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Vibrational Corrections to Magneto-Optical Rotation: A Computational Study

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Vibrational corrections to the Verdet constants of nine molecules (H_2, N_2, CO, H_2O, CH_4, benzene, toluene, *p*-xylene, and *o*-xylene) were calculated with pure density functional theory (DFT), hybrid DFT, and an approximate coupled-cluster theory. Comparisons are made for the accuracy of the vibrational averages among different methods and with respect to experimental data where available. It is found that vibrational corrections to magneto-optical rotation can be as large as 10% of the equilibrium value. Hybrid DFT with the B3LYP hybrid functional offers reasonable accuracy at a relatively inexpensive computational cost for accurate calculations of vibrationally averaged Verdet constants.

1. Introduction

One of the goals of theoretical chemistry is predicting the electronic structure and electric, magnetic, and mixed electric−magnetic response properties of new molecule-based materials from first principles. Unfortunately, at present wavefunction-based ab initio methods that are known to yield highly accurate response properties can be prohibitively expensive for systems with many atoms and properties that require large polarized diffuse basis sets. Furthermore, to be able to make direct comparisons of calculated molecular properties with experiment one should consider that the experimentally determined properties represent an average over a range of geometries due to the vibrational motion of molecules. Computing vibrational corrections requires more computational effort than calculating the property at the equilibrium geometry. Further factors that influence the outcome of experiment include solvation, intermolecular interactions or crystal packing, and the temperature dependence of the aforementioned effects.

Vibrational averaging has been shown to be a significant factor in the calculation of molecular properties derived from electric, magnetic, and mixed electric and magnetic perturbations.[1−23] The application of density functional theory (DFT) for predictions of molecular properties and their vibrational averages is particularly attractive because DFT has a comparatively low computational cost among the first-principles quantum-chemical methods and often provides reliable results. Furthermore, DFT-based vibrational frequencies are known to agree very well with experimental data,[24] which is obviously a highly important aspect for computations of vibrational averages. We have recently demonstrated by hybrid-DFT computations on a test set of 22 rigid chiral organic molecules that on average the zero-point vibrational correction of natural optical rotation is on the order of 20% of the corresponding calculated equilibrium value.[18] Therefore, vibrational effects are highly significant and should be considered when evaluating the agreement between theory and experiment for DFT and other quantum chemical methods. Our protocol for calculating vibrational averages of molecular properties was subsequently extended to consider their temperature dependence and applied to study the temperature dependence of the optical rotation of bicyclic chiral organic molecules.[23,25]

In the present work, we apply this technique to the calculation of the Verdet constant which is the material parameter that relates the magnitude of magneto-optical rotation (MOR, i.e., magnetic-field induced optical rotation) to the amplitude of the applied magnetic field (see section 2). The focus of this work will be to determine (i) the magnitude of zero-point and finite-temperature vibrational corrections on MOR at the molecular level and (ii) if DFT can be used to provide vibrational corrections of the correct magnitude at comparatively low computational cost. In combination with a highly accurate equilibrium value (i.e., obtained with a correlated ab initio method), the use of such DFT−derived vibrational corrections may significantly increase the predictive power of computational methods for computations of MOR. Interest in theoretical methods for magneto-optical phenomena is stirred by the possibilities of developing new valuable tools for examining molecular electronic structure. For example, the effect of circularly polarized light on nuclear magnetic resonance (NMR) spectra and its relation to the MOR properties has been studied previously.[26,27] It has been shown that this effect leads to shifts in the NMR spectrum, which may be used for the resolution enhancement of the NMR spectroscopy of more complicated molecules.

Calculations of Verdet constants have previously been performed using various theoretical techniques.[27−33] Most of the earlier work has dealt with rather small molecules because, as a quadratic response property, calculations of Verdet constants can be time-consuming and require high-quality basis sets. Bishop and Cybuslki[29] have studied the Verdet constant of H_2 and D_2, and Parkinson et al.[30] have calculated the Verdet constant of H_2, N_2, CO, and HF. The quadratic response function approach has further been applied within the multiconfiguration self-consistent field (SCF)[31] and coupled cluster[32] frameworks, respectively. In ref 33, a gauge-origin independent formulation of the Verdet constant has been presented for coupled cluster wave functions (using gauge-including atomic orbitals (GIAOs)).[34−36] Coriani et al. have provided the most accurate calculations of the Verdet constant to date using the CC3 method.[37] Krykunov et al.[38,39] have implemented the calculation of the Verdet constant for time-dependent density functional theory (TDDFT) with GIAOs. Other TDDFT implementations have become available during the past few years as well. For

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instance, Botek et al. have recently reported calculations of the Verdet constant of benzene, toluene, and *p*-xylene based on the B3LYP hybrid functional.[40]

In this article, we report the calculation of vibrationally averaged Verdet constants for nine molecules (H_2, N_2, CO, H_2O, CH_4, benzene, toluene, *p*-xylene, *o*-xylene) using "pure" (i.e., non-hybrid) DFT, hybrid DFT, and the approximate coupled-cluster theory. Comparisons are made to experimental data where available. After a brief description of the methodology used in this study, a discussion for trends, similarities, and differences between the nine molecules is given. Finally, the results are summarized, and conclusions are drawn.

2. Methodology and Computational Details

2.1. Verdet Constants. The MOR or Faraday effect[41,42] involves the propagation of linearly polarized light through a uniformly magnetized medium. Even for a non-chiral substance the polarization plane of light rotates if the light beam propagates parallel to the direction of an external magnetic field. The Verdet constant quantifies the observed magnitude of the rotation angle as a function of the applied magnetic field[43] and can be defined via

$$V(\omega) = \frac{\phi(\omega)}{B_\gamma l} \tag{1}$$

where ϕ is the rotation of the plane of polarization, B_γ is the magnitude of the magnetic field along the direction γ of propagation of light, and l is the path length through the medium. The Verdet constant is a material property that depends on the frequency of the incident light beam. For the present work, we consider the Verdet constant to be a molecular property.

In the transparent region of the spectrum, the rotation ϕ of a solution or a gas with freely rotating molecules is proportional to the change in the imaginary part of the frequency-dependent linear electric molecular polarizability $\alpha_{\alpha\beta}(\omega)$ due to the application of a static magnetic field.[44−46] As a result, the Verdet constant can be expressed as

$$V(\omega) = \omega C \epsilon_{\alpha\beta\gamma} \left(\frac{\partial \alpha^{i}_{\alpha\beta}(\omega)}{\partial B_\gamma} \right)_{B_\gamma = 0} \tag{2}$$

with $\alpha^{i}_{\alpha\beta}(\omega)$ and $\epsilon_{\alpha\beta\gamma}$ denoting the imaginary part of the frequency dependent linear polarizability and the third-rank Levi−Civita tensor, respectively, and the constant C in SI units is given by

$$C = \frac{2}{6}\left(\frac{1}{2c}\right)\left(\frac{2\pi N}{4\pi\epsilon_0}\right) \tag{3}$$

where ϵ_0 is the permittivity of free space and N is the number of molecules per unit volume. In atomic units, $C = 7.641\,77 \times 10^{-3} N$, which for an ideal gas at 273.15 K and a pressure of 1 atm ($N = 3.981\,39 \times 10^{-6} a_0^{-3}$) yields $C = 3.042\,49 \times 10^{-8}$. For the molecules H_2, N_2, CO, H_2O, and CH_4, we report the Verdet constants in atomic units to facilitate easy comparison with previously published experimental and calculated Verdet constants. In the case of benzene, toluene, *p*-xylene, and *o*-xylene, we report Verdet constants for the liquid phase, again to compare with previously published data more easily. In this case, C is obtained from the density of the liquid, but $V(\omega)$ is calculated without further considering intermolecular interactions. The results for the four liquids have been converted from atomic units to SI units of $\deg\cdot T^{-1}\cdot m^{-1}$. All frequencies ($\omega$) have been given in atomic units.

Verdet constants have been computed with three methods: pure (non-hybrid) DFT with an asymptotically correct Kohn−Sham potential (SAOP, see below), hybrid DFT using the popular B3LYP functional, and the approximate coupled-cluster method CC2. In some cases, a comparison with CCSD is made. The calculation of the Verdet constants with pure DFT was performed using the AOResponse module of the Amsterdam Density Functional (ADF) program developed in our group. Details of this implementation have been published previously.[38,39] The same diffuse polarized triple-ζ Slater-type basis "Vdiff" as in ref 39 has been applied. This basis set represents a good compromise between computational expense and the need for a large polarized basis set for this application. The statistical average of (model) orbital potentials (SAOP) has been used in these calculations. This is an asymptotically correct Kohn−Sham potential that has been successful in calculations of various dynamic response properties.[47−49] For hybrid DFT, the B3LYP hybrid functional[50,51] was used to calculate the Verdet constants. We have further determined Verdet constants with the CC2 approach. CC2 is an approximate coupled-cluster theory that is known to yield quite reliable excitation energies.[52−56] The Dalton 2.0 code was used for all quadratic response calculations based on B3LYP and CC2.[57−61] The Gaussian-type basis sets used for the calculations with the Dalton code include the augmented correlation consistent basis sets of the type aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ as provided in the Dalton basis set library. In all cases, we have calculated the Verdet constants at frequencies for which literature and experimental data are available.

2.2. Vibrational Averaging of Calculated Molecular Properties. For this work we have applied a recently developed program that calculates vibrationally averaged Verdet constants as a function of temperature.[22] This program is easily adapted to any standard quantum chemistry software that can calculate intramolecular forces and the property of interest analytically. The nuclear vibrational wave functions are described by harmonic oscillators with cubic anharmonicity included on a first-order perturbational level.

Previous work on vibrational averaging has been performed by a number of authors. Toyama et al. have examined vibrational effects on internuclear distances derived from a Taylor series expansion in normal coordinates.[62] Bishop et al. and Auer et al. have used perturbation theory to study vibrational effects on electric and magnetic properties.[63−67] Sundholm et al. have computed vibrational averages of NMR shielding tensors by solving the rovibrational Schrödinger equation with a finite-element method.[68] Similar techniques have been used by Christiansen et al. to calculate accurate polarizabilities.[69] Shielding surfaces have been used by Wigglesworth and co-workers to obtain accurate calculations of NMR shielding constants.[70] Ruud, Åstrand, Ruden, and others have calculated vibrational averages for a number of molecular properties using a Taylor series expansion about an effective geometry.[2−7,11−13,15−17] The zero-point vibrational corrections to polarizability and hyperpolarizability have also been determined using field-induced coordinates,[71] and Quinet et al. have computed zero-point vibrational averages of hyperpolarizability using analytical property derivatives.[9]

In this work, the temperature dependence of the Verdet constant (represented here as a general molecular property P) is modeled with an expression that includes to first-order effects due to both the anharmonicity of the potential energy surface as well as the curvature of the property surface:

$$\langle P\rangle_T = P_{\mathrm{e}} + \frac{1}{4}\sum_i \coth\left(\frac{\hbar\omega_i}{2kT}\right)\left(\frac{\partial^2 P}{\partial {q_i}^2}\right) - \frac{1}{4\hbar}\sum_i \frac{1}{\omega_i}\left(\frac{\partial P}{\partial q_i}\right)\sum_j \coth\left(\frac{\hbar\omega_j}{2kT}\right)k_{ijj} \qquad (4)$$

The first term in the vibrational correction involving the second derivatives of P represents the *property curvature* correction. The second term involving the cubic force constants k_{ijj} represents the vibrational *anharmonicity* correction. [The names of the terms used here differ from the terminology used by Bishop et al. and Quinet et al. (e.g., refs 63 and 9). The anharmonicity term corresponds to the mechanical anharmonicity term of refs 63 and 9, and the property curvature term corresponds to the electrical anharmonicity term of refs 63 and 9.] In eq 4, ω_i is the frequency of normal mode i. P_{e} is the property calculated at the equilibrium geometry, T is the temperature, k is the Boltzmann constant, and q_i are dimensionless normal coordinates. For $kT \gg \hbar\omega_i$, the hyperbolic cotangent factor increases linearly with temperature. As the temperature approaches 0 K, the coth factors decrease to 1, and the zero-point vibrational average is obtained.

For each molecule, we have calculated an optimized geometry using strict convergence criteria. Geometry optimization was carried out until the norm of the gradients converged to about $10^{-6}\ E_{\mathrm{h}}\ a_0^{-1}$. Grids with a mesh size smaller than the default were used for all DFT calculations. Using this optimized geometry, the frequencies and normal modes were then computed. In all cases the same basis sets were applied as those that were used in the subsequent Verdet constant computations. The results of the frequency calculations were used to construct a set of geometries corresponding to displacements along the normal coordinates q_i to obtain the derivatives in eq 4 by numerical differentiation.[18] For each normal mode, the displacement of each atom was limited such that the maximum displacement was 0.04 a_0. It has been shown previously that such a displacement magnitude yields reliable numerical derivatives in DFT calculations.[72] The Vosko−Wilk−Nusair (VWN)[73] functional along with the revised Perdew−Becke−Ernzerhof (revPBE)[74,75] gradient corrections were used for all geometry optimizations and vibrational frequency calculations for pure DFT with ADF because there is no corresponding energy expression for the SAOP potential. For the B3LYP computations the Turbomole 5.7[76] code was used for the optimizations and all gradient and frequency calculations. Additionally, the CC2 approach employing the resolution-of-the-identity (RI) approximation as implemented in Turbomole 5.7 was used for all optimizations and frequency and gradient calculations using this method.[52,53,77] Vibrational averaging calculations using this numerical differentiation technique can be quite demanding computationally, although the computations are trivially parallelized and therefore do not necessarily require a large turnaround time if a computing cluster is available. For example, for each wavelength considered here the vibrational average of the Verdet constant of p-xylene requires a total of 96 energy gradient and quadratic response function calculations in addition to the frequency and Verdet constant calculations at the equilibrium geometry. The computational effort may eventually be reduced for cases with a high symmetry, but in its present form the vibrational averaging protocol employed by us does not use symmetry.

TABLE 1: A Comparison of the Experimental V_{exp}, Calculated Literature V_{lit}, and the Equilibrium Verdet Constants for Three Computational Methods of Five Nonaromatic Molecules Used in This Study[a]

molecule	ω	V_{exp}	V_{lit}	V_{SAOP}[b]	V_{B3LYP}[c]	V_{CC2}[d]	V_{CC2}[e]	V_{CC2}[f]	V_{CCSD}[g]
H_2	0.11391	0.501[h]	0.456[i]	0.570	0.478	0.421	0.448	0.449	0.458
	0.08284	0.251[h]	0.229[j]	0.285	0.241	0.213	0.226	0.227	0.231
	0.06509	0.150[h]	0.139[j]	0.172	0.146	0.129	0.137	0.137	0.140
	0.05360	0.103[h]	0.093[j]	0.115	0.098	0.087	0.092	0.092	0.094
N_2	0.11391	0.492[h]	0.497[k]	0.511	0.464	0.429	0.454	0.461	
	0.08284	0.251[h]	0.252[k]	0.259	0.235	0.217	0.231	0.234	
	0.06509	0.152[h]	0.153[k]	0.157	0.142	0.132	0.140	0.142	
	0.05360	0.101[h]	0.103[k]	0.106	0.095	0.088	0.094	0.095	
CO	0.11391	0.895[h]	0.702[l]	0.928	0.899	0.856	0.884	0.886	
	0.08284	0.444[h]		0.452	0.434	0.418	0.432	0.434	
	0.06509	0.261[h]		0.270	0.258	0.249	0.259	0.259	
	0.05360	0.175[h]		0.180	0.172	0.166	0.173	0.173	
H_2O	0.11391	0.884[m]		0.865	0.897	0.901	0.922	0.939	
	0.08856	0.651[n]	0.918[o]	0.488	0.495	0.501	0.518	0.529	
	0.06509	0.281[m]		0.252	0.252	0.256	0.266	0.273	
	0.05695	0.211[m]		0.191	0.190	0.193	0.201	0.206	
CH_4	0.11391	1.36[h]	1.276[p]	1.499	1.320	1.225	1.247		
	0.08284	0.685[h]	0.639[p]	0.746	0.658	0.615	0.626		
	0.06509	0.408[h]	0.386[p]	0.449	0.396	0.371	0.378		
	0.05360	0.277[h]	0.259[p]	0.300	0.265	0.249	0.253		

[a] All Verdet constants are reported in units of au × 10^7. [b] SAOP/Vdiff//revPBE/Vdiff. [c] B3LYP/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ. [d] CC2/aug-cc-pVDZ//CC2/aug-cc-pVDZ. [e] CC2/aug-cc-pVTZ//CC2/aug-cc-pVTZ. [f] CC2/aug-cc-pVQZ//CC2/aug-cc-pVQZ. [g] CCSD/aug-cc-pVQZ//CCSD/aug-cc-pVQZ. [h] Reference 78. [i] CCSD/aug-cc-pV6Z from ref 33. [j] James-Coolidge type wave functions from ref 29. [k] CC3/aug-cc-pVQZ from ref 37. [l] SCF/ (11s7p4d)/[7s6p4d] basis for C and (11s7p4d)/[7s6p4d] for O from ref 30. [m] Reference 79. [n] Reference 80. [o] SAOP/ET2 from ref 39. [p] CC2/d-aug-cc-pVTZ from ref 37.

3. Results

For each one of the nine molecules, H_2, N_2, CO, H_2O, CH_4, benzene, toluene, o-xylene, and p-xylene, we have calculated the equilibrium Verdet constants and the corresponding zero-point vibrational averages at a number of frequencies. The data for the equilibrium Verdet constants for the five nonaromatic molecules considered in this study are given in Table 1. The corresponding zero-point vibrational corrections and vibrational averages are given in Tables 2 and 3. For H_2 and N_2 we have additionally calculated equilibrium Verdet constants, vibrational corrections, and vibrational averages on the basis of a variety of methods and basis sets, as shown in Tables 4 and 5. The equilibrium Verdet constants for the four aromatic molecules considered in this work are collected in Table 6. The zero-point vibrational corrections and vibrational averages for the aromatic molecules are shown in Tables 7 and 8, respectively. We have split up the set of molecules into the diatomic nonaromatic (H_2, N_2, and CO), polyatomic nonaromatic (H_2O and CH_4), and aromatic (benzene, toluene, o-xylene, p-xylene) molecules to facilitate the discussion.

3.1. H_2, N_2, and CO. As shown in Tables 1, 4, and 5 the Verdet constants for H_2, N_2, and CO at the equilibrium geometries calculated with SAOP/Vdiff are larger than the experimental data at all four frequencies. In contrast, hybrid DFT and the CC2 method underestimate the experimental Verdet constants for H_2 and N_2 at all frequencies examined here. The CO equilibrium Verdet constants are lower than experiment except for the highest frequency with B3LYP/aug-cc-pVDZ. Using CCSD with the aug-cc-pVQZ basis set yields Verdet constants at the equilibrium geometry of H_2 that are also smaller than the experimental values. However, this is not surprising as the equilibrium calculations do not include vibrational effects.

TABLE 2: A Comparison of the Vibrational Corrections to the Verdet Constants for Three Computational Methods of the Five Molecules Considered in This Study[a]

molecule	ω	$\Delta_a V_{SAOP}$[b]	$\Delta_p V_{SAOP}$[b]	ΔV_{SAOP}[b]	$\Delta_a V_{B3LYP}$[c]	$\Delta_p V_{B3LYP}$[c]	ΔV_{B3LYP}[c]	$\Delta_a V_{CC2}$[d]	$\Delta_p V_{CC2}$[d]	ΔV_{CC2}[d]
H_2	0.11391	0.044	0.023	0.067	0.031	0.009	0.040	0.028	0.009	0.037
	0.08284	0.021	0.010	0.031	0.015	0.004	0.019	0.014	0.004	0.018
	0.06509	0.013	0.006	0.019	0.009	0.003	0.012	0.008	0.002	0.010
	0.05360	0.008	0.004	0.012	0.006	0.002	0.008	0.006	0.002	0.008
N_2	0.11391	0.004	0.001	0.005	0.002	0.002	0.004	0.002	0.000	0.002
	0.08284	0.002	0.001	0.003	0.001	0.001	0.002	0.001	0.000	0.001
	0.06509	0.001	0.001	0.002	0.001	0.000	0.001	0.001	0.000	0.001
	0.05360	0.001	0.000	0.001	−0.001	−0.008	−0.009	0.000	0.000	0.000
CO	0.11391	0.004	0.004	0.008	0.002	0.004	0.006	0.004	0.004	0.008
	0.08284	0.002	0.002	0.004	0.001	0.002	0.003	0.002	0.002	0.004
	0.06509	0.001	0.001	0.002	0.000	0.001	0.001	0.001	0.001	0.002
	0.05360	0.001	0.001	0.002	0.000	0.001	0.001	0.001	0.001	0.002
H_2O	0.11391	0.042	0.026	0.068	0.049	0.032	0.081	0.056	0.036	0.092
	0.08856	0.023	0.014	0.037	0.026	0.016	0.042	0.029	0.018	0.047
	0.06509	0.011	0.007	0.019	0.013	0.008	0.021	0.015	0.009	0.024
	0.05695	0.009	0.005	0.014	0.009	0.006	0.015	0.011	0.006	0.017
CH_4	0.11391	0.064	0.224	0.288	0.051	0.077	0.128	0.048	0.068	0.116
	0.08284	0.031	0.106	0.137	0.025	0.036	0.061	0.024	0.033	0.057
	0.06509	0.018	0.062	0.080	0.015	0.021	0.036	0.014	0.019	0.033
	0.05360	0.012	0.041	0.053	0.010	0.014	0.024	0.009	0.013	0.022

[a] All corrections to the Verdet constants are reported in units of au × 10^7. [b] SAOP/Vdiff//revPBE/Vdiff. [c] B3LYP/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ. [d] CC2/aug-cc-pVDZ//CC2/aug-cc-pVDZ.

TABLE 3: Comparison of the Experimental V_{exp} and the Zero-Point Vibrationally Averaged Verdet Constants $\langle V \rangle_0$ for Three Computational Methods of the Five Nonaromatic Molecules Used in This Study[a]

molecule	ω	V_{exp}	$\langle V_{SAOP} \rangle_0$[b]	$\langle V_{B3LYP} \rangle_0$[c]	$\langle V_{CC2} \rangle_0$[d]	V_{CC2}[e] + ΔV_{B3LYP}[c]
H_2	0.11391	0.501[f]	0.637	0.518	0.458	0.489
	0.08284	0.251[f]	0.316	0.260	0.231	0.246
	0.06509	0.150[f]	0.191	0.158	0.139	0.149
	0.05360	0.103[f]	0.127	0.106	0.095	0.100
N_2	0.11391	0.492[f]	0.516	0.468	0.431	0.465
	0.08284	0.251[f]	0.262	0.236	0.218	0.236
	0.06509	0.152[f]	0.159	0.143	0.133	0.143
	0.05360	0.101[f]	0.107	0.086	0.088	0.086
CO	0.11391	0.895[f]	0.936	0.905	0.864	0.892
	0.08284	0.444[f]	0.456	0.436	0.421	0.437
	0.06509	0.261[f]	0.272	0.259	0.251	0.260
	0.05360	0.175[f]	0.182	0.173	0.168	0.174
H_2O	0.11391	0.884[g]	0.933	0.978	0.993	1.020
	0.08856	0.651[h]	0.525	0.537	0.548	0.571
	0.06509	0.281[g]	0.270	0.273	0.279	0.294
	0.05695	0.211[g]	0.205	0.205	0.211	0.221
CH_4	0.11391	1.36[f]	1.787	1.448	1.341	
	0.08284	0.685[f]	0.883	0.719	0.672	
	0.06509	0.408[f]	0.529	0.432	0.405	
	0.05360	0.277[f]	0.353	0.289	0.271	

[a] All Verdet Constants are Reported in Units of au × 10^7. [b] SAOP/Vdiff//revPBE/Vdiff. [c] B3LYP/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ. [d] CC2/aug-cc-pVDZ//CC2/aug-cc-pVDZ. [e] CC2/aug-cc-pVQZ//CC2/aug-cc-pVQZ. [f] Reference 78. [g] Reference 79. [h] Reference 80.

The zero-point vibrational average at this (full) CI level is in fact in excellent agreement with experiment, as shown in Table 4. As was already demonstrated by Bishop and Cybulski, excellent agreement is obtained between theory and experiment for H_2 when the vibrational average of the Verdet constant of H_2 is calculated at a high level of theory and a large basis set.[29] Interestingly, the equilibrium Verdet constants calculated with B3LYP/aug-cc-pVDZ for N_2 are very close in agreement with the much more expensive CC2 method with a triple-ζ basis set. In the table, we have also included the Verdet constant of N_2 calculated with the CC3 method by Coriani et al.[37] Note that better agreement with experiment is obtained when triple excitations are included in the equilibrium coupled-cluster calculations. For all three molecules, moving to a larger basis set with the CC2 method yields Verdet constants that are closer to experimental data.

For H_2, the vibrational corrections at the best theory and largest basis set examined here represent a correction that is almost 10% of the Verdet constant at the equilibrium geometry. This is in excellent agreement with the vibrational correction calculated in ref 29. The large zero-point vibrational correction calculated for the Verdet constant of H_2 is expected because of the low-mass of the hydrogen nuclei.

In contrast to H_2, the vibrational corrections to the Verdet constants of N_2 and CO are small as shown in Tables 2 and 5. Because of the heavier mass of these atoms and the much stiffer bonds, it is not surprising that the corrections are much smaller when compared to H_2. For DFT and CC2, the corrections for N_2 and CO are only about 1% of the equilibrium values. As the light frequency decreases, the vibrational corrections generally decrease until they become negligible roughly within the numerical precision of our approach. For CO, the corrections for pure SAOP/Vdiff and CC2/aug-cc-pVDZ are slightly larger than the corrections for B3LYP/aug-cc-pVDZ. The property curvature corrections are about equal in magnitude to the anharmonicity corrections. However, hybrid DFT indicates a slightly smaller anharmonicity correction than the calculations with pure DFT and CC2 show.

For H_2 and CO, the closest agreement with experiment (other than what is predicted by CCSD for H_2) is obtained when the vibrational corrections from B3LYP/aug-cc-pVDZ are added to the equilibrium Verdet constant calculated with CC2/aug-cc-pVQZ. It should be noted that very good results are also obtained using hybrid DFT for both the equilibrium calculation and the vibrational corrections.

In contrast to H_2 and CO, vibrational averages of the Verdet constants of N_2 calculated with pure DFT yield the best agreement with experiment, although the vibrational averages are slightly larger than experimental values. The vibrational averages calculated with B3LYP and CC2 even with the large aug-cc-pVTZ basis set are lower than the experimental Verdet constants and do not agree as well as the SAOP/Vdiff calcula-

TABLE 4: Comparison of Theories and Basis Sets for the Calculation of the Equilibrium Verdet Constants ($V(\omega)$), Zero-Point Vibrational Corrections ($\Delta V(\omega)$), and Zero-Point Vibrational Averages ($\langle V(\omega)\rangle_0$) of H_2[a]

	ω	SAOP/Vdiff	B3LYP/D[b]	CC2/D[b]	CC2/T[c]	CC2/Q[d]	FCI/Q[d]	expt[e]
$V(\omega)$	0.11391	0.570	0.478	0.421	0.448	0.449	0.458	0.501
	0.08284	0.285	0.241	0.213	0.226	0.227	0.231	0.251
	0.06509	0.172	0.146	0.129	0.137	0.137	0.140	0.150
	0.05360	0.115	0.098	0.087	0.092	0.092	0.094	0.103
$\Delta V(\omega)$	0.11391	0.067	0.040	0.037	0.043	0.043	0.043	
	0.08284	0.031	0.019	0.018	0.021	0.021	0.021	
	0.06509	0.019	0.012	0.010	0.012	0.012	0.012	
	0.05360	0.012	0.008	0.008	0.008	0.008	0.008	
$\langle V(\omega)\rangle_0$	0.11391	0.637	0.518	0.458	0.491	0.492	0.501	0.501
	0.08284	0.316	0.260	0.231	0.247	0.248	0.252	0.251
	0.06509	0.191	0.158	0.139	0.149	0.149	0.152	0.150
	0.05360	0.127	0.106	0.095	0.100	0.100	0.102	0.103

[a] All Verdet constants were calculated at the respective geometries given by the theory and basis set and are reported in units of au × 10^7. [b] aug-cc-pVDZ. [c] aug-cc-pVTZ. [d] aug-cc-pVQZ. [e] Reference 78.

TABLE 5: Comparison of Theories and Basis Sets for the Calculation of the Equilibrium Verdet Constants ($V(\omega)$), Zero-Point Vibrational Corrections ($\Delta V(\omega)$), and Zero-Point Vibrational Averages ($\langle V(\omega)\rangle_0$) of N_2[a]

	ω	SAOP/Vdiff	B3LYP/D[b]	CC2/D[b]	CC2/T[c]	expt.[d]
$V(\omega)$	0.11391	0.511	0.464	0.429	0.454	0.492
	0.08284	0.259	0.235	0.217	0.231	0.251
	0.06509	0.157	0.142	0.132	0.140	0.152
	0.05360	0.106	0.095	0.088	0.094	0.101
$\Delta V(\omega)$	0.11391	0.005	0.004	0.002	0.002	
	0.08284	0.003	0.002	0.001	0.001	
	0.06509	0.002	0.001	0.001	0.001	
	0.05360	0.001	−0.009	0.000	0.000	
$\langle V(\omega)\rangle_0$	0.11391	0.516	0.468	0.431	0.456	0.492
	0.08284	0.262	0.236	0.218	0.232	0.251
	0.06509	0.159	0.143	0.133	0.141	0.152
	0.05360	0.107	0.086	0.088	0.094	0.101

[a] All Verdet constants were calculated at the respective geometries given by the theory and basis set and are reported in units of au × 10^7. [b] aug-cc-pVDZ. [c] aug-cc-pVTZ. [d] Reference 78.

TABLE 6: Comparison of the Experimental V_{exp}, Calculated Literature V_{lit}, and Equilibrium Verdet Constants for Three Computational Methods for the Four Aromatic Molecules Used in This Study[a]

molecule	ω	V_{exp}[b]	V_{lit}[c]	V_{SAOP}[d]	V_{B3LYP}[e]	V_{B3LYP}[f]	V_{CC2}[g]
benzene	0.09113	816 ± 49	577	564	585	582	541
	0.04649	93 ± 5	129	128	132	131	
	0.02941	42 ± 2	50	48	51	51	
toluene	0.09113	709 ± 43	516	529	527	521	
	0.04649	73 ± 5	116	120	119	118	
	0.02941	29 ± 2	45	47	46	46	
p-xylene	0.09113	647 ± 39	454	495	468	458	
	0.04649	53 ± 6	103	113	107	105	
	0.02941	14 ± 6	40	44	42	41	
o-xylene	0.09113			549	530	526	
	0.04649			121	119	118	
	0.02941			48	46	46	

[a] All Verdet constants are in solution and are reported in units of deg·T^{-1}·m^{-1}. [b] Experimental data from ref 40. [c] Calculated data from ref 40. [d] SAOP/Vdiff//revPBE/Vdiff. [e] B3LYP/aug-cc-pVDZ//revPBE/Vdiff. [f] B3LYP/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ. [g] CC2/aug-cc-pVDZ//CC2/aug-cc-pVDZ.

tions. Most of the disparity between the CC2 Verdet constants and the experimental ones can be attributed to the neglect of triple excitations.[37] The vibrational averages calculated with pure DFT are in closest agreement with experiment most likely because of a fortuitous cancellation of errors.

TABLE 7: Comparison of the Zero-Point Vibrational Corrections of the Verdet Constants with Three Computational Methods for the Four Aromatic Molecules Used in This Study[a]

molecule	ω (E_h)	ΔV_{SAOP}[b]	ΔV_{B3LYP}[c]	ΔV_{CC2}[d]
benzene	0.09113	40.3	27.8	28.6
	0.04649	8.1	5.6	
	0.02941	3.0	2.2	
toluene	0.09113	26.4	26.9	
	0.04649	5.0	5.5	
	0.02941	1.9	2.1	
p-xylene	0.09113	25.2	33.1	
	0.04649	4.7	6.9	
	0.02941	1.8	2.6	
o-xylene	0.09113	46.7	40.9	
	0.04649	10.0	8.5	
	0.02941	4.0	3.3	

[a] All Verdet constants are in solution and are reported in units of deg·T^{-1}·m^{-1}. [b] SAOP/Vdiff//revPBE/Vdiff. [c] B3LYP/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ. [d] CC2/aug-cc-pVDZ//CC2/aug-cc-pVDZ.

TABLE 8. Comparison of the Experimental V_{exp}, Literature and Zero-Point Vibrationally Averaged Verdet Constants $\langle V\rangle_0$ for Three Computational Methods for the Four Aromatic Molecules Used in This Study[a]

molecule	ω (E_h)	V_{exp}[b]	$\langle V_{SAOP}\rangle_0$[c]	$\langle V_{B3LYP}\rangle_0$[d]	$\langle V_{CC2}\rangle_0$[e]
benzene	0.09113	816 ± 49	604	610	570
	0.04649	93 ± 5	136	137	
	0.02941	42 ± 2	51	53	
toluene	0.09113	709 ± 43	555	548	
	0.04649	73 ± 5	125	123	
	0.02941	29 ± 2	49	48	
p-xylene	0.09113	647 ± 39	520	491	
	0.04649	53 ± 6	117	112	
	0.02941	14 ± 6	46	44	
o-xylene	0.09113		596	567	
	0.04649		131	127	
	0.02941		52	49	

[a] All Verdet constants are in solution and are reported in units of deg·T^{-1}·m^{-1}. [b] Experimental data from ref 40. [c] SAOP/Vdiff//revPBE/Vdiff. [d] B3LYP/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ. [e] CC2/aug-cc-pVDZ//CC2/aug-cc-pVDZ.

For both H_2 and N_2, it can be seen in Tables 4 and 5 that changing the basis from double-ζ to triple-ζ yields improved agreement with experiment for the equilibrium and zero-point vibrationally averaged Verdet constants with CC2. This is reasonable because coupled-cluster methods require large basis sets to bring out the correlation corrections inherent in the theory. We have also calculated the vibrational corrections for CO at the CC2/aug-cc-pVTZ level, and similar behavior is observed in the calculation of the zero-point vibrational average for CO. Because of the relatively minor vibrational corrections for these molecules, the improvements to the vibrational averages of the Verdet constants of N_2 and CO offered by these larger basis sets result from more accurate equilibrium values.

3.2. H_2O and CH_4. The equilibrium Verdet constants for H_2O and CH_4 calculated at four frequencies are shown in Table 1. Contrary to the diatomics discussed so far, pure DFT underestimates the Verdet constant at all four frequencies for H_2O, while it yields larger Verdet constants than what is experimentally measured for CH_4. As with the diatomic molecules used for this study, CC2 also undervalues the Verdet constants with respect to experiment for these two molecules, except for H_2O at the highest frequency considered here ($\omega = 0.11391$). As larger basis sets are used, CC2 becomes closer to the experimental Verdet constants, except at this highest frequency, where it deviates more for H_2O. For water, the equilibrium Verdet constants calculated with B3LYP are overestimated at $\omega = 0.11391$ (but not as much as CC2) and are lower than the experimental values at the lower frequencies (slightly more than CC2). The trend observed for H_2O at the lower frequencies is also observed in CH_4 where the equilibrium Verdet constants are smaller than what is measured in experiment.

The zero-point vibrational corrections (Table 2) to H_2O and CH_4 are roughly the same relative (percentage) size as the corrections to H_2, that is, about 8−10%. For H_2O, the corrections for CC2 are the largest, whereas the corrections calculated with pure DFT are the smallest. Conversely, the vibrational corrections for methane are smallest for CC2 and largest for pure DFT. For water, it appears that the anharmonicity corrections are generally larger than the property curvature corrections by a factor of about 1.5. Once again, the opposite is true for CH_4, where the property curvature terms are larger than the anharmonicity contributions.

Shown in Table 3 are the vibrational averages of the Verdet constants of H_2O and CH_4. For both of these molecules, the vibrational averages calculated at the CC2 level overall yield results that are closest to experiment. For the highest frequency considered here, pure DFT gives the zero-point vibrational average that is closest to the experimental Verdet constant for H_2O, while it gives a zero-point vibrational average that is furthest away from experiment for CH_4. It should be noted that B3LYP yields reasonable vibrational averages for these two molecules. The vibrational averages of the Verdet constants calculated with B3LYP are generally larger than experiment (in contrast to CC2) for CH_4 and are generally smaller than experiment (similar to CC2) for H_2O. The notable exception to this statement is for the highest frequency in the table.

3.3. Benzene, Toluene, *p*-Xylene, and *o*-Xylene. From Table 6, it can be seen that the equilibrium Verdet constants for all aromatic molecules (where experimental data are available) calculated with pure DFT and hybrid DFT at $\omega = 0.09113$ fall short of the experimental values as measured by Botek et al. in ref 40. Even the CC2 method with the aug-cc-pVDZ basis set produces an equilibrium Verdet constant that is lower than what is measured in experiment. At lower frequencies, the opposite trend is observed. Here, the calculated equilibrium Verdet constants for benzene, toluene, and *p*-xylene are larger than their corresponding experimental values.

As expected from the general trends observed for the nonaromatic molecules, pure DFT yields equilibrium Verdet constants that are larger than the hybrid DFT functional used here for the aromatic molecules except benzene. Differing geometries are not the main reason for this behavior. Changing the geometry to the revPBE optimized one and calculating the Verdet constant with the B3LYP hybrid functional results in only a slight change of the Verdet constant of benzene, toluene, and *o*-xylene. The Verdet constant for *p*-xylene calculated with B3LYP/aug-cc-pVDZ at the revPBE equilibrium geometry has a greater relative change compared to that of the other three aromatic molecules.

The vibrational corrections to the Verdet constant of the aromatic molecules are shown in Table 7. The zero-point vibrational corrections range from about 5% of the equilibrium Verdet constants for benzene to about 8% of the equilibrium value for *o*-xylene as calculated with B3LYP and the aug-cc-pVDZ basis set. For pure DFT, the zero-point vibrational corrections are noticeably larger for benzene and quite similar for toluene in comparison with hybrid DFT. The corrections for benzene obtained with CC2 are very close to the B3LYP corrections for this molecule.

The zero-point vibrational averages of the Verdet constants of the aromatic molecules are shown in Table 8. At $\omega = 0.09113$ the vibrational averages of benzene, toluene, and *p*-xylene are closer to the experimental measurement than the calculated Verdet constants at the equilibrium geometries. Unfortunately, this is not the case for the other lower frequencies, where the vibrational corrections shift the calculated values slightly away from the experimental Verdet constants. For benzene, B3LYP tends to yield the best agreement with experiment. However, the difference between pure DFT and hybrid DFT is relatively small (6 $\mathrm{deg{\cdot}T^{-1}{\cdot}m^{-1}}$) at the highest frequency compared to the differences between the vibrational averages and the experimental data. For the highest frequency, pure DFT yields better agreement between theory and experiment for toluene and *p*-xylene. However, this may be due to the previously noted tendency for pure DFT to yield Verdet constants that are larger than expected. At the lower frequencies, this DFT artifact hurts the vibrational averages, which are generally larger than the experimental values. As a result, B3LYP yields Verdet constants that are slightly closer to experiment.

The intrinsic vibrational temperature dependence of the Verdet constants of benzene, toluene, *p*-xylene, and *o*-xylene calculated with the B3LYP hybrid functional and the aug-cc-pVDZ basis set at $\omega = 0.09113$ is shown in Table 9. Because considering intermolecular interactions between the molecules is beyond the scope of this study, the temperature-dependence calculations considered here are based on contributions that populations of excited vibrational states make to the anharmonicity changes to the potential energy and property curvature surfaces. The correction does not include the temperature dependence of the conversion factor C in eq 3 which depends on temperature via the density.

The data in Table 9 show that, as temperature increases, the anharmonicity correction decreases slightly. However, the opposite trend is calculated for the property curvature correction, where an increase is observed as temperature increases. The overall effect is to provide only a very slight increase in the vibrational average of the Verdet constant of the aromatic molecules as temperature increases.

For benzene, the property curvature correction is stronger than the anharmonicity correction by a factor of about 1.5, as also shown in Table 9. It is also calculated that the property curvature term dominates the correction by a factor close to 2 for toluene. For *p*-xylene the factor increases to 3, and for *o*-xylene, the factor is as large as 5. Similar to the nonaromatic molecules, a

TABLE 9: Intrinsic Vibrational Temperature Dependence of the Verdet Constants for the Aromatic Molecules at $\omega = 0.09113$ Calculated with B3LYP/aug-cc-pVDZ[a]

		0 K	100 K	200 K	300 K	400 K
benzene	$\Delta_a V$	11.2	11.2	11.1	11.0	11.0
	$\Delta_p V$	16.6	16.6	16.8	17.5	18.7
	ΔV	27.8	27.8	28.0	28.5	29.7
	$\langle V \rangle$	609.9	609.9	610.0	610.6	611.8
toluene	$\Delta_a V$	9.9	9.9	9.6	9.1	8.7
	$\Delta_p V$	17.0	17.1	17.7	18.8	20.4
	ΔV	26.9	26.9	27.2	27.9	29.0
	$\langle V \rangle$	548.1	548.1	548.4	549.1	550.2
p-xylene	$\Delta_a V$	8.9	8.9	8.5	8.0	7.5
	$\Delta_p V$	24.2	24.3	25.3	27.1	29.5
	ΔV	33.1	33.2	33.8	35.1	37.0
	$\langle V \rangle$	490.8	490.8	491.4	492.7	494.6
o-xylene	$\Delta_a V$	8.9	8.8	7.9	6.4	4.8
	$\Delta_p V$	32.0	32.1	33.0	34.7	37.2
	ΔV	40.9	40.9	40.8	41.1	42.0
	$\langle V \rangle$	567.1	567.1	567.1	567.4	568.3

[a] $\Delta_a V$ is the anharmonic correction, $\Delta_p V$ is the property curvature correction, ΔV is the total vibrational correction, and $\langle V \rangle$ is the vibrational average. All Verdet constants are in solution and are reported in units of deg·T^{-1}·m^{-1}. See text for details.

stronger contribution from the property curvature rather than the anharmonicity term is also observed with several of the nonaromatic molecules, with the notable exceptions of H_2 and H_2O.

4. Discussion

From analyzing the results of the computations, it is seen that pure DFT (SAOP/Vdiff) tends to overestimate the Verdet constants at the equilibrium geometries relative to the other computational methods. It has already been stated in ref 39 that the good agreement of the equilibrium Verdet constants with experiment is likely due to a fortuitous cancellation of errors, in large part from the neglect of vibrational corrections. Evidence of the overcorrection of the equilibrium value is prevalent in the calculations of the Verdet constants for seven out of the nine molecules examined here at all frequencies, where the equilibrium Verdet constants are higher than the calculations that employ hybrid DFT or CC2. The notable exceptions are H_2O and benzene, where SAOP/Vdiff equilibrium Verdet constants are lower than the B3LYP and CC2 results for H_2O and are lower than the B3LYP results for benzene. The reason behind the overestimation of the Verdet constants with pure DFT may be in part from the slight geometry differences that are calculated between pure DFT and hybrid DFT. For example, calculation of the Verdet constants of the aromatic molecules with B3LYP at the revPBE/Vdiff optimized geometry causes a slight increase in the Verdet constant relative to the calculation at the B3LYP/aug-cc-pVDZ optimized geometry. However, it should be noted that this small difference is not large enough to explain the roughly 10−20% differences calculated between the SAOP/Vdiff and the B3LYP/aug-cc-pVDZ equilibrium Verdet constants for molecules such as H_2 and CH_4. Therefore, most of the errors in pure DFT have to be attributed to errors in the response calculations arising from deficiencies in the exchange-correlation potential and the response kernel.

Because pure DFT tends to overestimate the magnitude of the Verdet constants, it is reasonable to expect the absolute vibrational corrections and the vibrational averages to be larger than expected as well when compared to the corrections and averages computed with B3LYP and CC2. This observation holds true for all molecules examined here except for H_2O and benzene. In the extreme case (CH_4), the vibrational corrections to the Verdet constant calculated with SAOP are more than twice as large as the corrections calculated with B3LYP. As a result, vibrational averages between the two methods result in a difference of almost 20% for methane. Because of larger corrections and larger equilibrium values, the vibrationally averaged Verdet constants of many of the molecules calculated with pure DFT are overestimated in comparison to the vibrational averages calculated with B3LYP or CC2. It should be noted that in some cases, such as the higher frequencies for toluene and *p*-xylene, the relatively larger equilibrium Verdet constants and vibrational corrections of the pure DFT calculations can lead to a slightly closer agreement between the vibrational averages and the experiment.

Although it is reasonable to expect the larger vibrational corrections to be compensated with a larger equilibrium Verdet constant for pure DFT when calculating *relative* vibrational corrections, this is not always the case. For example, the differences between the relative corrections between pure DFT and hybrid DFT for methane at $\omega = 0.11391$ are quite noticeable. SAOP/Vdiff predicts a relative correction that is almost double the 10% relative correction calculated with B3LYP/aug-cc-pVDZ.

This work demonstrates that vibrational corrections are important for accurate calculations of Verdet constants. It should be noted that when using approximate computational methods, one cannot expect vibrational corrections to account for all of the differences observed between the equilibrium Verdet constants and experimental measurement. Basis set effects and electron correlation are also responsible for these discrepancies. In particular, Coriani et al. have shown that CC triples terms are necessary for accurate predictions of the Verdet constants of N_2.[37] Because the vibrational corrections for the Verdet constant of N_2 are very small, this is a good test molecule for exposing the importance of electron correlation and other non-vibrational effects in the calculation of accurate Verdet constants. However, Coriani et al. have shown that CC3 does not account for the differences between theory and experiment for the Verdet constant of CH_4. In this work, we show that a vibrationally averaged Verdet constant using CC2 leads to much better agreement between theory and experiment. It is clear that the roughly 10% vibrational correction should not be neglected except for semi-quantitative estimates.

The vibrational corrections to the Verdet constants of the aromatic molecules examined here are all positive. These corrections help push the equilibrium Verdet constants toward their experimental measurements at the highest frequency considered here ($\omega = 0.09113$). However, this is not the case for the other lower frequencies, where the equilibrium Verdet constants are already larger than the experimental values. Botek et al. reported a similar observation in comparing the equilibrium Verdet constants of three aromatic molecules calculated by hybrid TDDFT with experimental data.[40] The disparity between the calculated and the experimental values may be attributed to inaccuracies in the prediction of the excitation energies and their transition dipole moments for the molecules, including contributions from higher energy excitations that can influence the Verdet constant at low frequencies. CC2 should yield more reliable excitation energies, but it is seen to afford a similar under-estimation of the Verdet constant of benzene at low frequencies as DFT. The effects of the medium were not considered in our calculations, and molecular interactions in the liquid phase for these aromatic molecules may contribute a large part to the discrepancies observed between theory and experiment.

Overall, it appears that B3LYP is the most practical method for calculating reasonably accurate vibrationally averaged Verdet constants. Although CC2 should be considered the more accurate method, it requires large basis sets to produce better agreement with experiment as shown by the differences in the calculation of the equilibrium Verdet constants with the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets with this method. From inspecting the vibrational averages to the Verdet constant, using the aug-cc-pVDZ basis set with B3LYP provides reasonable agreement with experiment. In many cases, B3LYP/aug-cc-pVDZ provides better agreement with experimental data as compared to CC2/aug-cc-pVDZ. We have also included a column in Table 3 illustrating the vibrational average produced when the B3LYP/aug-cc-pVDZ vibrational corrections are added to a more accurate CC2/aug-cc-pVQZ equilibrium calculation. The calculations are in good agreement with experiment but are only marginally better than the vibrational averages calculated with both B3LYP equilibrium values and B3LYP vibrational corrections. However, using the DFT-derived vibrational corrections along with an accurate correlated equilibrium value might be a practical approach in cases where DFT yields a somewhat deficient equilibrium value but the correct trends for displacements along the normal coordinates.

For larger molecules, the differences between the B3LYP and CC2 methods are rather significant with respect to the computational resources and time required for their calculation. The calculation of the vibrational average of the Verdet constant of benzene with CC2/aug-cc-pVDZ has been a formidable task. As we have shown in Table 7, the vibrational corrections obtained at the much more affordable hybrid DFT level are almost identical.

For most of the molecules in this study, the property curvature term dominates the vibrational corrections but is of the same order of magnitude as the anharmonicity term. The notable exceptions are H_2 and H_2O, where the anharmonicity term is larger than the property curvature term. The largest ratio between the two vibrational correction terms is observed in *o*-xylene, where the property curvature term is about four to five times larger than the anharmonicity term.

The intrinsic temperature dependence of the vibrational averages of the Verdet constants for the nonaromatic molecules examined in this study is completely negligible at temperatures below 400 K. This is due to the very small populations of excited vibrational states at these relatively low temperatures for small molecules. The calculation of the temperature dependence based on intrinsic vibrational effects of the Verdet constant for the aromatic molecules illustrates that there is generally a very slight increase in the Verdet constant. Most of this increase occurs from an increase in the property curvature correction as temperature increases. However, this increase is tempered by a reduction in the anharmonicity correction as temperature increases.

It should be noted that the overall temperature dependence of the intrinsic vibrational corrections is small compared to the temperature dependence of the Verdet constant based solely on the changes in the density of the liquid. For example, the density of toluene changes from 0.902 g/cm^3 at 255 K to 0.839 g/cm^3 at 323 K.[81] This corresponds to about a 7% change in the density over a temperature range of 68 K at ambient pressure. Because the calculation of the Verdet constant depends linearly on the number density N, the temperature dependence of the Verdet constant based on density changes alone may contribute largely to the temperature dependence of the Verdet constant observed in experiment. Although the vibrational corrections in this temperature range are clearly much less significant, calculation of the contributions to the temperature dependence from vibrational effects alone may help elucidate the overall temperature dependence behavior of Verdet constants independent from the density changes.

5. Conclusions

The data for the vibrational averages of the Verdet constant for the molecules used in this study illustrate that considering vibrational corrections to the Verdet constant yields better agreement with experiment in most cases. It has been shown that vibrational corrections to the Verdet constant can be as large as 10% of the equilibrium values. CH_4 has the largest relative correction, while N_2 has the smallest.

Pure DFT tends to overestimate Verdet constants for the small nonaromatic molecules examined here, and this overestimation can lead to a slightly larger than expected vibrational correction. B3LYP tends to provide good quality vibrational averages of the Verdet constant at a reasonable expense. Adding B3LYP vibrational corrections to equilibrium calculations of the Verdet constant at the CC2 level has yielded only marginal improvement over consistent B3LYP vibrational averages for the molecules considered here. Highly accurate methods need large basis sets to bring about their full potential. Using CC2 or a higher correlated method with basis sets larger than double-ζ with additional polarization functions may be expensive at this time even for equilibrium Verdet constant calculations. Additionally, accurate coupled-cluster calculations may require methods well beyond single and double excitations.

Although equilibrium and vibrational averages of the Verdet constant based on non-hybrid DFT using SAOP and the Vdiff basis set lead to higher deviations from experiment for the set of small molecules considered here, for the larger aromatic molecules the deviations from experiment using this method are approximately the same size as the deviations from experiment using B3LYP (and CC2 in the case of benzene). Pure DFT affords fast computations of vibrational corrections, though B3LYP should be slightly more accurate because hybrid DFT is known to provide an excellent force field that is necessary for accurate vibrational averages.[12] However, for very large systems, faster non-hybrid DFT may provide insight into the sign and magnitude of the vibrational corrections.

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