their dielectric counterpart.

Finally, in Fig. 9(b) (Appendix C), we directly compare the limiting dielectric spectra of type-A and type-B systems. Their high-frequency flanks are not identical due to the emergence of an excess wing in the case of type-A.

IV. DISCUSSION

Starting with the TFPI data, the emergence of a bi-modal relaxation spectrum reflecting a two-step correlation function with a stretched long-time decay sets in well above T_m. Even a non-glass forming liquid such as benzene displays such "glassy dynamics."[65] An α-peak scaling $\chi''(\omega\tau_\alpha)/\chi_o$ may cover a temperature range of about 150 K for some liquids, and in most cases, a CD function reproduces the α-peak. The extent of relaxation stretching varies strongly among the molecular liquids. There is no relationship between stretching and fragility,[9] in contrast to persisting claims. The master curve construction $\chi''(\omega\tau_\alpha)/\chi_o$ can be extended to temperatures down to T_g, for which the TFPI spectra no longer cover the α-peak, yet its high-frequency wing. This suggests a temperature independent high-frequency envelope, comprising also the excess wing. As discussed before,[23] the excess wing is nothing other than the "intermediate power law" or "nearly logarithmic decay" identified in OKE experiments[66] and has to be understood as an integral part of the α-relaxation since it scales with τ_α.[17,23,39] Due to the continuous crossover to the excess wing, it is not possible to define a clear-cut high-frequency power law exponent of the α-relaxation.

The corresponding PCS decays measured at low temperatures also show no indication that FTS fails, except for the lowest temperatures very close to T_g, for which instrumental artifacts may occur. Their stretching varies and is stronger compared to that of the TFPI decays. Correspondingly, the PCS spectra turn out to be broadened on the low-frequency flank, whereas they tend to agree with the TFPI spectra on the high-frequency flank. A Kohlrausch fit is usually superior, yielding values β_K = 0.52–0.73 (see Table I). This variation is somewhat larger than previously reported (β_K = 0.58 ± 0.06)[30] but smaller than that of the TFPI data. Within the error margin, five of the eight systems may be regarded as close to the generic relaxation function suggested by the Darmstadt group,[24] whereas three systems significantly depart. The difference in the relaxation stretching reported by the two techniques, i.e., $\Delta\beta_{CD}$, may be as large as $\Delta\beta_{CD}$ = 0.29 for salol or $\Delta\beta_{CD}$ = 0.24 for PC [Table I and Fig. 5(b), respectively]. Yet, there are also liquids for which $\Delta\beta_{CD}$ is rather small (e.g., m-TCP); that is, the spectral shape virtually does not change over the entire range of the glass transition. Importantly, we do not find indications that the spectral width changes within a narrow temperature interval to bridge the qualitatively different stretched decays probed by each of the two techniques. Thus, we face the possibility that a sharp transition occurs in a spectral gap currently not accessible by either technique and, thus, failed to be noticed so far (see also Ref. 28). The anticipated transition might occur in a time constant interval of ns, which is in the moderately supercooled regime. Or TFPI and PCS spectra reflect different contributions from fluctuations, which potentially cause a depolarized light scattering signal (see below).

Let us discuss the quality of our experiments. The TFPI technique was introduced in 1990,[67] and the first experiments suffered from artifacts at low intensity due to missing a narrowband filter for the Fabry–Perot optics. Only by applying such a filter are the higher orders of the TFPI spectrum sufficiently suppressed to allow for measurements of the extremely broad spectra characteristic of glass formers.[68–70] The TFPI spectra of glycerol, OTP, PC, and salol were investigated by several groups. A comparison of the stretching parameters is included in Table I. High agreement is found and confirms the trend that rather high β values are found. We note that in the case of an ionic glass former (CKN), the TFPI spectra were comparably broad ($\beta_{CD} \simeq 0.42$, $\beta_K \simeq 0.55$).[71] All PCS studies, in contrast, find stretching parameter systematically smaller than those from TFPI. For a given glass former, the PCS stretching parameters reported by different groups displays some scatter, which, however, is less than the "jump" observed (Table I). We note that most PCS studies did not apply the fast correlator employed by the Darmstadt and our group (cf. Sec. II). Still, the current precision of PCS experiments does not allow us to fully resolve the excess wing contribution (cf. Figs. 3 and 5).

Both techniques cannot easily be expanded to fill the gap in the MHz to GHz range needed to allow for a direct comparison of the full spectra and, thus, to monitor a possible crossover of the spectral widths. Employing a confocal FPI (CFPI), one is able to cover a frequency range of 10–400 MHz; however, it was only rarely applied.[8,72] In the case of an epoxy resin, TFPI, CFPI, and PCS were combined to cover the full dynamic range. No significant change of the stretching parameter as a function of temperature was found; β_K scattered in the range 0.55–0.62.[72] The spectral range can be extended by taking recourse to OKE experiments (10 MHz to 10 THz). A direct comparison between TFPI and OKE spectra demonstrated good agreement in the case of salol and benzophenone,[73,74] and similarly for OTP.[49] Another OKE study of salol reports a steady increase in the stretching parameter with temperature (Table I).[55] The experimental situation is not completely satisfying.

From a theoretical point of view, the question of what actually is probed by DLS is not fully answered. First TFPI experiments by the Cummins group analyzed the data in the frame of the mode coupling theory (MCT), and the spectra were interpreted as arising from the interaction-induced scattering mechanism (dipole-induced-dipole (DID) mechanism), which allowed the spectra to be related to the dynamics of density fluctuations addressed by MCT.[53,71] Generally, in depolarized backscattering geometry, DLS originates from both DID and orientational (self and collective) fluctuations. They cannot easily be separated. Later on, it was concluded that the relaxational part of TFPI spectra originates from the orientational fluctuations, whereas the high-frequency part around the boson peak and higher frequencies is dominated by the DID mechanism.[75] This refers to the α-peak; yet, regarding its high-frequency wing (excess wing) emerging at low temperatures, the situation was not addressed. Later on, in the case of a non-polar liquid it was found that density fluctuations are more important than orientational fluctuations. The spectra showed a low stretching parameter $\beta_K = 0.55$ ($\beta_{CD} = 0.42$).[76] It seems that the theoretical situation is not fully settled either, and it may be possible that the different contributions of the DLS signal show different frequency dependences, i.e., TFPI and PCS spectra may be differently affected.

Support that the TFPI spectra reflect the orientational self-part comes from ^{2}H NMR relaxometry,[13,14] which by its very nature probes solely the orientational self-part.[77] Plotting the single-frequency spin-lattice relaxation rate R_1 as a function of the time constant τ_α, the such rescaled rate $R_1(\tau_\alpha)$ reproduces the TFPI master curve $\chi''(\omega\tau_\alpha)/\chi_o$, both α-peak and excess wing.[13,20] For the case of glycerol, this is again documented in Fig. 5(a).[20,58] In order to understand this intriguing result, we proposed an envelope scaling extending strict FTS:[20] The TFPI spectrum compiled at the lowest temperatures, including the α-relaxation peak and excess wing, provides an envelope of all spectra observable at higher temperatures up to well above T_m. Alternatively, one could state that indeed FTS holds with a temperature independent spectral function including an α-peak and excess wing, which, upon increasing temperature, is more and more truncated at high frequencies by the fast/microscopic dynamics. Given the possibility of a dynamic transition in the ns range, however, a generalization of the NMR result has to be taken with caution. In the case of glycerol or m-TCP with a rather small $\Delta\beta$, the approach will work, but for systems such as salol or PC, one would expect a failure (Table I): $R_1(\tau_\alpha)$ would not reproduce the correct relaxation spectrum. In this case also, a master curve construction of the TFPI data for time constants slower than about 1 ns would be out of the question.

The claim stands that in the limit of low-polar liquids, PCS and dielectric spectra are expected to agree and consequently exhibit the generic relaxation stretching close to T_g.[24,28] This implies that the spectral shape of the self-part of the orientational correlation function is independent of the rank-l and that cross correlations do not appear in PCS. Plotting β_K as a function of the dielectric relaxation strength $\Delta\varepsilon$ on a log-scale, a saturation around $\beta_K = 0.55$ for low-polar liquids was indeed suggested.[17] As demonstrated here, the latter finding not only appears to hold for type-A glass formers but also for weakly polar type-B glass formers [Fig. 7(b)]: The α-relaxation peak exhibits an identical shape, yet its high-frequency flank differs among type-B and type-A systems [Fig. 9(a)]. The latter share an identical excess wing. In the case of the investigated type-B glass formers, an excess wing is missing; yet, there are systems that display both an excess wing and an α-peak.[20,59] The full α-relaxation of the type-B systems investigated is well reproduced by the generic spectrum reported by the Darmstadt group.[24,28] In contrast, the corresponding TFPI spectra are narrower, and we found two systems for which the PCS spectrum is narrower than their dielectric counterpart. Moreover, the dielectric spectra of type-B glass formers show a secondary relaxation of variable strength and time scale, but given the current precision and a possibly smaller relaxation strength, it may be difficult to probe by PCS (cf. DMP). Similar results were reported for an epoxy resin.[72] Yet, there are systems for which a secondary relaxation is well identified by PCS.[78]

Molecular dynamics studies suggest that there may be a l-dependence of the relaxation stretching; one finds a trend $\beta(l = 1) > \beta(l = 2)$.[79,80] This is, however, at variance with the present results: the DLS spectra of OTP and DMP are narrower than their dielectric counterparts. Regarding cross correlation effects, they are also documented for DLS; it is coherent scattering.[30,40] Possibly, their contributions may affect TFPI and PCS differently. Finally, one expects that the manifestation of cross correlation effects in dielectric spectra scales similarly with the dipole moment as does the self-correlation. However, it was shown that dipolar cross correlation contributions scale with both dipole density and the Kirkwood factor if the latter is larger than 1.[27,31] Low dipole moment liquids tend to display g_K values close to unity.[27,31] Thus, cross correlation appears to be negligible in weakly polar liquids, as in diluted systems.[28]

V. CONCLUSION

Relaxation spectra of molecular glass formers measured by tandem Fabry–Perot interferometry (TFPI) and by photon correlation spectroscopy (PCS) are re-investigated from above T_m down to T_g

to scrutinize the claim that a generic relaxation stretching is found close to T_g while individual stretching is established at high temperatures. In addition, we test the assertion that close to T_g, dielectric and PCS spectra of the α-relaxation become identical in the limit of low-polar systems.

The TFPI spectra reveal no change in the relaxation stretching covering a very large temperature range. They can be described by a CD function with parameters varying along $\beta_{CD} = 0.39–0.80$. The corresponding PCS decays measured close to T_g show no indication that FTS fails. However, their relaxation stretching varies too; a Kohlrausch fit is superior and provides $\beta_K = 0.52–0.73$. Three systems out of eight show larger deviations from the generic relaxation spectra recently reported. Compared to each other, TFPI and PCS appear to measure qualitatively different relaxation spectra, although the corresponding high-frequency flanks are quite similar over the entire temperature range. We do not find, however, any indication that the DLS stretching changes in a narrow temperature interval to bridge the different stretching reported by the two light scattering techniques. We are faced with two possibilities: (i) A sharp transition occurs in the ns range currently not accessible by either technique, or (ii) TFPI and PCS reflect different contributions from the different fluctuations potentially causing a depolarized light scattering signal.

The TFPI spectra allow constructing master curves $\chi''(\omega\tau_\alpha)/\chi_o$ down to T_g, which include α-relaxation and excess wing. In the case of glycerol, the master curve is reproduced by a single-frequency ^{2}H NMR spin–lattice relaxation rate when plotted as a function of the time constant τ_α. Explaining this finding, we re-iterate our proposal of an envelope scaling extending strict FTS. Altogether, this suggests that the excess wing appears as a genuine feature of the α-relaxation and no clear-cut power law can be identified in its high-frequency flank, and that the TFPI spectra reflect the self-part of the orientational fluctuations.

Comparing dielectric spectra of weakly polar liquids, the α-relaxation peak shows an identical spectral shape among the systems investigated. Its high-frequency flank, however, appears to be different for type-A and type-B glass formers: While type-A glass formers exhibit a non-power law high-frequency flank encompassing the excess wing, type-B systems show a clear-cut power law, and the full α-relaxation is reproduced by the generic spectrum. We find two systems for which the corresponding PCS spectrum is narrower than their dielectric counterpart. Also, a secondary relaxation well recognized in the dielectric spectra appears not to be probed by PCS.

ACKNOWLEDGMENTS

Many thanks to Ranko Richert (Arizona State University) for providing the dielectric spectra of DHIQ and TNB and to Thomas Blochowicz (Technische Universität Darmstadt) for providing the PCS data of glycerol and PC and for making available the generic relaxation spectrum. Finally, the financial support from the Deutsche Forschungsgemeinschaft (DFG) through Project No. RO907/22 is appreciated.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contribution

Ernst A. Rössler: Conceptualization (lead); Formal analysis (equal). **Manuel Becher**: Conceptualization (supporting); Formal analysis (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

APPENDIX A: 2-METHYL-TETRAHYDROFURAN

In Fig. 8, we display the data of 2-methyl-tetrahydrofuran in the time domain. While the TFPI decays follow FTS from 220 K down to 135 K and can be interpolated by a CD function, the typical two-step correlation function with a stretched long-time decay disappears at high temperatures (dashed lines), indicating the onset of "glassy dynamics" only below about 220 K. The PCS decays virtually follow FTS and can be fitted by a Kohlrausch function. The difference among the TFPI and PCS decays is marginal but systematic.

APPENDIX B: DECAHYDROISOQUINOLINE

The glass former decahydroisoquinoline (DHIQ) exhibits some spectral peculiarities. Its glass transition temperature is rather low (T_g = 179 K), and one recognizes the disappearance of "glassy dynamics" at the highest temperatures—see Fig. 9(a). Moreover, in comparison with most other glass formers studied here, the amplitude of the α-relaxation is low with respect to that of the fast dynamics, including the microscopic peak—see the inset of Fig. 9(a). To put it differently, the fast relaxations are relatively pronounced, relaxing about 40% of the correlation function, while typically only 10% are found (cf. Fig. 4). In addition to a damped oscillatory behavior at short times, one observes a very stretched decay extending over about two decades at the lowest temperature. It is not part of the α-relaxation, as it does not scale with the latter. Most analyses by the

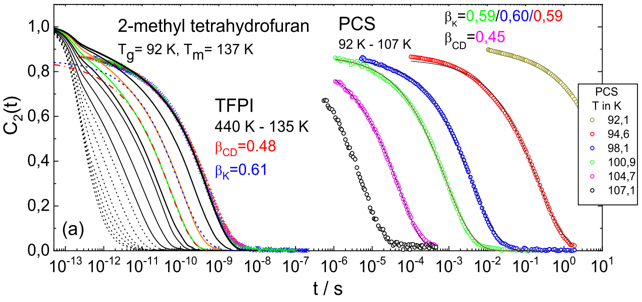

FIG. 8. Time domain representation of the TFPI (solid and dashed lines, at 440, 410, 380, 350, 320, 270, 240, 220, 200, 180, 170, 160, 150, 145, and 135 in K) and PCS data (open circles) of 2-methyl tetrahydrofuran; red dashed-dotted line: CD fit for T = 160 K (green data line); blue dashed line: Kohlrausch fit (orange data line); at T > 220 K, the two-step character of the decays disappears (dashed lines). PCS decays shifted to best coincide with TFPI decay at 135 K (colored crosses); stretching parameters of CD and Kohlrausch fits are indicated (color refers to the corresponding data and fit).

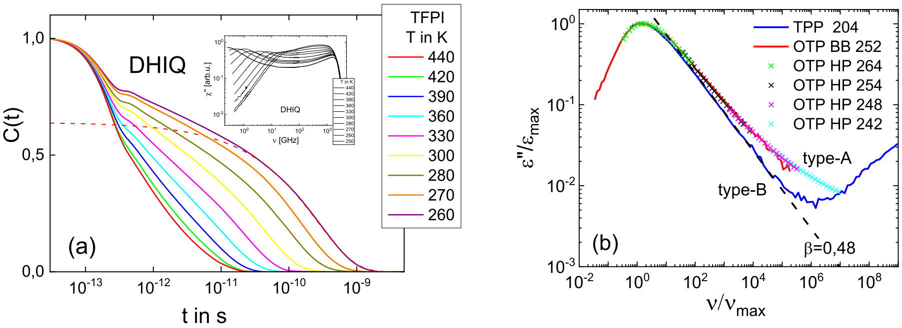

FIG. 9. (a) Time domain representation of the TFPI data of decahydroisoquinoline (DHIQ). Dashed line: CD interpolation with $\beta_{CD} = 0{,}56$. Note the extended fast relaxation, which cannot be attributed to the α-relaxation. The inset shows corresponding spectra. (b) Comparison of the dielectric spectral shape of the α-relaxation of type-A and type-B glass formers for the limit of weakly polar systems. In addition, we compare a broadband (BB) spectrum with data measured by a high-precision (HP) bridge. In the case of the type-B system, we added the power law interpolation of its high-frequency flank; the exponent value is indicated.

MCT are hampered by a low amplitude of the fast dynamics. This is different in the case of DHIQ.

APPENDIX C: LIMITING DIELECTRIC SPECTRA

In Fig. 9(b), the limiting dielectric spectra in the case of weakly polar systems of type-A (OTP) and type-B (TPP), respectively, glass formers are compared. The α-relaxation spectra close to T_g are similar but not identical. While type-A systems display a high-frequency excess wing, type-B systems investigated exhibit a clear-cut power-law behavior. The broadband (BB) spectrum of OTP was also measured by an Alpha-A analyzer (Novocontrol). It is compared to the dielectric spectra measured by an ultra-precision bridge (HP) covering about three decades (Andeen Hagerling 2700A).[20] No significant difference is observed. In the case of type-B, we included a power-law interpolation of the high-frequency flank of the α-relaxation.

REFERENCES

[1] P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, “Scaling in the relaxation of supercooled liquids,” Phys. Rev. Lett. **65**, 1108 (1990).

[2] P. Lunkenheimer, U. Schneider, R. Brand, and A. Loid, “Glassy dynamics,” Contemp. Phys. **41**, 15–36 (2000).

[3] T. Blochowicz, C. Gainaru, P. Medick, C. Tschirwitz, and E. A. Rössler, “The dynamic susceptibility in glass forming molecular liquids: The search for universal relaxation patterns II,” J. Chem. Phys. **124**, 134503 (2006).

[4] G. Floudas, M. Paluch, A. Grzybowski, and K. L. Ngai, *Molecular Dynamics of Glass-Forming Systems* (Springer, Heidelberg, 2011).

[5] N. Petzold, B. Schmidtke, R. Kahlau, D. Bock, R. Meier, B. Micko, D. Kruk, and E. A. Rössler, “Evolution of the dynamic susceptibility in molecular glass formers: Results from light scattering, dielectric spectroscopy, and NMR,” J. Chem. Phys. **138**, 12A510 (2013).

[6] *The Scaling of Relaxation Processes*, edited by F. Kremer and A. Loidl (Springer International Publishing, Cham, Switzerland, 2018).

[7] H. Z. Cummins, G. Li, Y. H. Hwang, G. Q. Shen, W. M. Du, J. Hernandez, and N. J. Tao, “Dynamics of supercooled liquids and glasses: Comparison of experiments with theoretical predictions,” Z. Phys. B **103**, 501–519 (1997).

[8] W. Steffen, A. Patkowski, H. Gläser, G. Meier, and E. W. Fischer, “Depolarized-light-scattering study of orthoterphenyl and comparison with the mode-coupling model,” Phys. Rev. B **49**, 2992–3002 (1998).

[9] B. Schmidtke, N. Petzold, B. Potzschner, H. Weingartner, and E. A. Rossler, “Relaxation stretching, fast dynamics, and activation energy: A comparison of molecular and ionic liquids as revealed by depolarized light scattering,” J. Phys. Chem. **118**, 7108–7118 (2014).

[10] R. Torre, P. Bartolini, and R. Pick, “Time-resolved optical Kerr effect in a fragile glass-forming liquid, salol,” Phys. Rev. E **57**, 1912–1920 (1998).

[11] G. Hinze, D. D. Brace, S. D. Gottke, and M. D. Fayer, “A detailed test of mode-coupling theory on all time scales: Time domain studies of structural relaxation in a supercooled liquid,” J. Chem. Phys. **113**, 3723–3733 (2000).

[12] R. Kimmich and N. Fatkullin, “Self-diffusion studies by intra-and inter-molecular spin-lattice relaxometry using field-cycling: Liquids, plastic crystals, porous media, and polymer segments,” Prog. Nucl. Magn. Reson. Spectrosc. **101**, 18 (2017).

[13] M. Flämig, M. Hofmann, N. Fatkullin, and E. A. Rössler, “NMR relaxometry: The canonical case of glycerol,” J. Phys. Chem. B **124**, 1557–1570 (2020).

[14] M. Becher, A. Lichtinger, R. Minikejew, M. Vogel, and E. A. Rössler, “NMR relaxometry accessing the relaxation spectrum in molecular glass formers,” Int. J. Mol. Sci. **23**, 5118 (2022).

[15] M. Paluch, J. Knapik, Z. Wojnarowska, A. Grzybowski, and K. L. Ngai, “Universal behavior of dielectric responses of glass formers: Role of dipole-dipole interactions,” Phys. Rev. Lett. **116**, 025702 (2016).

[16] A. I. Nielsen, T. Christensen, B. Jakobsen, K. Niss, N. B. Olsen, R. Richert, and J. C. Dyre, “Prevalence of approximate $\sqrt{t}$ relaxation for the dielectric α process in viscous organic liquids,” J. Chem. Phys. **130**, 154508 (2009).

[17] T. Körber, R. Stäglich, C. Gainaru, R. Böhmer, and E. A. Rössler, “Systematic differences in the relaxation stretching of polar molecular liquids probed by dielectric vs magnetic resonance and photon correlation spectroscopy,” J. Chem. Phys. **153**, 124510 (2020).

[18] C. Gainaru, R. Kahlau, E. A. Rössler, and R. Böhmer, “Evolution of excess wing and β-process in simple glass formers,” J. Chem. Phys. **131**, 184510 (2009).

[19] K. L. Ngai, P. Lunkenheimer, C. Leon, U. Schneider, R. Brand, and A. Loidl, “Nature and properties of the Johari–Goldstein β-relaxation in the equilibrium state of a class of glass-formers,” J. Chem. Phys. **115**, 1405–1413 (2001).

[20] E. A. Rössler and M. Becher, “Glass spectrum, excess wing phenomenon, and master curves in molecular glass formers: A multi-method approach,” J. Chem. Phys. **160**, 074501 (2024).

[21] A. Brodin, R. Bergman, J. Mattsson, and E. A. Rössler, “Light scattering and dielectric manifestations of secondary relaxations in molecular glassformers,” Eur. Phys. J. B-Condens. Matter **36**, 349 (2003).

[22] A. Brodin and E. A. Rössler, “Universal and non-universal features of the dynamic susceptibility of supercooled liquids,” J. Phys.: Condens. Matter **18**, 8481–8492 (2006).

[23] A. Brodin, C. Gainaru, V. Porokhonskyy, and E. A. Rössler, “Evolution of dynamic susceptibility in molecular glass formers—A critical assessment,” J. Phys.: Condens. Matter **19**, 205104 (2007).

[24] F. Pabst, J. P. Gabriel, T. Böhmer, P. Weigl, A. Helbling, T. Richter, P. Zourchang, T. Walther, and T. Blochowicz, "Generic structural relaxation in supercooled liquids," J. Phys. Chem. Lett. **12**, 3685–3690 (2021).

[25] F. Pabst, A. Helbling, J. Gabriel, P. Weigl, and T. Blochowicz, "Dipole-dipole correlations and the Debye process in the dielectric response of nonassociating glass forming liquids," Phys. Rev. E **102**, 010606 (2020).

[26] J. P. Gabriel, P. Zourchang, F. Pabst, A. Helbling, P. Weigl, T. Böhmer, and T. Blochowicz, "Intermolecular cross-correlations in the dielectric response of glycerol," Phys. Chem. Chem. Phys. **22**, 11644–11651 (2020).

[27] T. Böhmer, F. Pabst, J. P. Gabriel, and T. Blochowicz, "Dipolar order controls dielectric response of glass-forming liquids," Phys. Rev. Lett. **132**, 206101 (2024).

[28] T. Böhmer, F. Pabst, J. P. Gabriel, R. Zeißler, and T. Blochowicz, "On the spectral shape of the structural relaxation in supercooled liquids," J. Chem. Phys. **162**, 120902 (2025).

[29] K. Koperwas and M. Paluch, "Computational evidence for the crucial role of dipole cross-correlations in polar glass-forming liquids," Phys. Rev. Lett. **129**, 025501 (2022).

[30] K. Koperwas, J. Gapiński, Z. Wojnarowska, A. Patkowski, and M. Paluch, "Experimental examination of dipole-dipole cross-correlations by dielectric spectroscopy, depolarized dynamic light scattering, and computer simulations of molecular dynamics," Phys. Rev. E **109**, 034608 (2024).

[31] P.-M. Déjardin, S. V. Titov, and Y. Cornaton, "Linear complex susceptibility of long-range interacting dipoles with thermal agitation and weak external ac fields," Phys. Rev. B **99**, 024304 (2019).

[32] D. V. Matyushov and R. Richert, "From single-particle to collective dynamics in supercooled liquids," J. Phys. Chem. Lett. **14**, 4886–4891 (2023).

[33] N. Petzold and E. A. Rössler, "Light scattering study on the glass former o-terphenyl," J. Chem. Phys. **133**, 124512 (2010).

[34] Y.-H. Hwang and G. Q. Shen, "A study of α-relaxation in ortho-terphenyl by photon correlation spectroscopy," J. Phys.: Condens. Matter **11**, 1453 (1999).

[35] Y. Yang and K. A. Nelson, "T_c of the mode coupling theory evaluated from impulsive stimulated light scattering on salol," Phys. Rev. Lett. **74**, 4883–4886 (1995).

[36] P. Lunkenheimer and A. Loidl, "Dielectric spectroscopy of glass-forming materials: α-relaxation and excess wing," Chem. Phys. **284**, 205–219 (2002).

[37] J. Wiedersich, N. Surovtsev, and E. A. Rössler, "A comprehensive light scattering study of the glass former toluene," J. Chem. Phys. **113**, 1143–1153 (2000).

[38] J. Wiedersich, N. V. Surovtsev, V. N. Novikov, E. Rössler, and A. P. Sokolov, "Light scattering spectra of fast relaxation in silica and CKN glasses," Phys. Rev. B **64**, 064207 (2001).

[39] A. Brodin and E. A. Rössler, "Depolarized light scattering study of glycerol," Eur. Phys. J. B **44**, 3 (2005).

[40] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).

[41] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).

[42] C. J. F. Böttcher and P. Bordewijk, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1973), Vol. 2.

[43] R. Kahlau, D. Kruk, V. N. Novikov, and E. A. Rössler, "Generalization of the Cole–Davidson and Kohlrausch functions to describe the primary response of glass-forming systems," J. Phys.: Condens. Matter **22**, 365101 (2010).

[44] C. P. Lindsey and G. D. Patterson, "Detailed comparison of the Williams–Watts and Cole–Davidson functions," J. Chem. Phys. **73**, 3348–3357 (1980).

[45] B. Schmidtke, N. Petzold, R. Kahlau, and E. A. Rössler, "Reorientational dynamics in molecular liquids as revealed by dynamic light scattering: From boiling point to glass transition temperature," J. Chem. Phys. **139**, 84504 (2013).

[46] B. Schmidtke and E. A. Rössler, "Depolarized light scattering spectra of molecular liquids: Described in terms of mode coupling theory," J. Chem. Phys. **141**, 044511 (2014).

[47] J. Wuttke, J. Hernandez, G. Li, G. Coddens, H. Z. Cummins, F. Fujara, W. Petry, and H. Sillescu, "Neutron and light scattering study of supercooled glycerol," Phys. Rev. Lett. **72**, 3052–3055 (1994).

[48] H. Z. Cummins, Y. H. Hwang, G. Li, W. M. Du, W. Losert, and G. Q. Shen, "Relaxation dynamics in orthoterphenyl: Comparing β_K from extended mode coupling theory and phenomenological analyses," J. Non-Cryst. Solids **235–237**, 254–267 (1998).

[49] S. D. Gottke, D. D. Brace, G. Hinze, and M. D. Fayer, "Time domain optical studies of dynamics in supercooled *o*-Terphenyl: Comparison to mode coupling theory on fast and slow time scales," J. Phys. Chem. B **105**, 238 (2001).

[50] G. Fytas, C. H. Wang, D. Lilge, and T. Dorfmüller, "Homodyne light beating spectroscopy of *o*-terphenyl in the supercooled liquid state," J. Chem. Phys. **75**, 4247–4255 (1981).

[51] S. V. Adichtchev, S. Benkhof, T. Blochowicz, V. N. Novikov, E. Rössler, C. Tschirwitz, and J. Wiedersich, "Anomaly of the nonergodicity parameter and crossover to white noise in the fast relaxation spectrum of a simple glass former," Phys. Rev. Lett. **88**, 055703 (2002).

[52] W. M. Du, G. Li, H. Z. Cummins, M. Fuchs, J. Toulouse, and L. A. Knauss, "Light-scattering study of the liquid-glass transition in propylene carbonate," Phys. Rev E **49**, 2192–2205 (1994).

[53] G. Li, W. M. Du, A. Sakai, and H. Z. Cummins, "Light-scattering investigation of α and β relaxation near the liquid-glass transition of the molecular glass salol," Phys. Rev. A **46**, 3343–3356 (1992).

[54] L. Comez, S. Corezzi, D. Fioretto, H. Kriegs, A. Best, and W. Steffen, "Slow dynamics of salol: A pressure-and temperature-dependent light scattering study," Phys. Rev. E **70**, 011504 (2004).

[55] G. Hinze, R. S. Francis, and M. D. Fayer, "Translational–rotational coupling in supercooled liquids: Heterodyne detected density induced molecular alignment," J. Chem. Phys. **111**, 2710–2719 (1999).

[56] W. Götze, "Recent tests of the mode-coupling theory for glassy dynamics," J. Phys.: Condens. Matt. **11**, A1–A45 (1999).

[57] T. Blochowicz, C. Tschirwitz, S. Benkhof, and E. A. Rössler, "Susceptibility functions for slow relaxation processes in supercooled liquids and the search for universal relaxation patterns," J. Chem. Phys. **118**, 7544–7555 (2003).

[58] W. Schnauss, F. Fujara, and H. Sillescu, "The molecular dynamics around the glass transition and in the glassy state of molecular organic systems: A ^{2}H nuclear magnetic resonance (NMR) study," J. Chem. Phys. **97**, 1378–1389 (1992).

[59] A. Kudlik, S. Benkhof, T. Blochowicz, C. Tschirwitz, and E. Rössler, "The dielectric response of simple organic glass formers," J. Mol. Struct. **479**, 201–218 (1999).

[60] R. Richert, K. Duvvuri, and L.-T. Duong, "Dynamics of glass-forming liquids. VII. Dielectric relaxation of supercooled *tris*-naphthylbenzene, squalane, and decahydroisoquinoline," J. Chem. Phys. **118**, 1828 (2003).

[61] T. Körber, F. Krohn, C. Neuber, H.-W. Schmidt, and E. A. Rössler, "Reorientational dynamics of highly asymmetric binary non-polymeric mixtures—A dielectric spectroscopy study," Phys. Chem. Chem. Phys. **23**, 7200–7212 (2021).

[62] J. Hintermeyer, A. Herrmann, R. Kahlau, C. Goiceanu, and E. A. Rössler, "Molecular weight dependence of glassy dynamics in linear polymers revisited," Macromolecules **41**, 9335–9344 (2008).

[63] B. Pötzschner, F. Mohamed, C. Bächer, E. Wagner, A. Lichtinger, R. Minikejew, K. Kreger, H.-W. Schmidt, and E. A. Rössler, "Non-polymeric asymmetric binary glass-formers. I. Main relaxations studied by dielectric, ^{2}H NMR, and ^{31}P NMR spectroscopy," J. Chem. Phys. **146**, 164503 (2017).

[64] N. B. Olsen, T. Christensen, and J. C. Dyre, "Time-temperature superposition in viscous liquids," Phys. Rev. Lett. **86**, 1271–1274 (2001).

[65] S. Wiebel and J. Wuttke, "Structural relaxation and mode coupling in a non-glassforming liquid: Depolarized light scattering in benzene," New J. Phys. **4**, 56 (2002).

[66] H. Cang, V. N. Novikov, M. D. Fayer, and M. D. Fayer, "Experimental observation of a nearly logarithmic decay of the orientational correlation function in supercooled liquids on the picosecond-to-nanosecond time scales," Phys. Rev. Lett. **90**, 197401 (2003).

[67] G. Li, N. Tso, L. V. Hong, H. Z. Cummins, C. Dreyfus, M. Hebbache, R. M. Pick, and J. Vagner, "Acoustic anomaly and the Landau free energy of incommensurate K_2SeO_4," Phys. Rev. B **42**, 4406 (1990).

[68] N. V. Surovtsev, J. A. H. Wiedersich, V. N. Novikov, E. Rössler, and A. P. Sokolov, "Light-scattering spectra of fast relaxation in glasses," Phys. Rev. B **58**, 14 888–14 891 (1998).

[69] J. Gapiński, W. Steffen, A. Patkowski, A. P. Sokolov, A. Kisliuk, U. Buchenau, M. Russina, F. Mezei, and H. Schober, "Spectrum of fast dynamics in glass forming liquids: Does the 'knee' exist?," J. Chem. Phys. **110**, 2312–2315 (1999).

[70] H. C. Barshilia, G. Li, G. Q. Shen, and H. Z. Cummins, "Depolarized light scattering spectroscopy of $Ca_{0.4}$ $K_{0.6}(NO_3)_{1.4}$: A reexamination of the 'knee,'" Phys. Rev. E **59**, 5625–5628 (1999).

[71] G. Li, W. M. Du, X. K. Chen, H. Z. Cummins, and N. J. Tao, "Testing mode-coupling predictions for α and β relaxation in $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ near the liquid-glass transition by light scattering," Phys. Rev. A **45**, 3867–3879 (1992).

[72] L. Comez, D. Fioretto, L. Palmieri, L. Verdini, P. A. Rolla, J. Gapinski, T. Pakula, A. Patkowski, W. Steffen, and E. W. Fischer, "Light-scattering study of a supercooled epoxy resin," Phys. Rev. E **60**, 3086–3096 (1999).

[73] A. Brodin and E. A. Rössler, "Depolarized light scattering versus optical Kerr effect spectroscopy of supercooled liquids: Comparative analysis," J. Chem. Phys. **125**, 114502 (2006).

[74] A. Brodin and E. A. Rössler, "Depolarized light scattering versus optical Kerr effect. II. Insight into the dynamic susceptibility of molecular liquids," J. Chem. Phys. **126**, 244508 (2007).

[75] A. Patkowski, W. Steffen, H. Nilgens, E. W. Fischer, and R. Pecora, "Depolarized dynamic light scattering from three low molecular weight glass forming liquids: A test of the scattering mechanism," J. Chem. Phys. **106**, 8401–8408 (1997).

[76] G. Q. Shen, J. Toulouse, S. Beaufils, B. Bonello, Y. H. Hwang, P. Finkel, J. Hernandez, M. Bertault, M. Maglione, C. Ecolivet, and H. Z. Cummins, "Experimental studies of the liquid-glass transition in trimethylheptane," Phys. Rev E **62**, 783–792 (2000).

[77] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).

[78] J. Gabriel, F. Pabst, and T. Blochowicz, "Debye process and β-Relaxation in 1-Propanol probed by dielectric spectroscopy and depolarized dynamic light scattering," J. Phys. Chem. B **121**, 8847–8853 (2017).

[79] M. P. Eastwood, T. Chitra, J. M. Jumper, K. Palmo, A. C. Pan, and D. E. Shaw, "Rotational relaxation in *ortho*-Terphenyl: Using atomistic simulations to bridge theory and experiment," J. Phys. Chem. B **117**, 12898–12907 (2013).

[80] M. Vogel, private communication, Darmstadt (2025).