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A QM/MM and QM/QM/MM study of Kerr, Cotton–Mouton and Jones linear birefringences in liquid acetonitrile

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QM/MM and QM/QM/MM protocols are applied to the *ab initio* study of the three linear birefringences Kerr, Cotton–Mouton, and Jones, as shown by acetonitrile in the gas and pure liquid phases. The relevant first-order properties as well as linear, quadratic, and cubic frequency-dependent response functions were computed using time-dependent Kohn–Sham density-functional theory with use of the standard CAM-B3LYP functional. In the liquid phase, a series of room temperature (293.15 K) molecular dynamics snapshots were selected, for which averaged values of the observables were obtained at an optical wavelength of 632.8 nm. The birefringences were computed for electric and magnetic induction fields corresponding to the laboratory setup previously employed by Roth and Rikken in Phys. Rev. Lett. **85**, 4478, (2000). Under these conditions, acetonitrile is shown to exhibit a weak Jones response — in fact roughly 6.5 times smaller than the limit of detection of the apparatus employed in the measurements mentioned above. A comparison is made with the corresponding gas-phase results and an assessment is made of the index of measurability, estimating the degree of overlap of the three birefringences in actual measurements. For acetonitrile, it is shown that this index is a factor of 3.6 and 6.7 larger than that of methylcyclopentadienyl-Mn-tricarbonyl and cyclohexadienyl-Fe-tricarbonyl, respectively — two compounds reported in Phys. Rev. Lett. **85**, 4478, (2000) to exhibit a strong Jones signal.

1 Introduction

In particular during the last 15 years, a renewed interest has emerged for the Jones¹ and magnetoelectric^{2,3} birefringences. This optical effect reveals itself as an anisotropy of the refractive index as linearly polarized light traverses a medium perpendicular to externally applied electric and magnetic fields aligned parallel to one another (in the Jones linear birefringence) or perpendicular to each other (in the magnetoelectric linear birefringence), with the anisotropy being defined as the difference between polarization components tilted $\pm 45^\circ$ relative the external fields, and perpendicular to the direction of the incoming light

in Jones birefringence^{1,4} and coinciding with those of the two external fields in magnetoelectric birefringence.^{2,3} Although the two birefringences require different experimental setups, they are completely equivalent from the point of view of theory,^{4–6} and from now on we will only concentrate on Jones linear birefringence. The very first observation of the effect was conducted on liquids by Rikken *et al.*,⁷ and the endeavors at performing measurements on gaseous samples have since intensified. Reports have been made, presenting highly sophisticated and sensitive experimental equipment capable of observing the aforementioned effect in gases,⁸ and possibly also quantum vacuum-induced birefringence.⁹

Two closely related birefringences — denoted as the Kerr^{10–12} and Cotton–Mouton^{13–17} effects — are observable in the presence of electric (Kerr) or magnetic (Cotton–Mouton) fields. Here, the external fields are also aligned perpendicular to the direction of the incoming light, and the anisotropy is defined as the difference between the polarization components parallel and perpendicular to the external field, while maintaining perpendicularity with the direction of propagation of the light beam, as for the

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magneto-electric effect. The Kerr and Cotton–Mouton birefringences are therefore unavoidably present in any attempt at measuring the Jones effect. Since the magnitudes of the former ones are rooted in electric and magnetic dipole moment couplings, while the latter stems from higher-order moments, the Kerr and Cotton–Mouton effects will naturally be stronger and may screen the observation of the Jones effect. Thus, calculations will provide essential aid to identify ideal candidates, exhibiting possibly weak Kerr and Cotton–Mouton responses, but strong Jones signals.

In ref. 18 a series of systems (noble gases, furan homologues and monosubstituted benzenes) were theoretically analyzed in the gas phase. Property correlations were found between the birefringence and the atomic radius (for noble gases), or the dipole moment and the empirical para-Hammett constant (for benzene and eleven of its mono-substituted derivatives). The Jones constant (a measure of Jones birefringence) displayed a nearly perfect quadratic dependence on the atomic radius of the noble gases, and a linear dependence on both the dipole moment and the para-Hammett constant — with notable exceptions of nitroso- and nitrobenzene. Also based on the conclusions of ref. 18, it was clear that, with the current experimental facilities, it would prove a difficult task to perform a quantitative determination of the Jones birefringence in the gas phase.

On the other hand, it can be argued that the enhancement of the Jones effect in the condensed phase may help reach the conditions for detectability. Therefore, we have decided to investigate a system that could easily be subject to a measurement of linear birefringences in the liquid phase. A readily available and commonly employed system is acetonitrile — a popular solvent with a high dielectric constant (38.8) and a dipole moment of 3.92 D.¹⁹ Here we study its responses in both gas and liquid phases, determining the magnitude of the Kerr, Cotton–Mouton and Jones birefringences. To accurately describe the property in the liquid phase, we resort to the polarizable embedding (PE)^{20,21} and polarizable density embedding (PDE)²² response theory approaches, which are based on QM/MM and QM/QM/MM methodologies, respectively. This is to our knowledge the first application of such methodologies to mixed electric and magnetic high-order, frequency-dependent properties. Our aim is to reliably determine whether acetonitrile is a good candidate for an experimental attempt at observing the Jones birefringence in either of the two phases.

2 Theoretical methodology

In this section, the basic equations relating the observables to molecular response-theory tensors are given while the reader can consult the work of Rizzo and co-workers for a more comprehensive treatment.^{15,17,23–25}

2.1 The observables

The optical effects of interest in the present work are the Kerr, Cotton–Mouton and Jones linear birefringences. In a linear birefringence, the refractive index n of a medium builds an anisotropy Δn as light propagates through it in the presence of external elec-

tric E and/or magnetic induction B field(s) (or field gradients) aligned perpendicularly to the direction of the propagation of the light.¹⁷ As a consequence, a phase difference ϕ emerges, depending on the path length l , the wavelength of the radiation λ (related to the circular frequency ω by the relationship $\lambda = 2\pi c_0/\omega$, where c_0 denotes the speed of light *in vacuo*), and the refractive-index anisotropy. For small angles it can be written as

$$\phi \approx \frac{2\pi l}{\lambda} \Delta n \quad (1)$$

where, for the three linear birefringences identified by the subscripts K (Kerr), CM (Cotton–Mouton) and J (Jones), we have

$$\Delta n_K = n_{\parallel} - n_{\perp} = k_K \lambda E_x^2 \quad (2)$$

$$\Delta n_{CM} = n_{\parallel} - n_{\perp} = k_{CM} \lambda B_x^2 \quad (3)$$

$$\Delta n_J = n_{+45^\circ} - n_{-45^\circ} = k_J \lambda E_x B_x \quad (4)$$

for which the wavelength-dependent constants k_K , k_{CM} , and k_J have been introduced. In eqns (2)–(4) above, E_x and B_x are the electric and magnetic field-strengths along the x -axis — it is assumed that the light propagates along the z -axis. Since the observation of the Jones birefringence is of main interest here, we adopt the quantity

$$\eta_{\text{mea}} = \frac{|\Delta n_J|}{\sqrt{|\Delta n_K \Delta n_{CM}|}} = \frac{|k_J|}{\sqrt{|k_K k_{CM}|}} \quad (5)$$

as an index of measureability, as introduced by Rikken and co-workers in ref. 7. The larger the value of η_{mea} , the more intense is Jones response relative to the Kerr and Cotton–Mouton birefringences.

2.2 Definitions of response functions and operators

Tensors involved in the calculation of the Kerr effect are the permanent electric dipole moment, static and dynamic electric-dipole polarizability, and corresponding first- and second-order hyperpolarizabilities:

$$\mu_\alpha^{(0)} = \langle \hat{\mu}_\alpha \rangle \quad (6)$$

$$\alpha_{\alpha\beta}(0;0) = \alpha_{\alpha\beta}^{(0)} = -\langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta \rangle \rangle_0 \quad (7)$$

$$\alpha_{\alpha\beta}(-\omega; \omega) = \alpha_{\alpha\beta} = -\langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta \rangle \rangle_\omega \quad (8)$$

$$\beta_{\alpha\beta\gamma}(-\omega; \omega, 0) = \beta_{\alpha\beta\gamma} = \langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{\mu}_\gamma \rangle \rangle_{\omega,0} \quad (9)$$

$$\gamma_{\alpha\beta\gamma\delta}(-\omega; \omega, 0, 0) = \gamma_{\alpha\beta\gamma\delta} = -\langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{\mu}_\gamma, \hat{\mu}_\delta \rangle \rangle_{\omega,0,0} \quad (10)$$

To lowest order and in addition to the dynamic polarizability given in eqn (8), tensors involved in the description of the Cotton–Mouton effect¹⁶ are the magnetizability and hypermag-

netizabilities:

$$\xi_{\alpha\beta}^{(0)} = \langle \langle \hat{m}_\alpha; \hat{m}_\beta \rangle \rangle_0 - \langle \xi_{\alpha\beta} \rangle \quad (11)$$

$$\eta_{\alpha\beta\gamma\delta}^{\text{dia}}(-\omega; \omega, 0) = \eta_{\alpha\beta\gamma\delta}^{\text{dia}} = \langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{\xi}_{\gamma\delta} \rangle \rangle_{\omega,0} \quad (12)$$

$$\eta_{\alpha\beta\gamma\delta}^{\text{para}}(-\omega; \omega, 0, 0) = \eta_{\alpha\beta\gamma\delta}^{\text{para}} = -\langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{m}_\gamma, \hat{m}_\delta \rangle \rangle_{\omega,0,0} \quad (13)$$

Finally, in addition to the dipole moment in eqn (6), the anisotropy yielded by the Jones birefringence involves

$$G_{\alpha\beta\gamma}^{\text{dia}}(-\omega; \omega) = G_{\alpha\beta\gamma}^{\text{dia}} = -\langle \langle \hat{\mu}_\alpha; \hat{\xi}_{\beta\gamma}^{\text{dia}} \rangle \rangle_\omega \quad (14)$$

$$G_{\alpha\beta\gamma\delta}^{\text{dia}}(-\omega; \omega, 0) = G_{\alpha\beta\gamma\delta}^{\text{dia}} = \langle \langle \hat{\mu}_\alpha; \hat{\xi}_{\beta\gamma}^{\text{dia}}, \hat{\mu}_\delta \rangle \rangle_{\omega,0} \quad (15)$$

$$G_{\alpha\beta\gamma}^{\text{para}}(-\omega; \omega, 0) = G_{\alpha\beta\gamma}^{\text{para}} = \langle \langle \hat{\mu}_\alpha; \hat{m}_\beta, \hat{m}_\gamma \rangle \rangle_{\omega,0} \quad (16)$$

$$G_{\alpha\beta\gamma\delta}^{\text{para}}(-\omega; \omega, 0, 0) = G_{\alpha\beta\gamma\delta}^{\text{para}} = -\langle \langle \hat{\mu}_\alpha; \hat{m}_\beta, \hat{m}_\gamma, \hat{\mu}_\delta \rangle \rangle_{\omega,0,0} \quad (17)$$

$$a'_{\alpha\beta\gamma\delta}(-\omega; \omega, 0) = a'_{\alpha\beta\gamma\delta} = i\langle \langle \hat{\mu}_\alpha; \hat{q}_{\beta\gamma}, \hat{m}_\delta \rangle \rangle_{\omega,0} \quad (18)$$

$$a'_{\alpha\beta\gamma\delta\epsilon}(-\omega; \omega, 0, 0) = a'_{\alpha\beta\gamma\delta\epsilon} = -i\langle \langle \hat{\mu}_\alpha; \hat{q}_{\beta\gamma}, \hat{m}_\delta, \hat{\mu}_\epsilon \rangle \rangle_{\omega,0,0} \quad (19)$$

Above, single brackets $\langle \langle \hat{X} \rangle \rangle$ indicate first-order properties of the ground state, whereas double brackets $\langle \langle \hat{X}; \hat{Y}, \dots \rangle \rangle$ are used for linear, quadratic, and cubic frequency-dependent response functions.²⁶ The operators involved in eqns (6)–(19) are the electric dipole operator,

$$\hat{\mu}_\alpha = -e \sum_i \hat{r}_{i\alpha} \quad (20)$$

the traced electric quadrupole operator,

$$\hat{q}_{\alpha\beta} = -e \sum_i \hat{r}_{i\alpha} \hat{r}_{i\beta} \quad (21)$$

the magnetic dipole operator,

$$\hat{m}_\alpha = -\frac{e}{2m_e} \sum_i (\hat{r}_i \times \hat{p}_i)_\alpha \quad (22)$$

and the diamagnetic susceptibility operator,

$$\hat{\xi}_{\alpha\beta}^{\text{dia}} = \frac{e^2}{4m_e} \sum_i (\hat{r}_{i\alpha} \hat{r}_{i\beta} - \hat{r}_{i\delta} \hat{r}_{i\delta} \delta_{\alpha\beta}) \quad (23)$$

2.3 Kerr effect

For a molecular system exhibiting a permanent electric dipole, including the non-vanishing contributions up to quadratic order in the electric field-strength E_x , the Kerr constant [see eqn (2)] assumes the form

$$k_K = \frac{N}{60\epsilon_0\lambda} \times \left\{ K_0 + \frac{K_1}{T} + \frac{K_2}{T^2} \right\} \quad (24)$$

where ϵ_0 is the electric constant and N is the number density which for an ideal gas can be written as

$$N_{\text{gas}} = \frac{P}{kT} \quad (25)$$

with P denoting the pressure and k Boltzmann's constant. The terms involved in eqn (24) are

$$K_0 = \gamma_K \quad (26)$$

$$K_1 = \frac{1}{k} ([\beta\mu] + [\alpha\alpha]) \quad (27)$$

$$K_2 = \frac{1}{k^2} [\alpha\mu\mu] \quad (28)$$

and the tensor contractions taking place in eqns (26)–(28) are

$$\gamma_K = 3\gamma_{\alpha\beta\alpha\beta} - \gamma_{\alpha\alpha\beta\beta} \quad (29)$$

$$[\beta\mu] = 6\beta_{\alpha\beta\alpha}\mu_\beta^{(0)} - 2\beta_{\alpha\alpha\beta}\mu_\beta^{(0)} \quad (30)$$

$$[\alpha\alpha] = 3\alpha_{\alpha\beta}\alpha_{\alpha\beta}^{(0)} - \alpha_{\alpha\alpha}\alpha_{\beta\beta}^{(0)} \quad (31)$$

$$[\alpha\mu\mu] = 3\alpha_{\alpha\beta}\mu_\alpha^{(0)}\mu_\beta^{(0)} - \alpha_{\alpha\alpha}\mu_\beta^{(0)}\mu_\beta^{(0)} \quad (32)$$

See eqns (6)–(10) for tensor definitions regarding eqns (29)–(32). The anisotropy of the refractive index is

$$\Delta n_K = \frac{NE_x^2}{60\epsilon_0} \times \left\{ K_0 + \frac{K_1}{T} + \frac{K_2}{T^2} \right\} \quad (33)$$

From the definitions above, the following expressions can be used to obtain the anisotropy Δn_K and the Kerr constant k_K when the units for E_x , N , T and λ are those given explicitly in square brackets, whereas the terms K_n ($n=0,1,2$) are to be entered in atomic units $\times K^n$:

$$\Delta n_K = 1.17372 \times 10^{-55} \times (E_x[\frac{V}{m}])^2 \times N[\text{m}^{-3}] \quad (34)$$

$$\times \left\{ K_0 + \frac{K_1}{T[K]} + \frac{K_2}{(T[K])^2} \right\}$$

$$k_K[\frac{\text{m}}{\sqrt{2}}] = 1.17372 \times 10^{-46} \times \frac{N[\text{m}^{-3}]}{\lambda[\text{nm}]} \quad (35)$$

$$\times \left\{ K_0 + \frac{K_1}{T[K]} + \frac{K_2}{(T[K])^2} \right\}$$

Note that for an ideal gas at 1 atm and 293.15 K, $N = 2.50348 \times 10^{25} \text{ m}^{-3}$. Our reference for the value of fundamental physical constants is Ref. 27.

2.4 Cotton–Mouton effect

According to its usual definition, the Cotton–Mouton effect contains two main terms. Discarded additional terms, either contribute insignificantly (like those representing the anisotropy arising from the oscillating optical magnetic field) or depend on the permanent magnetic dipole moment that vanish in closed-shell

systems.¹⁶ Taking such approximations into account to quadratic order in the magnetic field-strength B_x , the Cotton–Mouton constant assumes the form

$$k_{\text{CM}} = \frac{N}{60\epsilon_0\lambda} \times \left\{ C_0 + \frac{C_1}{T} \right\} \quad (36)$$

The two terms in eqn (36) are defined as

$$C_0 = \eta_{\text{para}} + \eta_{\text{dia}} \quad (37)$$

$$C_1 = \frac{1}{k} [\alpha\xi] \quad (38)$$

where

$$\eta_{\text{para}} = 3\eta_{\alpha\beta\alpha\beta}^{\text{para}} - \eta_{\alpha\alpha\beta\beta}^{\text{para}} \quad (39)$$

$$\eta_{\text{dia}} = 3\eta_{\alpha\beta\alpha\beta}^{\text{dia}} - \eta_{\alpha\alpha\beta\beta}^{\text{dia}} \quad (40)$$

$$[\alpha\xi] = 3\alpha_{\alpha\beta}\xi_{\alpha\beta}^{(0)} - \alpha_{\alpha\alpha}\xi_{\beta\beta}^{(0)} \quad (41)$$

See eqns (8) and (11)–(13) for tensor definitions regarding eqns (39)–(41). The anisotropy of the refractive index is

$$\Delta n_{\text{CM}} = \frac{NB_x^2}{60\epsilon_0} \times \left\{ C_0 + \frac{C_1}{T} \right\} \quad (42)$$

Furthermore, the anisotropy Δn_{CM} and the Cotton–Mouton constant k_{CM} can be obtained by using the units for B_x , N , T and λ explicitly given in square brackets, whereas the terms C_n ($n=0,1$) should be entered in atomic units $\times K^n$:

$$\Delta n_{\text{CM}} = 5.61740 \times 10^{-43} \times (B_x[\text{T}])^2 \times N[\text{m}^{-3}] \times \left\{ C_0 + \frac{C_1}{T[\text{K}]} \right\} \quad (43)$$

$$k_{\text{CM}}[\text{m}^{-1}\text{T}^{-2}] = 5.61740 \times 10^{-34} \times \frac{N[\text{m}^{-3}]}{\lambda[\text{nm}]} \times \left\{ C_0 + \frac{C_1}{T[\text{K}]} \right\} \quad (44)$$

2.5 Jones effect

For molecules lacking permanent magnetic dipole moment, but exhibiting a permanent electric dipole moment, the Jones constant [see eqn (4)] is defined for non-vanishing contributions to lowest order in the field strengths E_x and B_x as

$$k_{\text{J}} = \frac{N}{30\epsilon_0 c_0 \lambda} \times \left\{ J_0 + \frac{J_1}{T} \right\} \quad (45)$$

where

$$J_0 = \mathcal{G}_{\text{para}}^{(3)} + \mathcal{G}_{\text{dia}}^{(3)} + \mathcal{A}'^{(3)} \quad (46)$$

$$J_1 = \frac{1}{k} \left(\mathcal{G}_{\text{para}}^{(2)} + \mathcal{G}_{\text{dia}}^{(2)} + \mathcal{A}'^{(2)} \right) \quad (47)$$

for which

$$\mathcal{G}_{\text{para}}^{(3)} = 3G_{\alpha\beta\alpha\beta}^{\text{para}} + 3G_{\alpha\beta\beta\alpha}^{\text{para}} - 2G_{\alpha\alpha\beta\beta}^{\text{para}} \quad (48)$$

$$\mathcal{G}_{\text{dia}}^{(3)} = 3G_{\alpha\beta\alpha\beta}^{\text{dia}} + 3G_{\alpha\beta\beta\alpha}^{\text{dia}} - 2G_{\alpha\alpha\beta\beta}^{\text{dia}} \quad (49)$$

$$\mathcal{A}'^{(3)} = -\frac{\omega}{2} \epsilon_{\alpha\beta\gamma} (a'_{\alpha\beta\delta\delta\gamma} + a'_{\alpha\beta\delta\gamma\delta}) \quad (50)$$

$$\mathcal{G}_{\text{para}}^{(2)} = \mu_{\alpha}^{(0)} (3G_{\alpha\beta\beta}^{\text{para}} + 3G_{\beta\beta\alpha}^{\text{para}} - 2G_{\beta\beta\alpha}^{\text{para}}) \quad (51)$$

$$\mathcal{G}_{\text{dia}}^{(2)} = \mu_{\alpha}^{(0)} (3G_{\alpha\beta\beta}^{\text{dia}} + 3G_{\beta\beta\alpha}^{\text{dia}} - 2G_{\beta\beta\alpha}^{\text{dia}}) \quad (52)$$

$$\mathcal{A}'^{(2)} = -\frac{\omega}{2} \epsilon_{\alpha\beta\gamma} (\mu_{\gamma}^{(0)} a'_{\alpha\beta\delta\delta} + \mu_{\delta}^{(0)} a'_{\alpha\beta\delta\gamma}) \quad (53)$$

Above, $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita alternating tensor. See eqns (6) and (14)–(19) for tensor definitions regarding eqns (48)–(53). The anisotropy of the refractive index is

$$\Delta n_{\text{J}} = \frac{NB_x E_x}{30\epsilon_0 c_0} \times \left\{ J_0 + \frac{J_1}{T} \right\} \quad (54)$$

which, along with the Jones constant k_{J} , are obtained through the relationships

$$\Delta n_{\text{J}} = 3.74752 \times 10^{-51} \times E_x \left[\frac{\text{V}}{\text{m}} \right] \times B_x[\text{T}] \times N[\text{m}^{-3}] \times \left\{ J_0 + \frac{J_1}{T[\text{K}]} \right\} \quad (55)$$

$$k_{\text{J}}[\text{V}^{-1}\text{T}^{-1}] = 3.74752 \times 10^{-42} \times \frac{N[\text{m}^{-3}]}{\lambda[\text{nm}]} \times \left\{ J_0 + \frac{J_1}{T[\text{K}]} \right\} \quad (56)$$

when the units for B_x , E_x , N , T and λ are those given explicitly in square brackets, whereas the terms J_n ($n=0,1$) are entered in atomic units $\times K^n$.

2.6 Local-field factors

The general view of a non-magnetic material such as a pure acetonitrile liquid is that induced magnetic moments by optical or static fields are negligible and no magnetic local-field effects need to be taken into account. However, the electric equivalent is certainly not negligible and should be accounted for. Moreover, in this study, the level of approximation is such that electric quadrupole-induced local-field effects are assumed to be negligible. The Onsager dielectric liquid model,²⁸ having the external fields as the reference fields, applies *cavity-field factors*, referred to in this work as *local-field factors* (LFF), to all dipole operators in any particular response function and first-order properties, resulting in effective response functions of the sort

$$\langle \langle \hat{\mu}_{\alpha}^{\omega\sigma}; \hat{\mu}_{\beta}^{\omega_1}, \hat{\mu}_{\gamma}^{\omega_2}, \hat{\mu}_{\delta}^{\omega_3} \rangle \rangle_{\text{eff}} = \quad (57)$$

$$f(\omega_{\sigma})f(\omega_1)f(\omega_2)f(\omega_3) \times \langle \langle \hat{\mu}_{\alpha}^{\omega\sigma}; \hat{\mu}_{\beta}^{\omega_1}, \hat{\mu}_{\gamma}^{\omega_2}, \hat{\mu}_{\delta}^{\omega_3} \rangle \rangle$$

for which the LFF are given by

$$f(\omega) = \frac{3}{2\epsilon_r(\omega) + 1} \quad (58)$$

where $\epsilon_r(\omega)$ is the relative permittivity. To linear order, the dynamic relative electric permittivity relates to the corresponding dynamic linear response function according to

$$\epsilon_r(\omega) = 1 + \frac{N}{\epsilon_0} \langle \alpha(\omega) \rangle \quad (59)$$

where $\langle \alpha(\omega) \rangle$ is the isotropically averaged frequency dependent molecular polarizability [see eqn (8)]. Due to nuclear alignment effects in the presence of a static electric field, the static electric relative permittivity is generally much higher than the dynamic one, in particular for highly dipolar samples. However, we currently do not model this process, and can only obtain theoretical values for the dynamic permittivity. Thus, we make use of experimentally measured values for $\epsilon_r(0)$ [measured at 298.5 K by Srinivasan and Kay²⁹] and $\epsilon_r(\omega)$ [measured at 293.15 K for $\lambda = 587.8$ nm by P. Pacák³⁰]. The latter one may be extrapolated to our wavelength of choice, 632.8 nm, by the dispersion formula obtained at 300 K by Moutzouris *et al.*³¹ Ultimately, considering the fact that $f(\omega) = f(-\omega)$, the effective anisotropies [see eqns (2)–(4)] become

$$\Delta n_{K,\text{eff}} = f(\omega)^2 f(0)^2 \times \Delta n_K \quad (60)$$

$$\Delta n_{\text{CM},\text{eff}} = f(\omega)^2 \times \Delta n_{\text{CM}} \quad (61)$$

$$\Delta n_{J,\text{eff}} = f(\omega) f(0) \times \Delta n_J \quad (62)$$

3 Computational details

3.1 Morphology

The molecular geometry of the isolated molecule (gas phase) has been optimized at a level of Kohn–Sham density-functional theory (DFT)^{32,33} in conjunction with the B3LYP exchange-correlation functional³⁴ and Dunning’s correlation-consistent basis set cc-pVTZ³⁵ using the quantum chemistry package DALTON.³⁶

The force field (OPLS) and acetonitrile box of liquid were obtained from www.virtualchemistry.org, referring to a benchmark study³⁷ for which the density had equilibrated at $T = 293.15$ K. Using GROMACS,^{38–41} an NVT MD simulation ran for 100 ns (1 fs time step) using periodic-boundary conditions and a Nosé–Hoover thermostat,^{42,43} from which 100 frames were extracted with intervals of 2 ps.

As mentioned, the molecular density in the gas phase is significantly lower compared to the liquid phase. For acetonitrile in particular, the density for the box of liquid is $N_{\text{liq}} = 1.11782 \times 10^{28} \text{ m}^{-3}$ (762.0 kg m^{-3}), corresponding to a ratio of

$$\frac{N_{\text{liq}}}{N_{\text{gas}}} = 446.51 \quad (63)$$

While this value of the liquid density is the one being used whenever the liquid density is referred to in the calculations, it should be noted that its value is 2.7% below the experimental value of 782.4 kg m^{-3} .⁴⁴

3.2 PE and PDE potentials

The choice of regions in the PE calculations is shown graphically in Fig. 1, where a droplet of liquid acetonitrile consisting of 1006 molecules is depicted. A quantum mechanical treatment is chosen for the red molecule placed in the center. The blue shell, with a radius of 1.5 nm, includes about 190 molecules (the exact number depends on the liquid configuration of each frame). In this region, atom-centered point charges and isotropic polarizabilities describe each molecule. The gray–green outer region enclosing the previous one extends to 2.68 nm, and only point charges at each atom were included in it. The atom-centered charges were obtained using the restrained electrostatic potential (RESP) scheme⁴⁵ with an ESP taken from Gaussian 09⁴⁶ at the B3LYP/6-31+G*⁴⁷ level of theory and fitted using the AmberTools’ Antechamber module.^{48,49} Atom-centered isotropic polarizabilities were obtained from the MOLCAS package⁵⁰ employing the LoProp scheme⁵¹ — also at the B3LYP/6-31+G* level of theory. The charges and polarizabilities were obtained for an isolated optimized acetonitrile molecule (gas phase).

Fig. 1 Spherical cut-out of liquid acetonitrile consisting of 1006 molecules. The red molecule placed in the center is treated quantum mechanically. The blue shell has a radius of 1.5 nm and consists of roughly 190 molecules depending on the liquid configuration of each frame, with point charges and isotropic polarizabilities at each atom. It is enclosed by the gray–green shell with a radius of 2.68 nm where only point charges at each atom are adopted.

The parameters were held constant for all molecules, motivated by the fact that geometric distortions are very small. In Fig. 2, the geometrical fluctuations at room temperature are illustrated for a reference solute molecule and 100 statistically uncorrelated snapshots. The bond angle fluctuates by no more than 0.1 deg and the bond lengths vary by less than 0.2 pm. Such fluctuations are minimal and do not significantly alter the charge distributions.

In the PDE calculations, the acetonitrile molecules in the inner shell explicitly exhibited their exact electron densities. Furthermore, due to technical reasons in the PDE calculations, all molecules (except the central fully quantum-mechanically treated molecule) were described by the atom-centered anisotropic po-

larizabilities. The electron density of each molecule was obtained from a B3LYP/6-31+G* calculation performed in Dalton³⁶, whereas the polarizabilities were produced using the Lo-Prop scheme⁵¹ also based on a B3LYP/6-31+G* calculation.

3.3 Response properties

Response properties for the isolated molecule and the liquid were calculated with the quantum-chemistry package DALTON³⁶ using PELib⁵² and Gen1Int⁵³ for the PE and PDE calculations. The CAM (Coulomb attenuated method)⁵⁴ extension to the B3LYP functional³⁴ was used in all cases. Basis sets employed for the isolated molecule corresponded to augmented variants of Dunning's correlation-consistent basis sets,³⁵ with increasing levels of augmentation (from double to quadruple) for cardinal numbers ranging from D to Q. The study of basis set convergence in the gas phase, see Table 1, led to the use of the double-augmented triple- ζ basis set in the liquid-phase study.

In the gas phase, the linear magnetizability related to the Cotton–Mouton effect included gauge-invariant atomic orbitals (GIAO), commonly also referred to as London orbitals. In the PE and PDE liquid environments, however, no such orbitals were available. Furthermore, the calculation of cubic response functions has not been implemented yet for the PDE model, thus any contributions to the three studied birefringences based on cubic response functions are absent for the PDE description of the liquid.

4 Results and discussion

4.1 Frontier analysis

In Fig. 3 we illustrate a frontier analysis, i.e., response property convergence with respect to the extension of the polarizable-shell radius for a single snapshot in the PE model. This study is similar to what has been presented before in the literature for other molecular properties.^{55–58} A zero shell radius refers to a non-polarizable medium and the negative radius refers to gas phase (isolated molecule) values. The various contributions to the Kerr effect, cf. eqns (26)–(28) for definitions, to the Cotton–Mouton effect, cf. eqns (37) and (38), and to the Jones effect, cf. eqns (46) and (47), can be safely claimed to be converged at a radius of approximately 1.5 nm. As mentioned above, this means that about 190 molecules need to be included in the polarizable region in order to obtain an appropriate description of the wide array of linear and nonlinear, electric and magnetic, response properties that are addressed in the present study.

In comparing gas- and liquid-phase data, it is seen that the use of a nonpolarizable embedding model provides in most cases a qualitatively correct picture of the solvation effects, in particular for the contributions involving the electric quadrupole operator in Jones birefringence ($\mathcal{A}^{(2)}$, $\mathcal{A}^{(3)}$ and $\mathcal{G}_{\text{dia}}^{(2)}$) and the $[\beta\alpha]$ and $[\alpha\mu\mu]$ contribution to Kerr.

We note that response properties obtained in the PDE environment were obtained for a fully polarizable solvent. However, the response properties produced in the PE environment are converged with respect to the radius of the polarizable shell, and may therefore legitimately be compared to the PDE results.

Fig. 2 Fluctuations of the C–C–N bond angle (top panel), C–C bond length (middle panel), and C–N bond length (bottom panel) for a selected solute molecule over 100 snapshots.

Fig. 3 Convergence of contributions to Kerr effect (top panel), Cotton–Mouton effect (mid panel), and Jones effect (bottom panel), with respect to the size of the polarizable-shell radius in the PE model. The dashed vertical line at 1.5 nm denotes the shell radius used for the calculation of MD room temperature averaged properties [see Fig. 4]. The data at the extreme left in each panel refer to gas phase results.

4.2 Statistical convergence

Alongside the QM/MM procedure to describe the medium, one hundred statistically uncorrelated snapshots were extracted from a room temperature molecular dynamics simulation to provide an appropriate averaging with respect to molecular configurations in the pure liquid. With structures adopted from these snapshots, the frequency-dependent linear, quadratic and cubic response functions given in eqns (6)–(19) were determined in the PE environment, while linear and quadratic response functions were also computed in the PDE environment. Fig. 4 shows the convergence behavior of the different contributions to the Kerr, Cotton–Mouton, and Jones effects with respect to an increasing number of snapshots/configurations in the PE model. Likewise, convergence of response properties in the PDE environment, where only the dominant contributions that depend on linear and quadratic response functions have been obtained, is shown in Fig. 5.

It is evident that a sizable number of snapshots, at least 60 or 70, needs to be included in the averaging procedure in order to reach the plateau where all contributions can be considered converged. This observation applies also if one focuses on the dominant contributions to the birefringences, namely K_2/T^2 , C_1/T and J_1/T for Kerr, Cotton–Mouton, and Jones, respectively. Since, as illustrated in Fig. 2, the intra-molecular motion is very small for a molecule as rigid as acetonitrile, the large property variations seen in Fig. 4 and Fig. 5 are predominantly due to direct solute–solvent interactions. A continuum approach is for this reason a less viable alternative.

Fig. 4 Convergence of contributions to the Kerr, Cotton–Mouton, and Jones effects for liquid acetonitrile with respect to number of room temperature MD snapshots in the PE model.

Fig. 5 Convergence of contributions to the Kerr, Cotton–Mouton, and Jones effects for liquid acetonitrile with respect to number of room temperature MD snapshots in the PDE model.

4.3 Local-field screening

Experimentally measured values of the relative permittivity are $\epsilon_r(0) = 35.95$ [measured at 298.5 K, see ref. 29] and $\epsilon_r(\omega) = 1.794$ [measured at 293.15 K and $\lambda = 587.8$ nm, see ref. 30], where the dynamic permittivity has been extrapolated to $\lambda = 632.8$ nm [formula obtained at 300 K, see ref. 31]. Using these permittivities, the effective anisotropies, eqns (60)–(62), are scaled by factors corresponding to

$$f(0) = 4.12 \times 10^{-2} \quad (64)$$

$$f(\omega) = 65.39 \times 10^{-2} \quad (65)$$

that results in global scaling factors of

$$\begin{aligned} \Delta n_{K,\text{eff}} &= f(\omega)^2 f(0)^2 \times \Delta n_K \\ &= 7.24 \times 10^{-4} \times \Delta n_K \end{aligned} \quad (66)$$

$$\begin{aligned} \Delta n_{CM,\text{eff}} &= f(\omega)^2 \times \Delta n_{CM} \\ &= 4.28 \times 10^{-1} \times \Delta n_{CM} \end{aligned} \quad (67)$$

$$\begin{aligned} \Delta n_{J,\text{eff}} &= f(\omega) f(0) \times \Delta n_J \\ &= 2.69 \times 10^{-2} \times \Delta n_J \end{aligned} \quad (68)$$

Taking the average of the calculated dynamic electric permittivity [see eqn (59)] over the 100 liquid snapshots yields a value of 1.661 in the PE environment, and 1.630 in the PDE environment. Evidently, our prediction of the dynamic permittivity for the pure acetonitrile liquid at 632.8 nm in the PE and PDE models are $\approx 7\%$ and $\approx 9\%$, respectively, off the experimental value of 1.794.

Regarding what scaling magnitudes can be expected, the Kerr effect is reduced by a little more than three orders of magnitudes, Cotton–Mouton is scaled by roughly half an order of magnitude, and the Jones effect is dampened by slightly less than two orders of magnitudes.

4.4 Molecular properties

In Table 1, we summarize results for the individual underlying contributions to the Kerr, Cotton–Mouton, and Jones birefringences of acetonitrile in gas and liquid phase for which the chosen optical wavelength is 632.8 nm and the temperature is set to 293.15 K. In the liquid phase, presented data refer to the converged averaged values after 100 snapshots in the PE and PDE models.

In the gas-phase calculations, we have employed correlation-consistent basis sets ranging from double to quadruple augmentation with cardinal numbers ranging from double to quadruple. Double- ζ basis sets are not expected to be sufficiently accurate for properties involving nonlinear, frequency-dependent response functions and this is clearly revealed in the calculations of, in particular, the terms in the Cotton–Mouton and Jones birefringences involving magnetic dipole and electric quadrupole interactions. The lowest order basis set that provides reliable results for all considered properties is the doubly-augmented

triple- ζ basis set and this is also the reason why we have chosen this basis set in the liquid-phase calculations that are considerably more expensive due to the need to perform an averaging over MD snapshot configurations and, to a lesser extent, due to the coupling between the QM and MM regions. Results at the double augmented triple- ζ level are in close agreement with those provided by the much larger quadruple augmented quadruple- ζ basis set — for the dominating contributions, we note: 3.94×10^8 vs. 3.94×10^8 for K_2/T^2 (largely dominating Kerr birefringence), -7.49×10^4 vs. -7.54×10^4 for C_1/T (Cotton–Mouton), -1.64×10^5 vs. -1.63×10^5 for J_1/T (Jones).

Concerning the linear magnetizability which in part constitutes the dominating contribution to the Cotton–Mouton effect [see eqn (38)], we observe a very slow convergence for basis sets without London-type orbitals (numbers not presented in Table 1) in both gas and liquid phases. However, the difference between gas-phase values without London orbitals and PE or PDE liquid-phase values is in fact converged at the doubly-augmented triple- ζ basis set. Thus, in an attempt to circumvent this convergence problem, we estimate the PE and PDE liquid-phase results for the temperature-dependent Cotton–Mouton term, C_1/T , as the gas-phase value with London orbitals, added to the observed shift from gas-phase calculations without London orbitals to liquid-phase calculations in the PE and PDE environments, respectively.

We note that, in absolute terms, all contributions — except the dominating Cotton–Mouton contribution — are initially enhanced in passing from gas phase to the liquid PE environment. Comparing data for liquid and gas phases at the level of a doubly-augmented triple- ζ basis set, we note that, for Kerr, K_2/T^2 increases by 54%, K_1/T by 114%, and K_0 by 23%; for Cotton–Mouton, C_1/T is reduced by 7% while C_0 is amplified by 38%; finally, for Jones, J_1/T increases by 21% and J_0 is amplified by 387%.

As was mentioned in the section for computational details, the calculation of cubic response functions is not yet implemented within our PDE environment module, and therefore the K_0 , C_0 and J_0 contributions are not presented at this level of approximation. Nonetheless, the dominant lower-order, temperature-dependent contributions were obtained. According to the PDE results, our estimations in going from gas to liquid phase are signal amplifications of 45% and 52% for the molecular Kerr properties K_2/T^2 and K_1/T^1 , respectively, 5% reduction for the Cotton–Mouton property C_1/T , and a 5% signal increase of the Jones property J_1/T .

Generally, the shift in going from gas phase to liquid phase is overestimated to a certain extent by the PE model in relation to the PDE model, but the overall picture is consistently preserved.

4.5 Anisotropies

The anisotropies and birefringence constants that are discussed here and listed in Table 1 are done so with local-field factors, as expressed in eqns (66)–(68). It is thus always the effective constants and anisotropies that are being presented, with the 'eff' subscript scrapped.

Table 1 Kerr, Cotton–Mouton, and Jones quantities for a photon wavelength of 632.8 nm and a temperature of 293.15 K. For the calculation of the birefringence constants and the anisotropies we assume an electric field-strength of 2.5×10^5 V/m and a magnetic field-strength of 17 T. Double to quadruple augmentation and cardinal numbers D to Q are combined for the isolated molecule (gas phase), while double augmentation and triple- ζ were used for the average over 100 frames taken in the liquid phase. Note that results reported for birefringence constants and corresponding anisotropies for the case of the polarizable embedding (PE) and polarizable-density embedding (PDE) models include local-field factors. Quantities k_K , k_{CM} , and k_J , are given in units of $[mV^{-2}]$, $[m^{-1}T^{-2}]$, and $[V^{-1}T^{-1}]$, respectively. Remaining quantities are given in atomic units with exception for the dimensionless anisotropies (Δn) and index of measureability (η_{mea}).

Basis	K_0 ($\times 10^4$)	K_1/T ($\times 10^5$)	K_2/T^2 ($\times 10^8$)	k_K ($\times 10^{-15}$)	Δn_K ($\times 10^{-11}$)	C_0 ($\times 10^2$)	C_1/T ($\times 10^4$)	k_{CM} ($\times 10^{-6}$)	Δn_{CM} ($\times 10^{-10}$)	J_0 ($\times 10^2$)	J_1/T ($\times 10^5$)	k_J ($\times 10^{-14}$)	Δn_J ($\times 10^{-14}$)	η_{mea} ($\times 10^{-4}$)
<u>Gas</u>														
dDZ	4.65	7.83	3.93	1.83	7.24	5.57	−7.52	−1.66	−3.03	−8.09	−1.65	−2.45	−6.60	4.45
tDZ	4.52	7.78	3.93	1.83	7.24	5.97	−8.44	−1.86	−3.40	−8.43	−1.65	−2.45	−6.60	4.20
qDZ	4.76	7.72	3.93	1.83	7.24	7.13	−8.52	−1.88	−3.43	−13.72	−1.64	−2.45	−6.59	4.18
dTZ	4.62	7.77	3.94	1.83	7.25	8.07	−7.49	−1.65	−3.01	−1.63	−1.64	−2.43	−6.53	4.42
tTZ	4.55	7.76	3.94	1.83	7.25	8.20	−7.48	−1.64	−3.01	−1.59	−1.64	−2.43	−6.53	4.42
qTZ	4.53	7.76	3.94	1.83	7.25	8.27	−7.37	−1.62	−2.96	−1.91	−1.64	−2.43	−6.53	4.46
dQZ	4.53	7.77	3.94	1.83	7.25	8.16	−7.49	−1.65	−3.01	−1.47	−1.63	−2.42	−6.52	4.41
tQZ	4.60	7.78	3.94	1.83	7.25	8.19	−7.49	−1.65	−3.01	−1.49	−1.63	−2.42	−6.52	4.41
qQZ	4.54	7.76	3.94	1.83	7.25	8.22	−7.54	−1.66	−3.03	−1.62	−1.63	−2.42	−6.52	4.40
<u>Liquid (PE)</u>														
dTZ	5.68	16.63	6.05	0.91	3.60	11.11	−6.99	−0.65	−1.20	−7.93	−1.98	−35.33	−95.01	144.74
<u>Liquid (PDE)</u>														
dTZ		11.79	5.70	0.86	3.39		−7.14	−0.68	−1.24		−1.73	−30.85	−82.97	127.93

The adopted photon wavelength is $\lambda = 632.8$ nm, and other assumptions include an electric field-strength of 2.5×10^5 V/m, a magnetic induction field-strength of 17 T and a temperature of 293.15 K. These values were chosen to correspond to a realistic proposal for an experimental verification.^{7,18}

We consider the PDE description of the liquid average over 100 snapshots to be our final estimates of the three linear birefringences. Consequently, the Kerr constant and anisotropy is found to be $k_K = 0.86 \times 10^{-15}$ and $\Delta n_K = 3.39 \times 10^{-11}$, respectively. Furthermore, the Cotton–Mouton observables are found to be $k_{CM} = -0.68 \times 10^{-6}$ and $\Delta n_{CM} = -1.24 \times 10^{-10}$. Finally, the Jones constant and the anisotropy become $k_J = -30.85 \times 10^{-14}$ and $\Delta n_J = -82.97 \times 10^{-14}$, respectively. In ref. 7 from the year of 2000, Roth and Rikken claim to have an apparatus limited to a resolution of $k_J = 2.0 \times 10^{-12}$, where they also reported findings of $k_J = 47 \times 10^{-12}$ and $k_J = 22 \times 10^{-12}$ for metallic complexes methylcyclopentadienyl-Mn-tricarbonyl and cyclohexadienyl-Fer-tricarbonyl (amongst other systems), that acted as the strongest sources of Jones birefringence. In light of these numbers and this technological restraint, the Jones constant predicted in this study for pure liquid acetonitrile is roughly 6.5 times too small for detection. It is possible, however, that the development of optical lines and detection apparata which has occurred in the last decade in the fast evolving field of laser spectroscopies might warrant a success in a possible attempt at a quantitative measurement of the Jones birefringence of acetonitrile.

4.6 Index of measureability

The last column of Table 1 presents the measureability index, η_{mea} , that is defined in eqn (5). Comparing gas-phase results

with results from the liquid average in the PDE environment, there is a great amplification in this measureability index. This seems largely to be due to the huge screening effect of the fields (local-field factors) suffered by the Kerr birefringence, in contrast to the lesser screening effect suffered by the Jones birefringence, since all individual contributions to the observables are of the same order going from gas to liquid. The measureability index, which is found to be 127.93×10^{-4} , is a factor of 3.6 greater than the best value found by Roth and Rikken in their study that sixteen years ago reported the first observation of magnetoelectric Jones birefringence⁷ ($\eta_{mea} = 36 \times 10^{-4}$ for a sample of methylcyclopentadienyl-Mn-tricarbonyl).

5 Conclusions

Quantum mechanics/molecular mechanics (QM/MM) and QM/QM/MM protocols have been applied to a first theoretical study of the three linear birefringences Kerr, Cotton–Mouton, and Jones, in the liquid phase. The relevant first-order properties, linear, quadratic, and cubic frequency-dependent response functions were calculated for acetonitrile in the form of a pure liquid by using time-dependent density-functional theory and the CAM-B3LYP functional. A series of molecular dynamics snapshots were considered as to obtain averaged values of the observables in a setup using an optical wavelength of 632.8 nm. The birefringence is computed at room temperature (293.15 K) for electric and magnetic induction fields corresponding to a setup previously employed in the laboratories (see ref. 7).

Comparison is made with gas-phase predictions and large enhancements are initially reported across the board for the underlying molecular properties in the liquid phase governed by the

PE model. However, the PE description of the liquid seems to be overestimating the effects as the more sophisticated description of the solvent density, the PDE model, generally predicts lower gas-to-liquid enhancements in contrast to the PE model.

Concerning measureability of Jones birefringence in liquid acetonitrile, it is found that this liquid exhibits a Jones response signal ($k_J = -30.85 \times 10^{-14}$) that is too weak for detection, according to the technological boundaries set up by Roth and Rikken back in 2000,⁷ and roughly 2 orders of magnitude lower than the best values reported for some metallic complexes. On the other hand, the index of measureability, estimating the degree of overlap of the three birefringences in measurements, is reported to be more than 3 times higher than the best value reported in ref. 7.

In conclusion, the Jones birefringence in liquid acetonitrile is predicted here to be about an order of magnitude too small for the detection apparatus employed in ref. 7, while at the same time suffering from little interference from the other two linear birefringences, Kerr and Cotton–Mouton, due to the very large measureability index.

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