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A Distributed Hyperpolarizability Model for Liquid Water

C. Neipert, B. Space[1]

Department of Chemistry,
University of South Florida,
4202 East Fowler Avenue, CHE205, Tampa, FL, USA, 33620-5250

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Abstract: In a recent work a novel, molecular dynamics (MD) based, theory was presented that provides a direct means to calculate the third order contributions to sum frequency vibrational spectroscopy (SFVS) at charged interfaces.[1] This contribution is described by a time correlation function (TCF) of the system's total hyperpolarizability (β) and dipole. A system's hyperpolarizability[2, 3, 4, 5] is difficult to calculate on the fly – no appropriate non-electronic structure (ES) techniques exist. In this work, such a model is developed for liquid water based on a formalism proposed previously.[1] The model is parametrized from and tested against, *ab initio* ES calculations. It was found that it is possible to reproduce the hyperpolarizability tensor of a gas phase water molecule and a water dimer accurately. Also, most relevant components of the hyperpolarizability derivative tensor of both the water and water dimer were also accurately fit, however, some elements were not able to be simultaneously reproduced. The model was also tested to assess whether or not it could reproduce the three non-zero condensed phase water hyperpolarizability tensor components. It was found that the model could capture two of the three relevant components.

Keywords: Hyperpolarizability, Water, Spectroscopy, SFG, SFVS, Dipole Interaction Model

Mathematics Subject Classification: Here must be added the AMS-MOS or PACS Numbers

PACS: Here must be added the AMS-MOS or PACS Numbers

1 Introduction

In a recent work[1] the first theoretical/computational molecularly detailed method to model both the second and third order contributions[6, 7] to the SFVS signature of charged interfaces was presented; probing these types of interfaces *via* interface specific optical techniques is fundamentally different than examining uncharged interfaces.[6, 7, 8, 9, 10, 11, 12] The presence of a static field associated with the charged species will both produce a more intense dipolar second order interface specific signal (due to ordering at the interface), and a distinct non-interface specific third order signal (due to contributions from regions into which the static field penetrates); these contributions are unable to be independently resolved experimentally, but have distinct physical origins.

Prior studies[8, 10, 9, 13, 14, 15, 16, 17, 18, 19, 20] used a semi-classical approach to calculate appropriate (quantum corrected) TCF's that describe a particular type of vibrational spectroscopy.

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[1] Corresponding author. E-mail: space@cas.usf.edu

Specifically, classical MD is employed to capture the dynamics of a given liquid system. The trajectories generated from the MD are then input into a spectroscopic model (SM) that supplements the MD potential. This permits the calculation of the system's dipole, polarizability, and associated derivatives along the trajectory that are then used to construct the relevant TCF. Because our primary focus is to calculate vibrational spectroscopic lineshapes, the system's electric moment derivatives must be accurate. Consider the Maclauran expansion of the dipole operator matrix element, μ_{ab}, around coordinate $\mathbf{r}$: $\mu_{ab} = \mu_o \delta_{ab} + \mu' \mathbf{r}_{ab} + \mathcal{O}(\mathbf{r}^2)$. A resonant spectroscopic signal for a given experiment stems from the perturbing field(s) inducing a transition between states (*i.e.* $a \neq b$). Thus, it is the electric moment derivatives that provide a window into the complex dynamics of the system *via* spectroscopy when considering intramolecular vibrations.[8, 9, 20, 21, 22]

It is possible to model the electric moments and derivatives (parametrized with *ab initio* calculations and/or experimental data) directly in an MD simulation that are required to compute TCF's that correspond to a specific type of vibrational spectroscopy.[23, 24] However, in practice, it is substantially easier to employ MD supplemented with a detailed spectroscopic model used only to calculate the TCF using the MD trajectory as input. Note, an MD simulation that accurately models the system's electric moments, but not necessarily the system's electric moment derivatives, will still accurately capture the dynamics of the system; the system's electric moment derivatives correspond to relatively small changes in an atom's local environment, and therefore do not significantly change the system forces.[25, 8] Such an approach has been demonstrated to be highly effective in understanding condensed phase spectroscopy of water, other liquids, and interfaces.[9, 10, 14, 15, 16, 17, 18, 19]

Calculating the third order contribution to SFVS studies at charged interfaces involves computation and correlation of the system's static hyperpolarizability and dipole at every step along the MD trajectory. A system's hyperpolarizability and hyperpolarizability derivatives are difficult quantities to calculate, and they have generally been calculated with ES methods and, usually, only reliably for small molecules.[2, 3] In calculating the requisite SFVS TCF, long dynamics runs – involving hundreds on thousands of MD configurations – are required. This consideration makes ES evaluation of the hyperpolarizability computationally intractable. Thus, the purpose of this work is to develop and rigorously test the extended SM that captures the condensed phase hyperpolarizability, and assess this new SM's applicability for future use in modeling third order optical effects at charged interfaces. Because the primary focus here is in modeling aqueous liquids and interfaces, the model was parameterized and tested on liquid water.

2 Constructing a SM for the Dipole Polarizability

The SM used in previous studies,[8, 9, 10, 14, 15, 16, 17, 18, 19] and its extension here, are based upon a generalization of the Thole modified Applequist point atomic polarizability formalism.[3, 8, 9, 10, 15, 26, 27, 28, 29, 30, 31, 32, 33, 34] Within this genre of spectroscopic model, a system is first broken down into the types of molecules that comprise it, and then into the atoms that comprise the specific sets of the different molecular species. Neglecting hyperpolarizability and higher order moments for now,[35] each atom type within a like group of molecular species is assigned an intrinsic point polarizability (α) along with point polarizability derivatives parametrized as a function of molecular geometry, for example as a displacement from an equilibrium bond length: $\alpha = \alpha_o + \alpha' \Delta r$. These atomic values are chosen such that when the atoms comprising a particular isolated molecular species are allowed to interact *via* the SM formalism, the molecule's electric moments and their derivatives – as compared with experimental and/or detailed ES calculations – are accurately reproduced.

In fitting the SM for a particular molecular species, the zeroth order (μ_o, α_o) terms are parametrized first, and are based upon a molecule's equilibrium gas phase configuration. The first order (derivative) terms are subsequently parametrized using high level ES in which the electric moments are calculated for small displacements (*e.g.*, $\mathcal{O}(E^{-5}\mathring{A})$) from a given molecule's equilibrium configuration. Due to the SM's natural incorporation of the electric moment derivatives and explicit account of many-body interactions *via* a many-body interaction tensor[26, 27, 31, 36] the SM, parametrized to gas phase data, is able to accurately capture the complexity of condensed phase phenomenon without additional fitting.[8, 9, 10, 14, 15, 16, 17, 18, 19]

Note, it is typical within a Thole/Applequist type model that the atomic polarizabilities are represented as points that interact to reproduce the molecular polarizability tensor. However, the intrinsic atomic polarizability can be more generally modeled as a tensor.[34, 36]

Denoting Cartesian tensor components with superscript Greek indices and atomic sites with Roman indices, the mathematical representation of the outlined formalism is given as follows:

$$\mu_i^\beta = \alpha_{o,i}\left[E_i^{(0),\beta} + \sum_{j\neq i}^{N} T_{ij}^{\beta\gamma}\mu_j^\gamma\right] \tag{1}$$

$$T_{ij} = \nabla_{r_i}\nabla_{r_j}\frac{1}{r_{ij}} \tag{2}$$

$$\alpha_{ik}^{eff,\beta\zeta} = \alpha_{o,i}\left[\delta_{\beta\zeta}\delta_{ik} + \sum_{j\neq i}^{N} T_{ij}^{\beta\gamma}\alpha_{jk}^{eff,\gamma\zeta}\right] \tag{3}$$

In Equation 1, N is the number of atomic sites in the system. Further, each atomic site i has an associated point charge, q_i, and intrinsic point polarizability, $\alpha_{o,i}$. $E_i^{(0),\beta}$ represents the electric field component at site i, and is a sum of two contributions: the field created at site i due to all q_j's and the field strength at site i due to any externally applied field. $T_{ij}^{\beta\gamma}$ (Equation 2, r_{ij} is the distance between atomic sites i and j) is the multipole interaction tensor which accounts for dipole induced dipole effects. Finally, μ_i^β is the induced-dipole moment component that arises from both $E_i^{(0),\beta}$ and $T^{\beta\gamma}$ contributions. Note, the effective polarizability between atomic site i and k, $\alpha_{ik}^{eff,\beta\zeta}$, is found *via* matrix inversion or direct iteration of Equation 3;[26, 31] the associated system polarizability tensor is a sum of the various $\alpha_{ik}^{eff,\beta\zeta}$ components.

3 Extension of the SM to Model Condensed Phase Hyperpolarizabilities

To construct a SM that permits calculation of a condensed phase system's hyperpolarizability, β, the Thole/Applequist methodology was formally extended in a previous work.[1] Specifically, tensor hyperpolarizabilities are assigned to each atomic (or other assigned) site such that when they interact, they reproduce the equilibrium gas phase hyperpolarizability tensor for a given molecule. When these sites further interact in the condensed phase, the hyperpolarizability can then be calculated without additional considerations. Given the lack of available experimental data, the model is constructed to reproduce detailed ES calculations using an appropriate, high level, basis set.[3, 36] The SM is constructed to give the effective hyperpolarizability (intrinsic + interaction effects), β_{ijk}^{eff}, as sums over the products of the intrinsic (point) and effective (tensor) polarizability elements of the system. The entire process is analogous to the Applequist/Thole many-body polarization method we use to calculate the polarizability in the SM, Equation 3.[36] The computational effort is not significantly increased beyond the solving of Equation 3 because the most demanding step is still the solution of the many-body polarization equations.

ES	x	y	z
O	0.	0.	-0.065565653769
H1	0.7569498491	0.	0.5202848504
H2	-0.7569498491	0.	0.5202848504
rOH	0.957180		

Table 1: The equilibrium configuration of an isolated water molecule used in ES calculations. Units are in Angstroms. These Cartesian coordinates give an angle of 104.5 degrees.

SM	x	y	z
O.	0.	0.	0.
H1	0.8179551669	0.	0.5752961881
H2	-0.8179551669	0.	0.5752961881
rOH	1.0		

Table 2: The equilibrium configuration of an isolated water molecule used in the SM calculations. Units are in Angstroms. These Cartesian coordinates give an angle of 109.47 degrees, consistent with the flexible simple point charge (SPC) MD model.

Denoting Cartesian tensor components with superscript Greek indices and atomic sites with Roman indices, the total effective hyperpolarizability (intrinsic + interaction effects), β_{ijk}^{eff}, is given by:[1, 36]

$$\beta_{ijk}^{eff,\alpha\beta\gamma} = \sum_n \beta_n^{\zeta\epsilon\mu} \frac{\alpha_{ni}^{eff,\mu\alpha}}{\alpha_n} \frac{\alpha_{nj}^{eff,\epsilon\beta}}{\alpha_n} \frac{\alpha_{nk}^{eff,\zeta\gamma}}{\alpha_n} \tag{4}$$

In Equation 4, $\beta_n^{\zeta\epsilon\mu}$ is the intrinsic hyperpolarizability tensor associated with atomic site n, $\alpha_{ni}^{eff,\mu\alpha}$ is the total effective polarizability tensor component between atomic site i and n, and α_n is the intrinsic point polarizability associated with atomic site n.[36] Note, it was originally proposed[1] to approximate the intrinsic hyperpolarizabilities of each atom as a point hyperpolarizability. This was found to be an insufficient approximation – at least for modeling the hyperpolarizability of water.

Using the above formalism, the extended SM was implemented to model the hyperpolarizability of water. To our knowledge, only a few experimental determinations[37, 38, 39, 40] have investigated the hyperpolarizability of gaseous or liquid water. Further, only one of the referenced works was conducted recently,[39] and the various determinations used somewhat different techniques and gave a range of values. Thus, the published experimental values for the hyperpolarizability of water were used as a rough guide; for parametrization and rigorous comparison purposes, density functional theory ES calculations were performed with PCGAMESS[41] at the aug-cc-pvqz/B3LYP5 level to calculate gas phase values – the values obtained were in agreement with experimentally determined values. Additionally, the condensed phase values calculated *via* the new extended SM were compared to other theoretical ES investigations and gave similar values.[2, 3]

The equilibrium water configurations along with the polarizability parameters used in the ES and extended SM calculations are those detailed in Table 1 and 2 respectively. The relevant dipole (the permanent dipole of 1.84 Debye is represented by atomic point charges) and polarizability parameters used in the extended SM for water are presented in Table 3. Further, the damping

	q	α_o	α'
oxygen:	-.6446	1.307	0.353
hydrogen:	0.3223	0.157	0.885

Table 3: The SM parameters for the permanent charges, polarizability (Å$^3/e$), and polarizability derivative (Å$^2/e$).

ES	x	y	z	SM	x	y	z
x	1.512355	0.	0.	x	1.562470	0.	0.
y	0.	1.441227	0.	y	0.	1.31758	0.
z	0.	0.	1.469676	z	0.	0.	1.424445
$\langle\alpha\rangle$	1.47442			$\langle\alpha\rangle$	1.434832		

Table 4: The polarizability tensor (Å^3/e) of an isolated water molecule calculated *via* ES and SM.

factor requisite in the SM/extended SM to prevent unphysically large values[31] when two atoms approach a distance of $(4\alpha_i\alpha_j)^{1/6}$ was 1.887Å.

Because accurately capturing the polarizability is essential to accurately model the hyperpolarizability (and for calculating spectroscopically relevant TCF's), the parameters given in Table 3 are also fit to reproduce the gas phase polarizability tensor of water (and its derivatives). The results are summarized in Tables 4 and 5 respectively. This polarizability model was additionally tested for water dimers, and exhibited nearly the same percent error for each of the corresponding polarizability and polarizability derivative tensor components as compared to results obtained from the isolated water molecule calculations.

Next, the intrinsic hyperpolarizability tensors of oxygen and hydrogen were determined such that when they interacted *via* the extended SM, the gas phase hyperpolarizability tensor of water, calculated using by ES, was reproduced. The best fit intrinsic hyperpolarizability tensor parameters associated with the oxygen and hydrogen are presented in Table 6. Table 6 also compares the interaction hyperpolarizability tensor of a single water molecule computed *via* ES and extended SM methods. Agreement between the two methods is remarkable.

Subsequently, the intrinsic hyperpolarizability derivative tensors of oxygen and hydrogen were parametrized. Introduction of the hyperpolarizability derivative tensors allows the total hyperpolarizability to be expressed as a function of both displacement from equilibrium bond length (Δr) and angle ($\Delta\theta$): $\beta^{ijk} = \beta_o^{ijk} + \beta_r'^{ijk}\Delta r + \beta_\theta'^{ijk}\Delta\theta$. Extensive global scan methods were employed in pursuit of finding a composition of the hyperpolarizability derivative tensors for oxygen and hydrogen that would reproduce the derivatives of all ijk tensor components of the system β, but none where found. However, third order SFVS signals depend only on the system's change in the total hyperpolarizability in three specific directions: β^{zxz}, β^{xxz}, and β^{zzz}. Further, the most common SFVS measurement is taken in the so called SSP direction (depending on the XXZ element in a coordinate system with z normal to the interface) because it typically gives by far the most intense signal. Therefore, while not ideal, it is sufficient to have a model that captures the system's hyperpolarizability derivative tensor in the XXZ direction because our primary goal is to ultimately calculate the third order contribution to SFVS at charged interfaces. Table 7 gives the non-zero hyperpolarizability derivative tensor parameters for oxygen and hydrogen that best reproduced the interaction hyperpolarizability tensor of gaseous water. There were several global fits that reproduced the XXZ component of the interaction hyperpolarizability derivative tensor. The set of parameters that was selected was chosen based upon its ability to also reproduce the

α_{ij}	xx	yy	zz	xz=zx	xy=yx	yz=zx
Ox:ES	–	–	–	1.080	–	–
Ox:SM	–	–	–	1.080	–	–
%Error	–	–	–	0.	–	–
Oz:ES	-1.479	-0.463	-1.282	–	–	–
Oz:SM	-1.508	-0.475	-1.254	–	–	–
%Error	1.961	2.592	-2.184	–	–	–
H1x:ES	1.281	0.401	0.672	–	–	0.543
H1x:SM	1.345	0.339	0.635	–	–	0.540
%Error	5.00	15.461	5.82	–	–	0.552
H1z:ES	0.691	0.230	0.575	–	–	0.420
H1z:SM	.754	0.238	0.627	–	–	0.464
%Error	9.117	3.478	-8.293	–	–	10.476
H2x:ES	-1.388	-0.405	-0.803	–	–	-0.543
H2x:SM	-1.345	-0.339	-0.635	–	–	-0.540
%Error	3.098	16.296	20.922	–	–	-0.552
H2z:ES	0.691	0.230	0.575	–	–	0.420
H2z:SM	0.754	0.238	0.627	–	–	0.464
%Error	9.117	3.478	9.043	–	–	10.476

Table 5: Polarizability derivative matrix. ES and SM are compared for the 9 coordinate displacements. Note only derivatives with a rounded order of magnitude ≥ 0.1 Å$^2/e$ for both ES and SM are presented here. That is why y coordinate displacements are not shown.

	$\epsilon_{xxz}\beta^{xxz}$	$\epsilon_{yyz}\beta^{yyz}$	β^{zzz}
O	0.679	-0.271	0.059
H	-0.6725	0.6875	-0.8625
ES	-0.5733135	-0.2205550	-0.6087189
SM	-0.5733011	-0.2205574	-0.6087125
%Error	-0.0022	0.0011	-0.0011

Table 6: The non-zero intrinsic hyperpolarizability tensor parameters of oxygen and hydrogen used in the extended SM calculations are given. The non-zero interaction hyperpolarizability (Å^5/e) tensor elements of an equilibrium configuration isolated water molecule are also listed for both ES and extended SM methods along with their percent error. Note, ϵ symbolizes the hyperpolarizability is fully symmetric with respect to all superscripts.

	$\beta_r'^{xxz}$	$\beta_r'^{yyz}$	$\beta_r'^{zzz}$
O	6.300	-0.650	5.260
H	3.75	37.95	-0.5
	$\beta_\theta'^{xxz}$	$\beta_\theta'^{yyz}$	$\beta_\theta'^{zzz}$
O	3.750	0.	3.0
H	8.933	0.	-35.8

Table 7: The hyperpolarizability derivative parameters for the extended SM of gaseous water are shown. Units are in Å$^4/e$ for β_r' and Å$^5/(e$ radian) for β_θ'.

Displacement	Component	ES	SM	%Difference
Ox:	β'^{zxz}	0.535820	0.536980	0.11598
Oz:	β'^{xxz}	1.371292	1.382532	-0.23294
Oz:	β'^{zzz}	0.866077	0.863747	1.123897
H1x:	β'^{xxz}	-1.34889	-1.34932	-0.0433224
H1x:	β'^{zzz}	-0.491203	-0.491037	0.016639
H1x:	β'^{zzx}	-0.267954	-0.268592	-0.063821
H1z:	β'^{xxz}	-0.685743	-0.691192	-0.54485
H1z:	β'^{zzz}	-0.433137	-0.8431843	0.129398
H1z:	β'^{zzx}	-0.5627319	-2.002802	-144.007
H2x:	β'^{xxz}	1.348770	1.349364	0.059449
H2x:	β'^{zzz}	0.491239	0.49072155	-0.05070
H2x:	β'^{zzx}	-0.26790	-0.268388	-0.04881
H2z:	β'^{xxz}	-0.68574	-0.6911921	-0.54514
H2z:	β'^{zzz}	-0.433117	-0.4318426	0.127441
H2z:	β'^{zzx}	0.562732	2.002801	144.007

Table 8: The hyperpolarizability derivative components of gaseous water that are relevant to third order SFVS and non-zero for a given displacement are listed for both ES and extended SM calculation methods. The percent error between extended SM and ES methods is also listed. Note, the first column designates the coordinate that was displaced as described in the text, and units are in Å$^4/e$.

two other relevant directions (ZXZ and ZZZ) in the majority of coordinate displacements.

Table 8 lists the resultant interaction hyperpolarizability derivative tensor in the XXZ, ZXZ, and ZZZ directions calculated using ES and extended SM methods. Note, only the derivatives that have an order of magnitude ≥ 0.1Å$^4/e$ in the SFVS relevant directions are given in Table 8.

In pursuit of further testing the extended SM, the total hyperpolarizability of a water dimer (the two molecules were parallel to each other and 5 $\mathring{A}$ apart) was calculated using both ES and extended SM methods. The same coordinate displacement method, detailed previously, was implemented to obtain the hyperpolarizability derivative matrix. In this case, all 18 possible displacements were tested. The results of ES and extended SM methods were compared to determine whether the extended SM was capable of capturing the influence of the additional interactions affect on the system hyperpolarizability. The XXZ hyperpolarizability derivative tensor element calculated *via* extended SM exhibits at most a 2.4% difference from the ES determinations, and this difference is as small as .16%. The ZZZ and ZZX hyperpolarizability tensor elements are not reproduced as well as the XXZ element. In general, most of the ZZZ and ZZX derivative tensor elements are within a percent difference of 2-3%. However, there are outliers that fall far from the ES value – as high as 139% difference in the ZZX direction.

The model was further tested by accessing its ability to capture the hyperpolarizability tensor components of condensed phase water as compared to two other detailed, ES based, theoretical investigations.[2, 3] The system configurations were generated using CM3D,[43] an MD code developed at the Center for Molecular Modeling at the University of Pennsylvania. Specifically, microcanonical MD of 64 water molecules was performed at a density of 1.0 g /cm^3 and an average temperature of 298K. Using well equilibrated configurations, the hyperpolarizability tensor elements were calculated.

The XXZ and YYZ components of the hyperpolarizability tensor compare well with the other ES based theoretical investigations. Specifically, the change of sign that is associated with the hyperpolarizability tensor of water going from the gas phase to the condensed phase is reproduced and this is a major accomplishment for our classical polarization model. Our method calculates β^{XXZ}=0.18 a.u. ($Bohr^5/e$) and β^{YYZ}=10.60 a.u.. Values calculated by Jensen (Kusalik et. al) using various ES techniques fall in the range of β^{XXZ}=0.14-0.81 (4.1-5.7) a.u. and β^{YYZ}=7.5-9.03 (10.9-18.8) a.u.. For reasons that are presently unclear, the β^{ZZZ} component calculated by our model does not appear to be captured accurately – the trademark change of sign is not present in this direction. Our model calculates β^{ZZZ}=-42.175 a.u. while the other investigations got positive values of about 10.0 a.u..[2, 3]

4 Conclusion

The extended SM does remarkably well in reproducing the most relevant component to third order SFVS – the XXZ component of the system hyperpolarizability derivative tensor for a water, a water dimer, and condensed phase water. For calculations involving one and two water molecules, the total system hyperpolarizability calculated *via* ES and extended SM agree well. For calculations involving condensed phase water, only two of the three non-zero hyperpolarizability tensor components could be reproduced. To date, no other molecularly detailed, on the fly, computationally tractable technique has been able to do as well in reproducing a system's hyperpolarizability, let alone the hyperpolarizability derivatives and for a system as complicated as water. Further investigation and refinement of this model is clearly required, but the initial results are quite promising. Specifically, because the total system hyperpolarizability is a function of intrinsic and system polarizability elements, it is reasonable that the extended SM be modified to incorporate atomic (site) intrinsic polarizability tensors instead of this quantity being represented as a point polarizability.

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