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Molecular-dynamics study of liquid water in strong laser fields

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Effects of an intense laser field on liquid water are investigated by using classical molecular-dynamics computer simulations and a water model SPC-FP, which for the first time includes both flexible intramolecular bonds and instantaneous electronic polarization effects. Comparisons with the field-off system are made throughout. Under the influence of the strong external torque, both the liquid structure and the intramolecular geometry are distorted. These effects significantly change the dynamical behavior of the liquid compared with the field-off system. The presence of the intense electric field furthermore gives rise to a nonlinear response of the medium. We estimate the nonlinear index of refraction and give a brief discussion of self-focusing and supercontinuum generation.

I. INTRODUCTION

The recent development of high-power lasers and supercomputers allows one to study experimentally and theoretically responses of a molecular liquid to a strong electromagnetic field. Such responses reflect a competition of the natural thermal motion of the molecules with the aligning effect of the field and give rise to observable changes of the liquid structure, the thermodynamics, the transport properties, and the spectroscopic and dielectric characteristics. In a very strong field, some features of the molecular liquid, which are otherwise hidden, can be revealed.

The molecular-dynamics (MD) method has the advantage of providing an exact numerical solution of the many-body classical equations of motion. Through a comparison of the simulation results with corresponding experiments, the method then becomes a useful tool for testing existing models as to their utility in various types of problems [1]. It may also predict unknown properties, and this can pave the way for future advances in theory and experimental research.

Computer MD simulations describing the effects of an externally applied intense force field on a molecular liquid were initiated by Evans in a series of publications [2–5]. More recently, this type of investigation has been continued by others [6–8]. Much of this work focused attention on the resulting nonlinear dynamical effects.

One of the world's most important substances is liquid water, and since the seminal work of Barker and Watts [9] and Rahman and Stillinger [10], various bursts of activity attempting to cast further light on this problem have occurred. Beginning in the late 1980s, with the general accessibility of supercomputers, new activity in this area is increasing once more, with the use of more realistic water models than were possible in past works. However, the plethora of complexities associated with this substance gives rise to nearly prohibitive computer intensiveness, even with present-day supercomputer technology. Adequate statistics in simulations of liquid water under varying thermodynamic and interactive conditions, particularly in partial ensembles in the presence of localized perturbations, are sometimes difficult to achieve.

Using novel laboratory and moving frame cross correlation functions, the effects of a circularly polarized external field on a rigid five-site liquid-water model have been evaluated by Evans, Lie, and Clementi [6]. However, two modifications of this model seem essential when the applied field is strong relative to the random intermolecular interactions, and consequently when local anisotropy is of significance. These two modifications are the inclusion of (1) flexibility in the intermolecular geometry, and (2) instantaneously responsive dynamic electrical polarization.

In this paper, we investigate the effects of a linearly polarized external electrical field on a relatively simple liquid-water-like model developed in our laboratory [11]. This model, which we call SPC-FP, is a simple point-charge model of the type developed by Berendsen *et al.* [12], but which also encompasses flexibility (F) in intramolecular bonding and electronic polarization (P). This model has been optimized to give a reasonable description of the thermodynamic and dielectric properties of unperturbed bulk water at 298 K. It employs an ensemble of molecules, which in their isolated state have the correct gas-phase structure and dipole moment of the water molecule. Under the influence of liquid-state perturbations, an average molecular dipole moment and geometry in the liquid state are achieved that are in good agreement with these experimental liquid-state properties. However, as in most other water models, including polarizable ones [13,14], the liquid structure, as evidenced by the radial distribution functions (RDF), is not accurately represented. For example, the oxygen-oxygen first RDF peak may be too high and sharp, as they are in the much-used rigid ST2 [15] and TIP4P models [16], or, with a good first peak, the subsidiary peaks may be too flat or missing. This latter situation is the case with the SPC-FP model.

It is known that some of the faults in three-point models can be cured by using tighter angular-dependent interactions [17] than those intrinsically arising from the

Coulomb and Lennard-Jones terms in these models, and also by using anharmonic intramolecular potential functions [18], which allow larger molecular distortions and dipole moment changes under the influence of perturbations. However, our mission here is not to develop the ultimate three-point model for liquid water, but rather to assess in a computationally tractable way the combined effects of bond flexibility and instantaneously responsive polarizability on a liquid-water-like substance under strong electrical perturbations. The lessons learned from this type of calculation will be of value in future work where more realistic models of liquid water can be used.

II. MOLECULAR-DYNAMICS SIMULATION

The standard constant-volume MD algorithm [19,20] was modified by including a uniaxial electric field externally applied along the x axis of the laboratory frame

$$E(t)=E_0\sin\lambda t \ , \tag{1}$$

where $E_0=1$ V/Å and $\omega=0.2\pi\times10^{15}\ \mathrm{s}^{-1}$ (wavelength $\lambda=3\mu\mathrm{m}$, optical period 10 fs). This laser field generates an external mechanical torque on each molecule in the ensemble and consequently results in a tendency for its alignment.

To describe the electronic polarization effect, we employ a technique similar to that in earlier work [7,8,11]. The point charges in the SPC-FP model are instantaneously varied in magnitude according to the strength and direction of the total electric field to which the molecule is subjected. In the present problem this electrical field is a result of both the applied field along the x direction and fluctuating fields from the neighboring molecules. Since the strength of the fluctuating field at any given molecular site varies negligibly between the short integration time steps (0.25 fs) used, this procedure provides stable solutions without iterations [21]. The method is more approximate than that of Sprik and Klein [13], but is much simpler, allowing also in a tractable computational algorithm the introduction of bond flexibility, which we believe to be of equal importance as polarization. In fact, the results to be presented in this paper show that the interplay between bond flexibility and electronic polarization is required to attain a realistic picture.

Table I summarizes the molecular parameters used in the computation. Here, A and B are, respectively, the repulsive and attractive parameters in a 12-6 Lennard-Jones potential centered on each oxygen atom, q_i (i=O or H) correspond to the point charges of an isolated molecule, and α is the effective microscopic polarizability, from which the variations in the point charges are derived [11]. The long-range electrostatic interactions are corrected by the reaction field with conducting boundary condition [22]. This is an acceptable approximation for moderately to highly polar substances such as water. In addition, this method is computationally economical and results in almost identical dielectric properties compared with an Ewald-type lattice summation [23]. The simulation system contains 256 water molecules and is extended through periodic boundary conditions with the minimum image convention. The water molecules in the ensemble are geometrically flexible through the use of intramolecular harmonic binding potentials [24,25].

TABLE I. Parameters used for the intermolecular potential function. ϵ is the electron charge; the polarizability α is an effective quantity for the liquid state and differs from the gas-phase value of 1.444 Å^3 [31].

A (eV Å^{12})	B (eV Å^6)	$q_O^0(\epsilon)$	$q_H^0(\epsilon)$	α (Å^3)
30 158.482	26.036	-0.65	±0.325	1.271

A steady state can be reached when the systematic external torque is balanced by the stochastic intermolecular interactions. The temperature of the sample is maintained near 298 K by a continuous velocity-rescaling routine [26,27] executed on each atom in the system. The effect of this artificial thermostat effectively removes the extra deterministic contributions to the rotational, vibrational, and translational kinetic energies introduced by the strong external torque. Data are evaluated over 1.312×10^5 time steps, each having 0.25-fs duration. This short time step is necessary to preserve the fidelity of the motions of the low-mass hydrogen atoms and to allow accurate tracking of the high-frequency laser field. Also, as mentioned above, the short time step helps to keep successive variations of the point polarization charges to low values, providing stability of the computations without iterations. Depending on the type of data calculated, from 0.1–0.2 CPU seconds per time step are required on the CRAY YMP/832 at the Pittsburgh Supercomputing Center.

Field-off calculations, taken directly from Ref. [11] under identical thermodynamic conditions, are also reported, not only in order to compare with field-off experimental quantities in bulk water, thus providing an assessment of the faithfulness of the model, but also to compare the effects when there is no external field with those occurring when the field is present (field on).

III. LIQUID STRUCTURE

As a consequence of the molecular alignment in the field, the normal liquid structure is destroyed. As mentioned earlier, the second peak of the oxygen-oxygen RDF is too flat in the SPC-FP model, so this model is not very accurate for non-nearest-neighbor structure. However, for first neighbors, the results indicate very strong field effects on the latent nearest-neighbor bonding in the normal liquid. This strong effect can be seen from the radial distribution functions portrayed in Fig. 1. It is apparent that the first peaks of the O $\cdots$ O, O $\cdots$ H, and H $\cdots$ H RDF's become more prominent and shift towards shorter distances in the strong field. The molecular alignment apparently tends to destroy the existing structures in ordinary tetrahedral water groupings and forms new groupings with different configurations, including various "bifurcated" structures [28–30]. Both experiment [29] and theory [30] have demonstrated that the presence of a symmetrical or asymmetrical bifurcated OH_2:::OH_2 water-water bond is enhanced in a strong electrical field because of the tendency to form structures with large dipole moments. This effect is indicated in the O ⋯ H RDF of Fig. 1(b), where a 70% enhancement of the first peak intensity is observed. The intensity would be about 100% greater if all the local tetrahedral structures in the normal liquid were replaced by bifurcated structures in the perturbed liquid, so this is indeed a very large effect.

The enhancements and shifts of the radial distribution functions in the presence of an externally applied field can also be found in nonpolar, but polarizable, liquids such as carbon disulphide [7]. This compression phenomenon, which tends to squeeze out molecular atoms from regions normally having low radial density, seems therefore to be a general tendency.

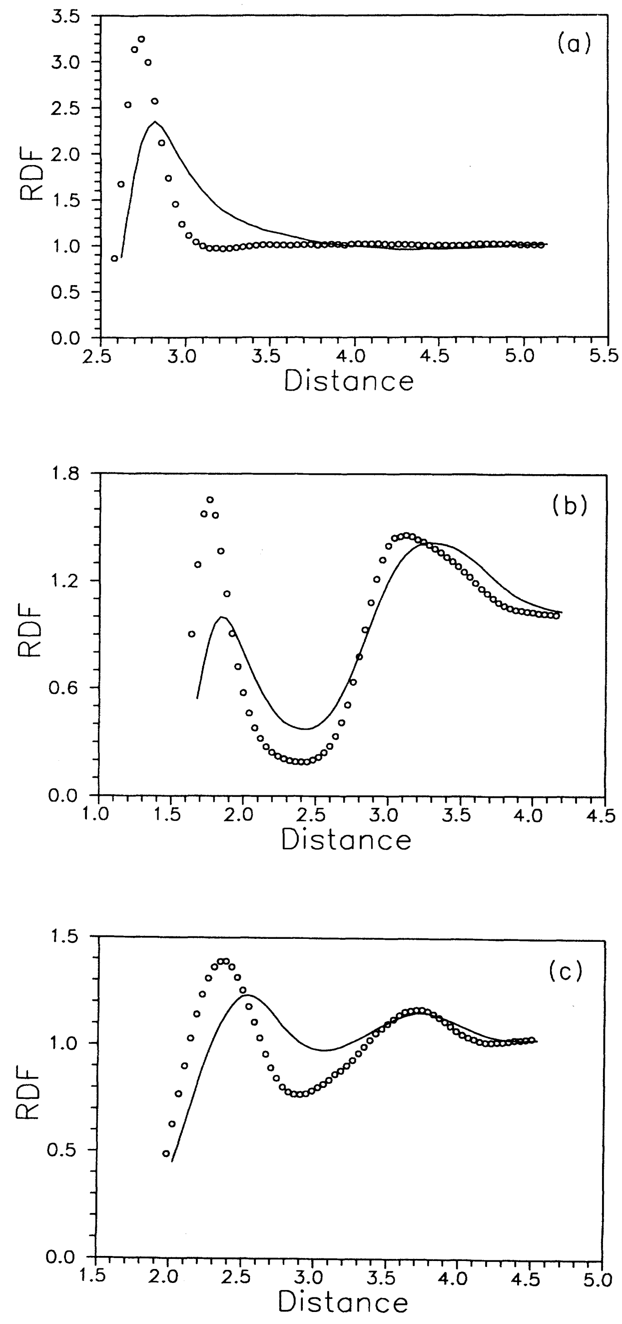

FIG. 1. Radial distribution functions. Solid curves, field-off ensemble; symbols, field-on ensemble. (a) O ⋯ O, (b) O ⋯ H, (c) H ⋯ H. Distance scales in angstroms.

Table II indicates the distortion of the intramolecular geometry upon application of the field. On average, the O—H bond length is stretched while the H—O—H bond angle contracts. These effects would be even more prominent if less stiff, more realistic anharmonic bond coupling were used [18]. Again, the effect is to increase the molecular dipole moment in the field.

Also given in Table II is the mean internal energy. This is an interesting parameter. Evans, Lie, and Clementi [6] have shown that the mean internal energy of their rigid five-site water model at equilibrium was raised by 40% from field-off to field-on conditions. However, the data given in Table II provide an opposite conclusion. This difference is caused directly by the inclusion of electric polarization and bond flexibility in the SPC-FP water model. While partial molecular alignment in the field has a tendency to bring like charges closer together, and thus to raise the internal energy, the simultaneously increased molecular dipole moment and the greater ability to form bifurcated bonds in the flexible model result in a net lowering of the energy. If the lowering of the entropy of water in the field is not too great, the rather strong stabilization of the internal energy would mean that field-on water has a lower vapor pressure than normal liquid water. This may be an experimentally observable property.

The effect of the induced dipole moment on the internal energy is clearly demonstrated by comparing Fig. 2, where the time evolution of the mean internal energy is plotted, with Fig. 3, which depicts the induced-dipole-moment autocorrelation functions (IDMCF). The internal energy variations in Fig. 2 follow almost exactly the variations of the longitudinal component (parallel to the field) of the induced dipole moment in Fig. 3, the minimum energy occurring when the induced dipole moment reaches a maximum. Both of these variations track the 10-fs optical period of the laser.

IV. DYNAMICAL PROPERTIES

Distortion of the normal liquid structure in the field substantially changes the dynamical properties of water.

TABLE II. Properties of SPC-FP water in field-off and field-on states.

	$\langle r_{OH} \rangle$ Å	$\langle (H—O—H) \rangle$ (deg)	U (eV)	$\bar{\mu}$ (D)	G_K
field off[a]	0.966	102.8	−0.430	2.4	
field off[b]	0.966	101.0	−0.426	2.44	2.65
field on[c]	0.976	100.1	−0.570	2.60	57.38

[a] Experiment, liquid phase 0.1 MPa and 298 K [31].

[b] SPC-FP model, Ref. [11]. The density of this model at 298 K is 0.997 g/cm^3 and the pressure is about 1 atm (0.1 MPa). In the absence of liquid-state interactions, the parameters used in this model also give the correct gas-phase structure and dipole moment.

[c] This work.

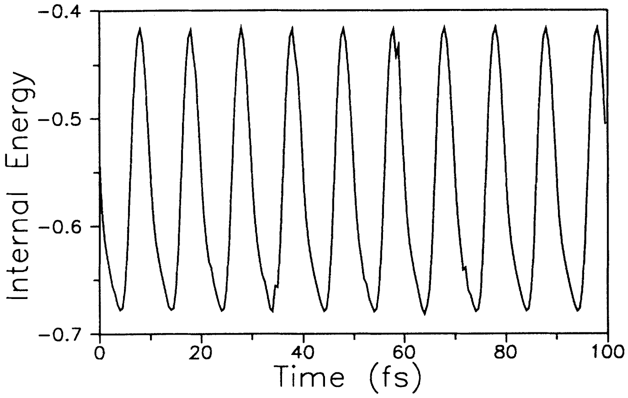

FIG. 2. Time evolution of the internal field-on energy (in units of eV). Note that the optical period of the laser is 10 fs.

As depicted in Fig. 4, the center-of-mass velocity autocorrelation functions (CMVCF) for the longitudinal and transverse components are completely different. Both deviate from the unperturbed CMVCF, even though the applied electric field does not have a direct influence on the motion of the center of mass of an electrically neutral molecule. Perturbations along the field direction are transmitted to orthogonal directions by the anisotropic intermolecular coupling. It is also clear from Fig. 4 that the perturbed liquid structure strongly resists the diffusion of water molecules along the field direction. This is partly caused by the formation of bifurcated bonds, which, as mentioned above, give rise to stronger intermolecular interactions in the field than do ordinary linear hydrogen bonds, $HOH \cdots OH_2$. The 10-fs laser period is also noticeable in the longitudinal component of the CMVCF.

The orientational autocorrelation functions (OCF) of the molecular bisector vector are compared in Fig. 5 for the longitudinal and transverse components in the field-on and field-off ensembles. The much slower relaxation of the field-on OCF, particularly for the longitudinal component, illustrates the molecular alignment effect introduced by the external torque. Also apparent in Fig. 5 are small-amplitude oscillations of the field-on OCF's, reflecting the fact that these moleculars vibrate around their equilibrium positions in concert with the 10-fs laser period as they attempt to reorient. The different dynamical behaviors for components parallel and orthogonal to the field provide direct evidence that the linearly polarized laser beam gives rise to a measurable anistropy in the molecular liquid.

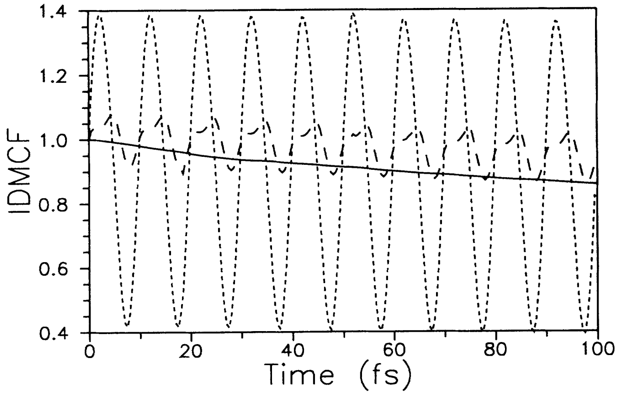

FIG. 3. Time-dependent induced-dipole-moment autocorrelation functions. The solid curves is the field-off ensemble; the long dashes represent components transverse to the field $\frac{1}{2}[\langle M_y(0)M_y(t)\rangle/\langle M_y(0)^2\rangle+\langle M_z(0)M_z(t)\rangle/\langle M_z(0)^2\rangle]$; and the short dashes represent the longitudinal component along the field direction $\langle M_x(0)M_x(t)\rangle/\langle M_x(0)^2\rangle$. The angular brackets represent the ensemble average.

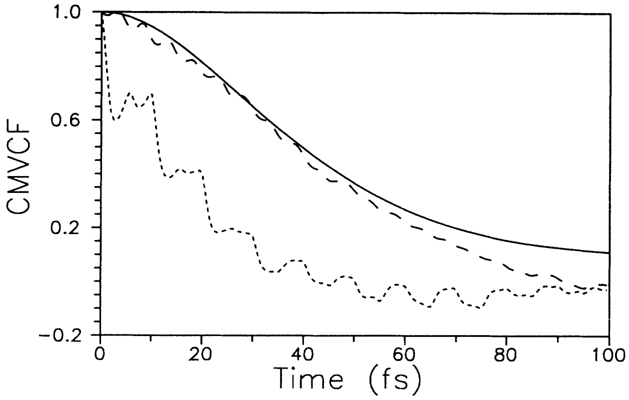

FIG. 4. Time-dependent center-of-mass translational velocity autocorrelation functions. The solid curve is the field-off ensemble, the long dashes represent the transverse components, while the short dashes are the longitudinal components. The definitions of the longitudinal and transverse components are as in the Fig. 3 caption.

The liquid-state intramolecular vibrational spectrum can be calculated from the Fourier transform of the VCF's for the oxygen and hydrogen atoms [11]. Owing

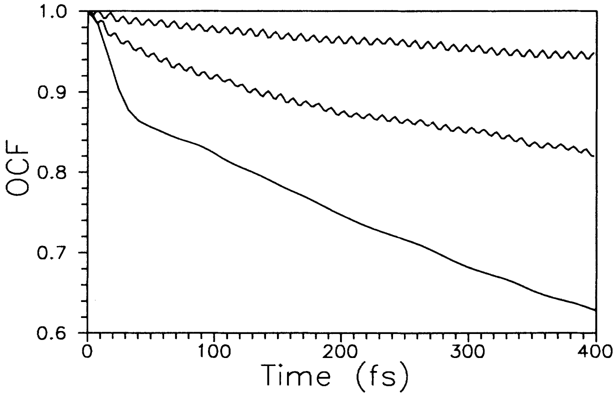

FIG. 5. Time-dependent orientational autocorrelation functions of the molecular bisector vector. Upper curve, longitudinal component; middle curve, transverse component; lower curve, field-off ensemble. The longitudinal and transverse components are defined as in the Fig. 3 caption.

to the structural changes caused by the intense laser light, the vibrational frequencies of the water molecules are depressed from 1802 to 1764 cm^{-1} for the bending mode, and from 3875 to 3527 cm^{-1} and 4080 to 3779 cm^{-1} for the symmetric and asymmetric stretching modes, respectively. These changes are significant. The corresponding gas phase values are 1594.59, 3656.65, and 3755.79 cm^{-1} [31]. Our assumption of purely classical harmonic intramolecular forces is the source of too high a value for each of the frequencies. However, we believe that the frequency depressions by the laser field should be experimentally observable, and the calculated differences would very likely be close to the true values. A part of the field effect lowering the vibrational frequencies must result from molecular alignment, which creates predominantly bifurcated OH_2:::OH_2 bonds having longer O—H bond lengths and smaller H—O—H bond angles. In fact, a correlation between the red shifts of the stretching frequencies and the average elongation of the O—H bonds in a type of field-perturbed water has already been observed in some concentrated electrolyte solutions [32].

In addition to the above peaks in the vibrational spectrum, we observe a new strong band centered at 3441 cm^{-1}. This is the resonant frequency of oscillating dipole moments in the water molecules. These oscillating dipoles induced by the incident beam act as sources of secondary radiation, such as Rayleigh and Raman scattering [33].

V. NONLINEAR OPTICS

The dielectric properties of a substance can be significantly changed in an intense laser field. This effect can give rise to a nonlinear response of certain optical characteristics. In this section we investigate at a molecular level the nonlinear response of liquid water to an intense laser beam. Though our work here is still in a preliminary stage, to the best of our knowledge, this is the first molecular-dynamics study concerning nonlinear-optical phenomena in water.

The autocorrelation functions of the longitudinal and transverse components of the induced dipole moment per molecule were compared in Fig. 3 with the same quantities measured for the field-off ensemble. When there is no external field, the induced dipole moment arises only from fields derived from neighboring molecules. In the laser field, not only the longitudinal autocorrelation function, but also, somewhat less clearly, the transverse ones are seen to oscillate with the period of the laser light oscillations. The transfer of information between longitudinal and transverse components occurs because of mode coupling. As would be expected, however, the transverse components of the induced dipole moment caused by the field are affected to a much less extent. Also, a small time lag is apparent, since mode coupling involves nuclear motions which are intrinsically slower than the electronic response. These kinds of effects were also found in our earlier simulations of flexible-polarizable carbon disulfide in laser fields [8].

In dielectrics, the electric displacement D is related to the applied electric field strength E and the polarization vector P through the fundamental relation [34] $P=D-\epsilon_0 E$, where $\epsilon_0=8.854\times10^{-12}$ $\mathrm{F\,m}^{-1}$. For a periodic field, D must be periodic in time. However, D is not necessarily in phase with E because of the relatively slow response of the dielectric to the fast alternation of the electric field. It is customary then to introduce a complex dielectric constant [35]

$$\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega) , \tag{2}$$

the real part of which represents the dielectric dispersion, while the imaginary part gives the dielectric loss. Both of course are frequency dependent. Employing a least-squares fit of the calculated time-dependent polarization per unit volume to [7,8,36]

$$P(t)=P_0+P_1\sin\omega t+P_2\cos\omega t , \tag{3}$$

we obtain $\epsilon_1=1.787$ and $\epsilon_2=0.097$ when the 3-μm laser beam having $E_0=1$ V/Å passes through SPC-FP water under normal thermodynamic conditions. Note that the wavelength we have chosen for the incident light is within the first prominent absorption band of liquid water in the infrared region [37]. This absorption band, centered near 2.92 μm, having a maximum value of the imaginary refractive index [38], $k\approx0.3$, arises from the resonance with the forced vibration of the water dipole moment. The calculated wave number, 3441 cm^{-1}, of this forced vibration is very close to the experimentally measured value of 3425 cm^{-1} [37].

Considering the relationships between the dielectric and optical constants [35]

$$\epsilon_1=n^2-k^2 , \tag{4}$$

$$\epsilon_2=2nk , \tag{5}$$

we find for SPC-FP water real and imaginary indices of refraction $n=1.337$ and $k=0.036$. The latter quantity, and thus ϵ_2, is obviously too low. This can be attributed in part at least to the assumption of an instantaneous polarization mechanism. The calculated value of n is only a bit larger than the experimental value of $n=1.327$ measured at $\lambda=2.92\mu$ and at $T=20\,^{\circ}\mathrm{C}$ [37]. This is also close to the value found for visible light. Throughout the visible and infrared regions [38] $k\ll n$, and thus n is not very sensitive to the value of k. According to Eq. (4), with the calculated value of $\epsilon_1=1.787$, n would range between 1.337 and 1.370 for k lying between 0.036 and 0.3.

Actually, a difference in the index of refraction in weak and intense light is expected because of the medium's nonlinear response, which is field-intensity dependent. In fact, we could use the difference between our calculated and experimental values of n very crudely to estimate these nonlinear effects. Because of the uncertainties that are probably inherent in the validity of ϵ_1 from the SPC-FP model, and the uncertainty in k already noted, such a calculation should only be considered as an outline of what may be possible in the future with better modeling. By neglecting higher-order nonlinear contributions, so that $n=n_0+n_1\overline{E}_0$, the resulting first-order nonlinear index of refraction n_1 is found to be 1.8×10^{-13} esu. By comparison, for carbon disulphide near $\lambda=1\ \mu$m, the experimental value of the nonlinear refractive index n_1 is 1.1×10^{-11} esu [39,40].

The experimental n_1 for pure water has been estimated to be about 220 times smaller than that of CS_2 [41]. In other words, a rough "experimental" value for the nonlinear index of refraction for pure water is 5×10^{-14} esu, not quite one third of our calculated value. Since there is a large statistical uncertainty in the calculation of n_1 as a difference between two large numbers, the agreement in sign and magnitude could be fortuitous. One goal of more realistic water models of the future would be to improve on this type of calculation.

VI. SUPERCONTINUUM GENERATION

A topic of very active interest in recent years is self-focusing and supercontinuum generation in condensed matter [41]. The latter gives rise to the generation of a broad-band "white light" continuum when intense ultrafast laser pulses propagate through media. Water is one of the most common liquids used to generate such a continuum [42]. When a laser beam possessing a Gaussian profile propagates through a medium with large high-order susceptibilities, the index of refraction of the medium at the central part of the beam becomes larger than that near the periphery of the profile. This nonuniformly distributed index of refraction acts like a convex lens that refracts the laser beam towards the center, further perturbing the medium, and thus producing a self-focusing effect. Self-focusing can significantly lower the thresholds for Raman scattering and supercontinuum generation, but a nonlinear absorption can also saturate the nonlinear susceptibility [39].

As indicated in Table II, under the influence of the applied electric field, the average dipole moment per molecule is increased by about 6%. This increment, mainly caused by the partially aligned neighboring molecules, gives rise to the positive nonlinear index of refraction described above. In fact, the degree of molecular alignment can be evaluated from

$$G_K=\left[\sum_{i=1}^{N}\mu_i/|\mu_i|\right]^2\Big/N\ . \tag{6}$$

As indicated in Table II, for the system studied here, G_K is $\sim$22 times larger than that measured in the field-off liquid.

For substances with spatially inhomogeneous polarizability, such as carbon disulphide, the molecular alignment contributes additionally to the enhancement of the index of refraction because of more efficient polarization along the molecular axis than normal to this axis [40]. Compounded with the large primary polarizability, this is presumably the reason why self-focusing occurs in liquid carbon disulphide even at moderate laser power levels [43,44]. Information on the field intensity dependence of the dielectric dispersion and loss for carbon disulphide can be extracted from Fig. 14 of Ref. [7]. See also Sec. 5 of Ref. [8].

VII. CLOSING REMARKS

In order to test the effects of flexible molecular bonds and instantaneously responsive "electronic" polarization on models for liquid water, we have studied in this paper the effects of an intense laser field on a recently developed, computationally simple SPC-FP model [11] of water. As a consequence of the tendency for molecular alignment, the liquid structure is distorted by forming a large number of bifurcated hydrogen bonds. The presence of these bonds, and presumably other nonconventional, more compact hydrogen bonding structures, is probably the reason for reversed intuition for many properties of liquid water, such as higher than bulk density near air-water interfaces [45].

On average, in the presence of a strong field, the O—H bond becomes longer and the H—O—H bond angle contracts, increasing the molecular dipole moment. These distortions, both intramolecular and intermolecular, induce spatial inhomogeneity, which significantly resists diffusion and slows down orientational relaxation, principally along the field direction.

The normal molecular vibrational modes of liquid water in a strong field, partly because of the molecular structure distortions (i.e., stretched O—H bonds), are found to have measurably lower frequencies relative to those in the field-off ensemble. This is in agreement with the red shifts observed in aqueous solutions with high concentrations of electrolyte [32]. There also appears a new band arising from the forced vibration of the molecular dipole moment under the influence of the incident light.

From the calculated time-dependent induced dipole moment, we are able to determine dielectric and optical properties of the molecular liquid at a given frequency and field intensity. Through a comparison of the calculated index of refraction with the experimental value measured for field-off pure water, we crudely estimate the first-order nonlinear index of refraction. This positive nonlinear index is a cause of the self-focusing phenomenon, which effectively reduces the threshold for supercontinuum generation.

In order to achieve a measure of realism in molecular-dynamics calculations of water, particularly under perturbations by electric fields, the additions of both instantaneously responsive polarizability and flexible molecular bonding seem essential. An electronically stiff water model would either fail to produce, or poorly estimate, the phenomena described in this paper, since polarization in a stiff model occurs only through dipole orientations, which require rather slow and unresponsive rotations of entire molecules.

At the present stage of computer power, the computationally intensive additions of both bond and "electronic" flexibility cause severe limitations in the range of models and results that can be obtained, even with an otherwise simplified water model of the type used here. The field-on data reported in this paper consumed only about seven

CPU hours on the CRAY YMP/832. This is not prohibitively long, and thus further embellishments of the model can be made [46]. However, statistical accuracy for partial ensembles of water molecules in the neighborhood of localized perturbations, such as surfaces, dissolved ions, or biological systems, would be inadequate unless much longer run times could be used.

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