PHYSICAL REVIEW A VOLUME 38, NUMBER 11 DECEMBER 1, 1988

Molecular-dynamics study of nonpolar molecular liquids in intense laser fields

S.-B. Zhu, J. Lee, and G. W. Robinson
Picosecond and Quantum Radiation Laboratory, P.O. Box 4260, Texas Tech University, Lubbock, Texas 79409

(Received 18 April 1988)

An electric polarization model for molecular liquids is proposed. This model is applied to liquid carbon disulphide in intense far-infrared laser fields. Changes in the liquid structure, in various time-dependent correlation functions, and in the dielectric properties of the optical medium are investigated. These changes are most profound at frequencies near the rotational resonance. When the perturbation is very strong, the molecular liquid becomes anisotropic and its polarization is saturated.

I. INTRODUCTION

When a very strong external force field is applied to a molecular liquid, the natural thermal motion of the molecules is placed in competition with the aligning effect of the field. The standard theoretical approach to this problem is based on a stochastic differential equation. This equation is typically written in isotropic configuration space for the variation of the probability density of a rigid dipole moment undergoing purely rotational Brownian motion under the influence of a unidirectional external field.[1-3] An extension has been made by Grigolini and Evans[4] to the non-Markovian case where the external field can become arbitrarily large. Recent advances in computer simulation techniques[5-10] enable us to probe more deeply into the fundamental physical characteristics of the molecular liquid state when such an applied field is present.

For a linear centrosymmetric molecule, such as CS_2, the lowest nonzero multipole moment is the quadrupole. However, it is known experimentally that the CS_2 molecule is highly polarizable.[11] The resulting induced dipole would be expected to exert an important influence on the liquid structure and other properties, especially when there exists an intense external electric field.

The principal purpose of this work is first to present an electric polarization model, and then to apply this model to the behavior of a nonpolar molecular liquid, specifically carbon disulphide, in far-infrared laser fields. Our aim is not to reproduce any available experimental data, but rather to predict the possible changes of the molecular liquid structure and other properties that could be of theoretical interest when such liquids are subjected to an ultrahigh field.

A complete quantum-mechanical description of a complex molecular system is generally impossible, at least for the current generation of computers. Nevertheless, classical and semiclassical methods often provide a good approximation for the description of molecular dynamics in electromagnetic fields.[12,13] Furthermore, liquid carbon disulfide would be expected to have few quantum ramifications. A full classical treatment will therefore be the subject of the present paper.

II. ELECTRIC POLARIZATION MODEL AND MOLECULAR-DYNAMICS SCHEME

In the presence of a strong electric field E, a molecule i is distorted in such a way that the component of the dipole moment in the x direction is

$$D_x^i = \mu_x^i + \alpha_{xj}^i E_j + \tfrac{1}{2}\beta_{xjk}^i E_j E_k + \tfrac{1}{3} A_{xjk}^i E'_{jk} + \cdots \ , \quad (1)$$

where μ_x^i is the permanent dipole moment, E'_{jk} is a field gradient, α_{xj}^i and A_{xjk}^i are components of the dipole and quadrupole polarizabilities, respectively, and β_{xjk}^i is a component of the first hyperpolarizability.[14] For a linear centrosymmetric molecule, $\mu_x^i = 0$. In addition, the polarization is generally anisotropic.

By neglecting the nonlinear optical polarizabilities, to the first order of approximation, we have

$$D_x^i(r_i) = \alpha_{xj}^i E_j(r_i) \ . \quad (2)$$

Here r_i is the position vector of the ith molecule. The polarizability may be modulated by internal vibrational motions. We keep only the linear term in the Taylor expansion of the polarizability,

$$\alpha_{xj} = \alpha_{xj}^{(0)} + \left[\frac{d\alpha}{dq} \right]_{xj} q \ , \quad (3)$$

where q is the normal coordinate and $\alpha_{xj}^{(0)}$ is the polarizability at $q = 0$.

Recently, we proposed a three-center Lennard-Jones (3CLJ) plus point-charge potential model for liquid CS_2. Intramolecular vibrational motions are explicitly included using a harmonic potential.[15] The Lennard-Jones parameters, the fractional charges, and the force constants are given in Table I. This model has proved reasonable for reproducing field-free experimental results, and will be employed to represent liquid carbon disulphide in the present work. To model the polarization, we place point charges on the sulfur atoms and allow them to vary according to the electric field component parallel to the molecular axis. Let $Q^i_{(t)}$ represent the instantaneous point charge on one of the sulfur atoms of the ith molecule. It contains a constant part, the value of which is given in Table I, and a variable part,

TABLE I. Molecular parameters.[a,b]

σ_{CC}	3.20 Å
σ_{SS}	3.52 Å
$\epsilon_{\mathrm{CC}}/k_B$	51 K
$\epsilon_{\mathrm{SS}}/k_B$	198.9 K
Q_{C}	$-0.308e$
Q_{S}	$0.154e$
K_1	7.5×10^5 dyn/cm
K_2	6×10^4 dyn/cm
K_0/r_e^2	2.34×10^6 dyn/cm

[a] $e=4.803\times10^{-10}$ esu.

[b] $r_e=1.56$ Å.

$$\Delta Q^i(t)=\frac{\alpha^{\parallel}E^i(t)\cos\theta^i(t)}{d^i(t)}\ , \tag{4}$$

with $d^i(t)$ and $\theta^i(t)$ being the instantaneous S-S distance and angle of inclination of the ith $\mathrm{CS_2}$ molecule with respect to the applied field. The charge variation on the other sulfur atom equals $-\Delta Q^i(t)$ to preserve electrical neutrality.

The normal component of the electric field will induce a dipole moment perpendicular to the molecular axis,

$$D_{\perp}^i(t)=\alpha^{\perp}E^i(t)\sin\theta^i(t)\ . \tag{5}$$

In the above equations, the superscripts $\perp$ and $||$ denote the normal and parallel components, respectively.

To save computational effort, we combine the effect of the normal component of the induced dipole moment into the variation of the point charges on the sulfur through an equivalent mechanical torque.[16] In this case, Eq. (4) may be rewritten

$$\Delta Q^i(t)=\frac{(\alpha^{\parallel}-\alpha^{\perp})E^i(t)\cos\theta^i(t)}{d^i(t)}\ . \tag{6}$$

When the wavelength of the external electric field is in the millimeter regime, the time scale of the field variations is of the same order as or longer than that of the nuclear motions. For such oscillatory fields, it is therefore reasonable to assume that the point charges on the sulfur redistribute instantly.

This polarization model differs in two aspects from the one suggested by Watts,[10] which also models the polarization using a variable particle charge on each atom. First, in this work, the point charges vary according to the applied electric fields and the instantaneous S-S distances, rather than depending only on the time-dependent bond lengths, as in the Watts model. Furthermore, in the Watts model there is no explicit relationship between the induced dipole moment and the polarizability. Second, the induced dipole moments in the present work are anisotropic instead of isotropic. This improvement is essential in the dynamics of linear molecules, since it influences, in fact, reduces, the effective torques applied to these molecules.

Our polarization model also provides an improvement on Evan's model,[5–9] in which the relation between the induced dipole moment and the polarizability is taken into account. However, in Evan's model, the externally applied field has no direct influence on the internal vibrational motions, and the electrostatic interactions from the induced dipole moments of the neighboring molecules are not included in the equation of motion.

Assuming the applied laser radiation is monochromatic with angular frequency ω, we write the equation of motion in the following form:

$$m_i\frac{d^2r_i}{dt^2}=-\nabla_i\phi+Q^i(t)[E_0\hat{\mathbf{x}}\cos\omega t+E_i^{\mathrm{loc}}(t)]\ . \tag{7}$$

Here

$$E_i^{\mathrm{loc}}(t)\equiv\sum_{j\neq i}\frac{Q^j(t)}{r_{ij}^3}(r_i-r_j)$$

represents the force field arising from the instantaneous moments of other molecules, $\hat{\mathbf{x}}$ is the unit vector along the externally applied field direction, and ϕ is the total mechanical potential energy. In general, this kind of equation of motion must be solved in a self-consistent fashion,[17] since $Q^i(t)=Q_0^i+\Delta Q^i(t)$ depends on the instantaneous values of $Q^j(t)$ $(j\neq i)$, as can be seen from Eq. (6) where $E^i(t)\equiv|E_0\hat{\mathbf{x}}\cos\omega t+E_i^{\mathrm{loc}}(t)|$ contains the values of electrostatic contributions from $Q^j(t)$. We neglect for the present the secondary (in comparison with that of the incident laser field) non-pair-additive interaction of molecular polarizability[18] in Eq. (6), that is, $E^i(t)=E_0\cos\omega t$, so that Eq. (7) can be solved in a standard algorithm. However, its contribution to the induced dipole moment and to $E_i^{\mathrm{loc}}(t)$ in Eq. (7) is still taken into account. Ignoring the electric field caused by other molecules in Eq. (6) does not introduce significant error since in all cases $E_0\gg E_i^{\mathrm{loc}}$.

The nonequilibrium molecular-dynamics method was used together with the third-order $P(r)E(a)C(r)E(a)C(v)$ algorithm.[19] We held the temperature constant by applying a "thermostat." This was done by rescaling the velocities at every time step[20] so that

$$\sum_{i=1}^{N}m_iv_i=0 \tag{8}$$

and

$$\tfrac{1}{2}\sum_{i=1}^{N}m_iv_i^2=\tfrac{3}{2}Nk_BT\ . \tag{9}$$

The rate of the kinetic energy so removed is indicative of the laser power absorbed.

III. APPLICATION OF THE MODEL

In this section we will apply the proposed model to study the changes in structure and other properties of liquid carbon disulphide under the influence of intense far-infrared fields, and to probe how these changes relate to the frequency and the intensity of the laser radiation. For this purpose, we have carried out nonequilibrium molecular-dynamics simulation with the aid of the Cray X-MP/48 supercomputer. Eight cases including three different laser peak intensities and six different frequencies are studied. These cases correspond to rather extreme conditions. They may not be realizable by currently available experimental techniques, but are useful in describing the model and for illustrating the possible direction and magnitudes of such effects for future experimental work. The entire study required about 35 CPU hours. For each system under study, 256 CS_2 molecules are taken in a cubic cell of side $L=29.47$ Å, with density $\rho=1.26$ g/cm^3, and temperature $T=298$ K. Ordinary periodic boundary conditions are employed. The long-range interaction is taken into account by the momentary reaction-field method.[21] A time step of 1.25 fs is used in the numerical integration of the equations of motion. To conserve computer time, the intermolecular forces are calculated every second step because of their relatively slow variation.

A. Structure and orientational order

As a consequence of the competition between the random thermal motion and the aligning motion of the external electric field, the structure of the molecular liquid is changed. These changes are field-, frequency-, and intensity-dependent. The rotational angular velocity correlation time τ_c for CS_2 at 293 K is 0.103 ps (Ref. 22) corresponding to a resonant frequency of 9.71 THz. When $\nu=8-10$ THz, which is close to this rotational resonance, the aligning motion of CS_2 molecules becomes much more efficient than at other frequencies. We will focus our discussion on the variation of the liquid structure at these particularly important frequencies.

Figure 1 depicts the first peaks of the C-C, C-S, and S-S radial distribution functions in the presence of the laser field with $\nu=8$ THz and $E_0=10(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$, that is, 1.46×10^5 esu/cm. These peaks are seen to shift towards shorter distances in the presence of the field. The shifts become more significant as the laser field increases in strength. The splitting of the first peak of the C-S distribution function [Fig. 1(b)] also becomes more prominent as a result of molecular alignment in the field.

Figure 2 illustrates the behavior of the computed running coordination number,

$$n_{CC}(r)=4\pi\rho_C\int_0^r s^2 g_{CC}(s)ds \ . \tag{10}$$

The first shell of neighbors with r taken at the first minimum in $g_{CC}(r)$ contains 11.15 molecules compared with 12.41 molecules for the unperturbed liquid, since the first minimum shifts towards shorter distances in the presence of the applied field. These results clearly demonstrate that substantial deviations in structure from the field-off case are present.

To provide a complete description of orientational ordering in the molecular liquid, we define a position-dependent angular correlation function (PDACF) by multiplying $g_{CC}(r)$ by the second-order Legendre polynomial $P_2(\cos\psi)$ over all coordinates. We thus obtain the Kirkwood G_2 factor,

$$G_2=\langle (N-1)P_2(\cos\psi)\rangle \ , \tag{11}$$

which enters the theoretical expressions for a number of observable properties, including the integrated intensity

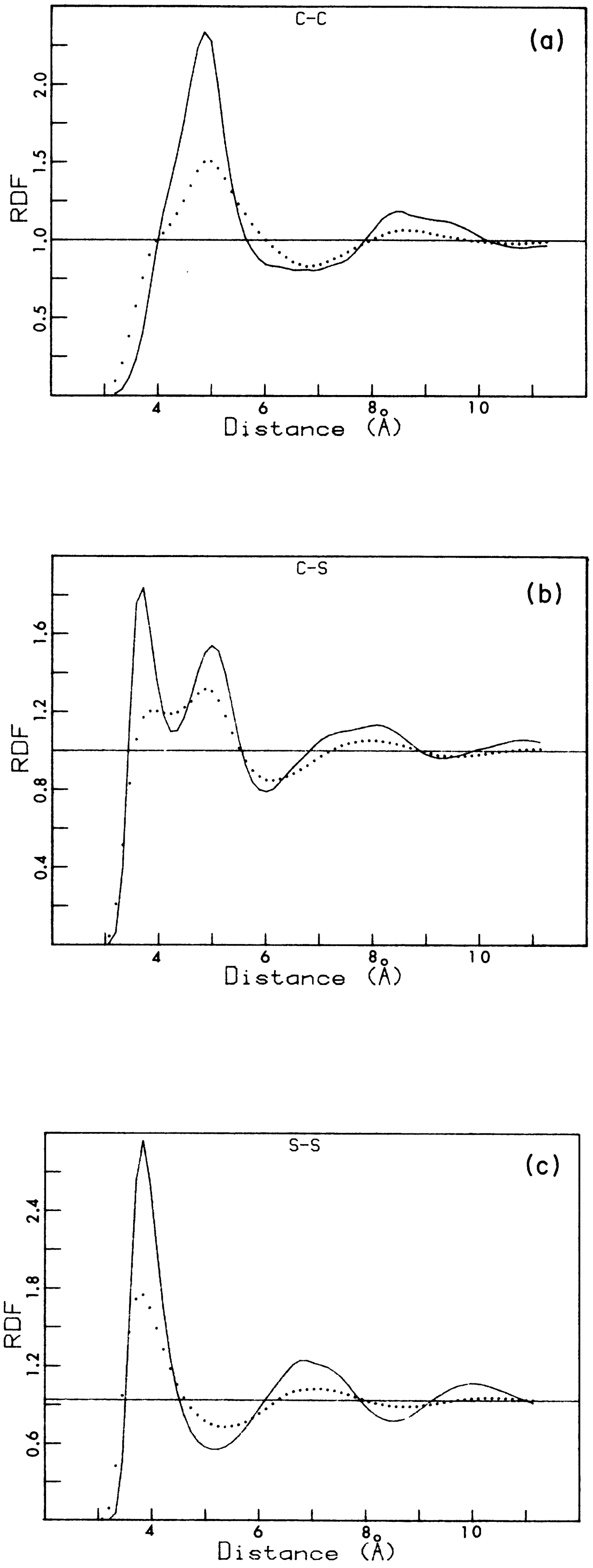

FIG. 1. Nuclear radial distribution functions. Dotted curves, field off; solid curves, field on. (a) C-C. (b) C-S. (c) S-S.

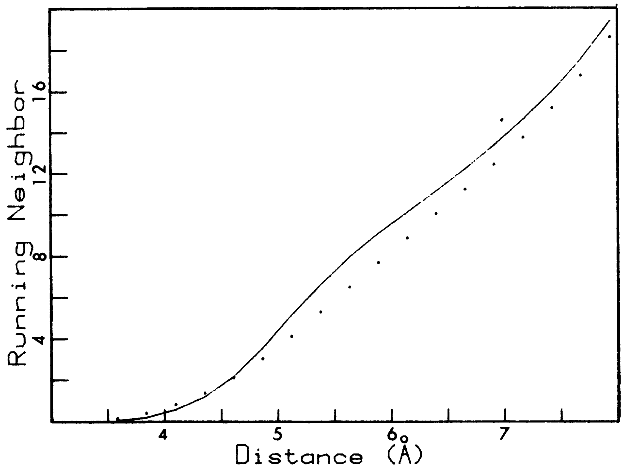

FIG. 2. Running coordination number. Dotted curve, field off, solid curve, field on.

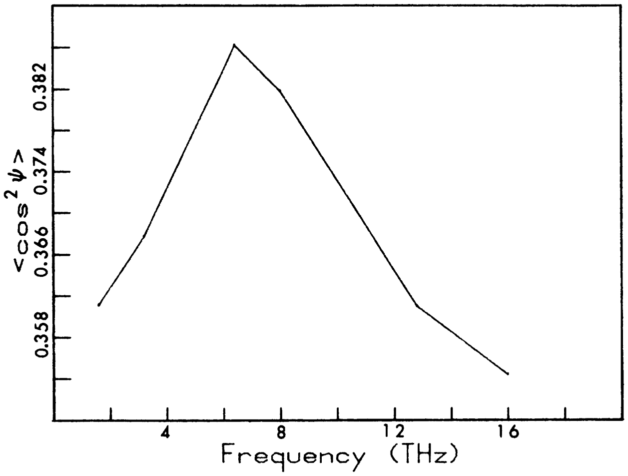

FIG. 4. Frequency dependence of $\langle \cos^2\psi \rangle$.

of depolarized scattered light.[23] See Fig. 3. The stronger orientational correlation corresponds to a much greater Kirkwood G_2 factor. In the presence of the field, liquid carbon disulphide is no longer isotropic in space. By reference to the frequency dependence of the mean values of $\langle \cos^2\psi \rangle$ shown in Fig. 4, it is evident that the resonant frequency indeed lies in the neighborhood of 8–10 THz. For random orientation, $\langle \cos^2\psi \rangle = \frac{1}{3}$.

B. Time-dependent correlation functions

The purpose of this section is to investigate the effect of the applied laser field on the various time autocorrelation functions (ACF) of theoretical interest. Again, these effects are most prominent near the rotational resonance.

The center-of-mass velocity autocorrelation function (CMVACF) and the angular velocity autocorrelation function (AVACF) in the presence of the laser field with frequency near the rotational resonance ($\nu = 8$ THz in the laboratory frame) are shown in Figs. 5 and 6. For comparison, the field-off results are also plotted. It is seen clearly in these figures that as the externally applied torque increases in strength, the ACF's decay more rapidly at early times. Oscillation may eventually develop if the applied field is sufficiently strong. This field strength is probably beyond the limit of present day laser sources.

Similar results have been observed by Evans.[5–9] He has pointed out that the oscillatory structure of the angular velocity autocorrelation function means that the far-infrared absorption is sharpened and shifted to high frequencies in comparison with the field-off case.[9] If the external torque is much larger than the internal torque, the orientational dynamics will become coherent, as in an ideal gas, but with much higher far-infrared peak frequency.[5]

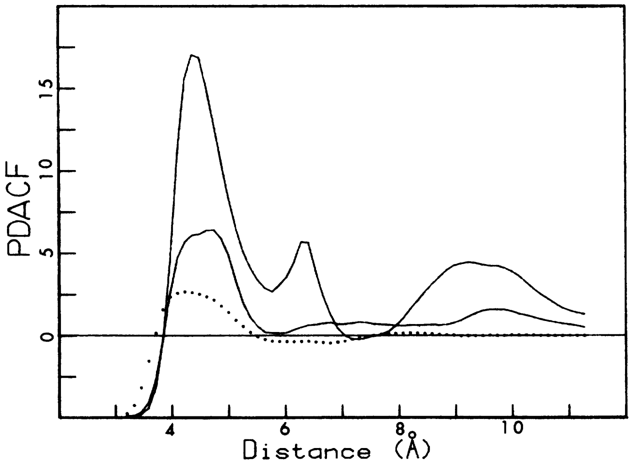

FIG. 3. The average value of $P_2(\cos\phi)$ as a function of r. Dotted curve, field off; lower solid curve, applied field $E_0 = 10(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$, $\omega = 8$ THz; upper solid curve, applied field $E_0 = 50(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$, $\omega = 8$ THz.

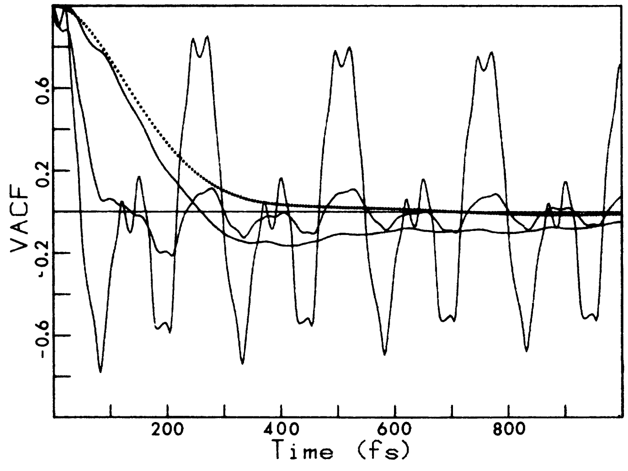

FIG. 5. Center-of-mass velocity autocorrelation functions. Dotted curve, field off; solid curves, (1) $E_0 = 10(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$, (2) $E_0 = 50(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$, (3) $E_0 = 90(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$.

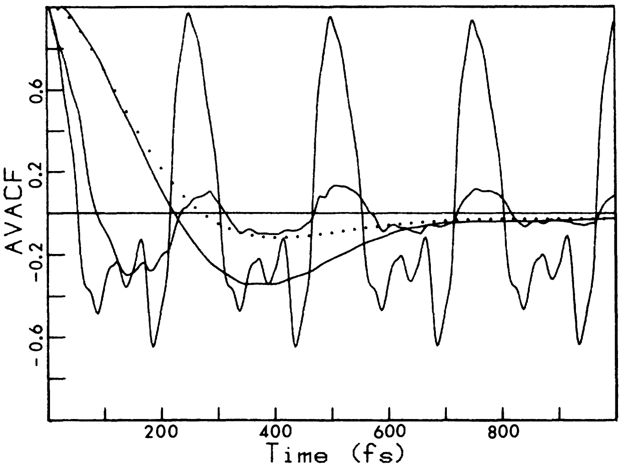

FIG. 6. Angular velocity autocorrelation functions. Symbols are the same as for Fig. 5.

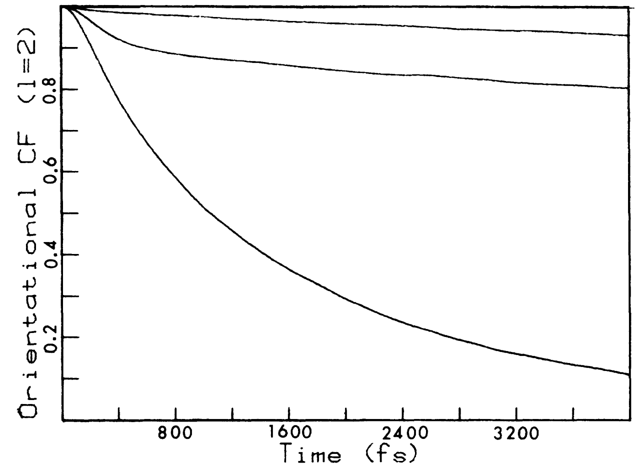

FIG. 8. Same as for Fig. 7, but $l=2$.

It is abundantly clear from Figs. 7 and 8 that the effect of the externally applied torque is to align the CS_2 molecules. Under the influence of intense far-infrared laser radiation, the molecules vibrate rapidly around their equilibrium positions. With an increase of field strength, the amplitude of the vibration becomes smaller but the frequency becomes higher. For a very strong field, the alignment of the molecules is saturated, and the orientational correlation function becomes purely oscillatory.

It should be noted that the curves in Figs. 5–8 are the average values of different components. Because of the anisotropy of the molecular liquid developed under the influence of the laser light, the behavior of the ACF's along the field direction is completely different from that along the other two directions. Examples are given in Figs. 9–11. As the applied field becomes very strong, the field-parallel ACF's become oscillatory with the period of the laser light. The field-perpendicular ACF's also become oscillatory, but at half the laser frequency. The difference between the components of the orientational correlation function along different directions is significant even in the weaker perturbation cases (Fig. 11). The orthogonal components in Figs. 9–11 are averages over the y and z directions. Beating effects for the VACF and AVACF are clearly recognizable. The two components strengthen each other at every odd period of the laser radiation, but weaken each other every even period.

C. Dielectric properties

The dielectric properties of a substance are interpreted in terms of the molecules which compose it, and their electric moments, both permanent and induced. In gen-

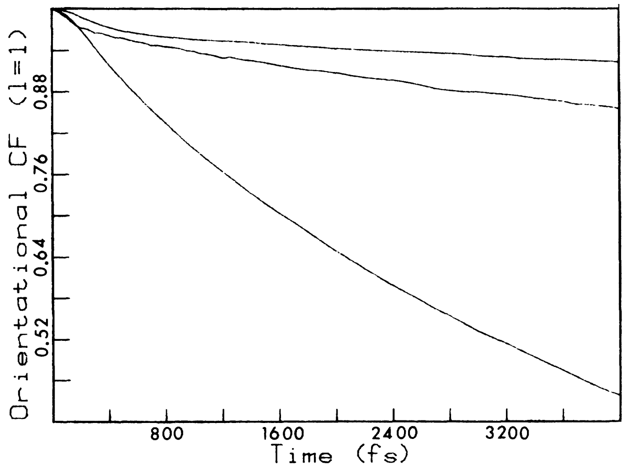

FIG. 7. Orientational correlation functions ($l=1$). Curves from lower to upper correspond to $E_0=0$, $E_0=10$, and $E_0=50(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$, respectively.

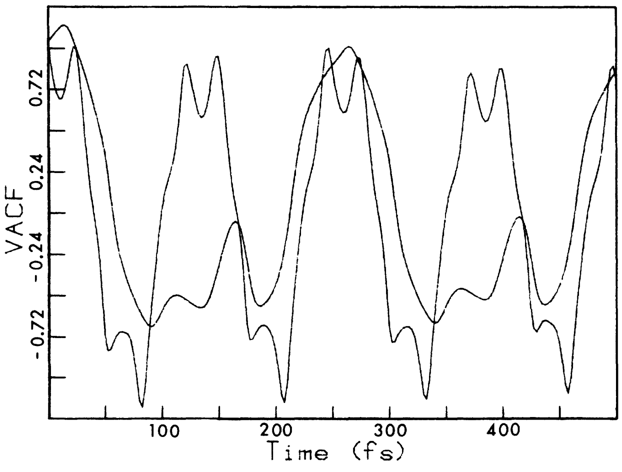

FIG. 9. Center-of-mass velocity autocorrelation functions, $E_0=90(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$, $\omega=8$ THz. Curve 1, component along the field direction; curve 2, component orthogonal to the field direction.

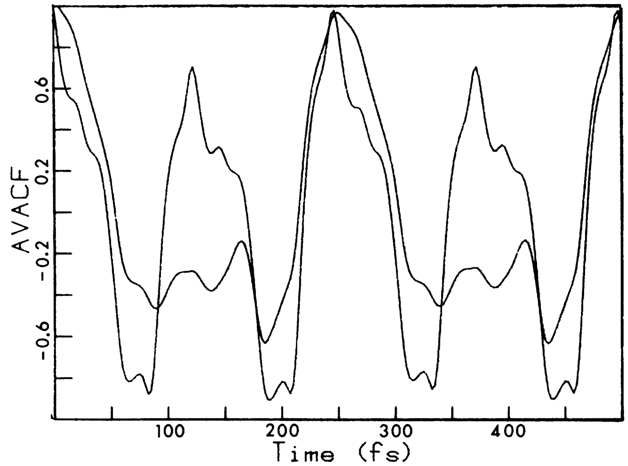

FIG. 10. Angular velocity autocorrelation functions, $E_0=90(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$, $\omega=8$ THz. Curve 1, component along the field direction; curve 2, component orthogonal to the field direction.

eral, the induced dipole moment is made up of an electronic distortion contribution which is almost an instantaneous response to the application of the electric field, together with a dipole orientational contribution, which is a relatively slow response. Since the carbon disulphide molecule is linear and centrosymmetric, but highly polarizable, and the far-infrared laser radiation, in general, is near the frequencies of nuclear oscillations,[24] the first contribution predominates at steady state. As a result, the total induced dipole moment autocorrelation function along the field direction,

$$C_M(t)=\langle M_x(0)M_x(t)\rangle/\langle M_x(0)^2\rangle\ , \tag{12}$$

$$M_x=\sum_{i=1}^{N} D_x^i$$

follows the alternation of the external field almost completely.

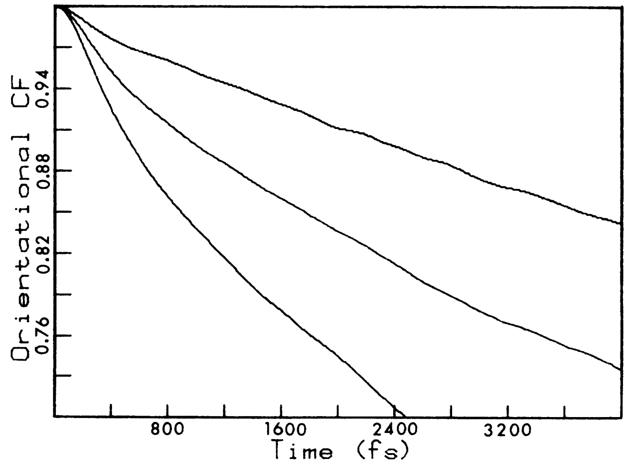

FIG. 11. Orientational correlation functions $(l=1)$, $E_0=10(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$, $\omega=10$ THz. Lower curve, component along the field direction; middle curve, average of different components; upper curve, component orthogonal to the field direction.

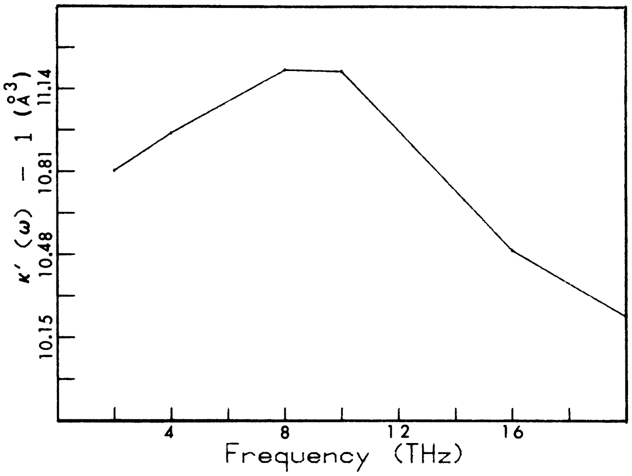

FIG. 12. $\kappa'(\omega)-1$ at constant field strength $E_0=10(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$.

If we separate the polarization into in-phase and out-of-phase components,

$$P(t)=P_0+P_r\cos\omega t+P_i\sin\omega t\ , \tag{13}$$

by a least-square fit[10] we obtain the dielectric dispersion (the real component) and the dielectric loss (the imaginary component) at the given frequency. Frequency variations of the complex relative permittivity of the liquid medium,

$$\kappa'(\omega)=1+P_r/E \tag{14}$$

and

$$\kappa''(\omega)=P_i/E\ , \tag{15}$$

according to the MD calculations are plotted in Figs. 12 and 13. In Eqs. (14) and (15), E is the macroscopic elec-

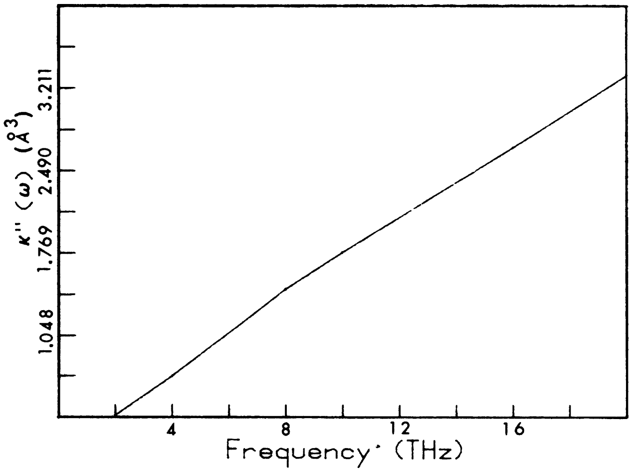

FIG. 13. $\kappa''(\omega)$ at constant field strength $E_0=10(\epsilon_{CC}/\sigma_{CC}^3)^{1/2}$.

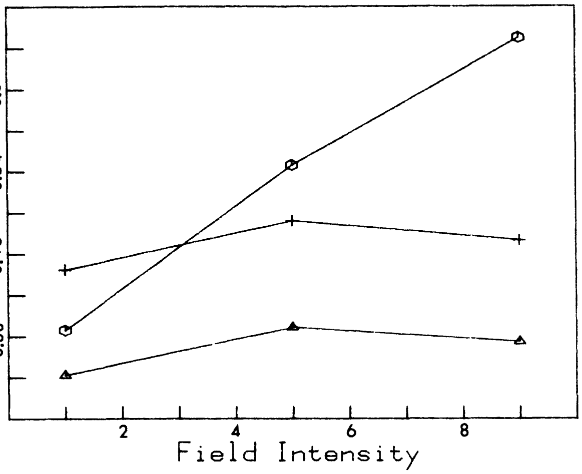

FIG. 14. Field intensity dependence of (1) $\kappa'-1$ (△); (2) κ'' (+); (3) $\langle\cos^2\psi\rangle$ (○) $\omega=8$ THz.

tric field, which includes the contribution from the external field E_0 and the fluctuating contribution from the environmental polarization. For all cases studied in this work $E \approx E_0$. For example, when $E_0=10(\epsilon_{\mathrm{CC}}/\sigma_{\mathrm{cc}}^3)^{1/2}$, $|E-E_0|/E_0 \lesssim 0.01$. There is no power absorption maximum observed in the frequency range of 2–20 THz. When the laser frequency increases from 10 to 20 THz, the real part of the relative permittivity decreases, which is an indication of the anomalous dispersion.

Because of the nonlinear effect in the optical medium, the dielectric constant and the index of refraction depend on the laser intensity. The best values of the complex permittivity as a function of the field strength at $\nu=8$ THz are given in Fig. 14. Both the real and imaginary parts of the permittivity are seen to have reached their maximum values near 50 $(\epsilon_{\mathrm{CC}}/\sigma_{\mathrm{CC}}^3)^{1/2}$. For a better appreciation of the saturation effect, we also demonstrate in Fig. 14 the field intensity dependence of $\langle\cos^2\psi\rangle$.

IV. SUMMARY AND CONCLUSIONS

This work proposes an electric polarization model of liquid carbon disulfide that introduces variable point charges associated with the sulfur atoms. The variation of these charges is assumed to follow the externally applied electric field instantly. In general, the polarization is anisotropic. Contributions from both the normal and the orthogonal components of the applied field are considered. This model is then used to simulate liquid carbon disulfide in intense far infrared laser fields with the aid of nonequilibrium molecular dynamics using the Cray X-MP/48 supercomputer. Changes in the liquid structure, various time-dependent correlation functions, and the dielectric properties of the optical medium are investigated. These changes appear the most profound at frequencies near the rotational resonance. In the presence of this strong perturbation, the molecular liquid becomes anisotropic in space. Saturation effects may be observed as the externally applied torque considerably exceeds the random intermolecular interactions from the thermal motion. The model, besides being useful for nonpolar molecules, should be applicable to polar molecular liquids as well. In this work we have confined the investigations to steady-state characteristics. Transient behavior of molecular liquids can be studied using the same model.

ACKNOWLEDGMENTS

We acknowledge financial support of the National Science Foundation (Grant No. CHE8611381) and the R. A. Welch Foundation (Grant Nos. D-0005 and D-1094). Supercomputer time was furnished by the Pittsburgh Supercomputing Center, to which we express thanks.

---

[1] H. Benoit, Ann. Phys. **6**, 561 (1951).

[2] R. Ullman, J. Chem. Phys. **56**, 1869 (1972).

[3] W. R. Coffey and B. V. Paranjape, Proc. R. Irish Acad. **78A**, 17 (1976).

[4] P. Grigolini and M. W. Evans, J. Chem. Soc. Faraday Trans. II **76**, 761 (1980).

[5] M. W. Evans, J. Chem. Phys. **76**, 5473 (1982).

[6] M. W. Evans, J. Chem. Phys. **76**, 5480 (1982).

[7] M. W. Evans, J. Chem. Phys. **77**, 4632 (1982).

[8] M. W. Evans, J. Chem. Phys. **78**, 925 (1983).

[9] M. W. Evans, J. Chem. Phys. **78**, 5403 (1983).

[10] R. O. Watts, Chem. Phys. **80**, 211 (1981).

[11] M. P. Bogaard, A. D. Buckingham, R. K. Pierens, and A. H. White, J. Chem. Soc., Faraday Trans. 1 **74**, 3008 (1978).

[12] D. W. Noid, M. L. Koszykowski, R. A. Marcus, and J. D. MacDonald, Chem. Phys. Lett. **51**, 540 (1977).

[13] W. H. Miller, J. Chem. Phys. **69**, 2188 (1978).

[14] A. D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967).

[15] S.-B. Zhu, J. Lee, and G. W. Robinson, Mol. Phys. **65**, 65 (1988).

[16] S.-B. Zhu (unpublished).

[17] J. A. Barker, Proc. R. Soc. London, Ser. A **219**, 367 (1953).

[18] A. van der Avoird, P. E. S. Wormer, F. Mulder, and R. M. Berns, in Vol. 93 of *Topics in Current Chemistry*, edited by M. J. S. Dewar *et al.* (Springer-Verlag, Berlin, 1980).

[19] D. Beeman, J. Comput. Phys. **20**, 130 (1976).

[20] D. Brown and J. H. R. Clarke, Mol. Phys. **51**, 1243 (1984).

[21] W. F. Van Gunsteren, H. J. C. Berendsen, and J. A. C. Rullmann, Discuss. Faraday Soc. **66**, 58 (1978).

[22] T. I. Cox, M. R. Battaglia, and P. A. Madden, Mol. Phys. **38**, 1539 (1979).

[23] M. R. Battaglia, T. I. Cox, and P. A. Madden, Mol. Phys. **37**, 1413 (1979).

[24] H. Frohlich, *Theory of Dielectrics* (Oxford University Press, London, 1958).