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Density-Functional-Based Determination of Vibrational Polarizabilities in Molecules within the Double-Harmonic Approximation: Derivation and Application

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Abstract: We present a nonperturbative derivation for the primary contribution to the vibrational polarizability for molecules, clusters, and other finite systems. Using a double-harmonic approximation and a finite-field approach the vibrational polarizability is calculated within the generalized gradient approximation to the density functional theory for a variety of molecules and clusters. The agreement between theory and experiment is quite good. The results show that for small ionic molecules and clusters, inclusion of the vibrational polarizability is necessary to achieve agreement with experiment.

I. Introduction

Materials with high dielectric constants have many important technological applications. Predicting the *total* second-order molecular polarizability is one capability that is required for the computational design of materials with high dielectric constants. The second largest contribution to the static second-order polarizability tensor is usually due to field-induced atomic relaxation. As the effect is of interest to several fields of research, a common terminology is lacking. This effect has been referred to as the displacement-, atomic-, nuclear-, relaxation-, or vibrational polarizability. Here we adopt the latter term and determine this effect within the double harmonic approximation.[1−4] For an in-depth review of recent efforts related to many aspects of polarizability calculations the interested reader is especially referred to ref 1. As discussed below, this effect is governed by the dynamic effective charge tensor which is known to account for infrared intensities of vibrational modes in molecules and clusters. The goal of this paper is to provide a database of calculations on the vibrational polarizability on small, medium, and large molecules. In doing so, we hope to show

that DFT provides an excellent and efficient means for identifying molecules for which the vibrational polarizability may be important and worthy of study within higher level quantum mechanical treatments. Also through these examples we compare to other calculations and experiment and attempt to identify some of the other competing factors that affect the total polarizability of a molecule. Also, through comparison between DFT and HF we identify some cases where reasonably large deviations between the two approaches appear. We note that there has been a significant amount of work aimed at in-depth studies of polarizabilities and vibrational polarizabilities on particular molecules. These careful studies have examined the accuracy as a function of basis sets and level of correlation and have been largely focused on conventional (Hartree−Fock and beyond) quantum-chemistry approaches rather than density-functional approaches.[5−7]

The dynamic effective charge tensor describes how the total dipole moment of a molecule or other finite system changes due to an atomic displacement. For a simple dipole consisting of two point charges $\pm Q$, the change of the dipole per unit change of the separation is just Q. For crystals, the local dipole is not necessarily a well-defined notion, and effective charge tensors come in multiple forms.[8] However, the lowest nonzero moment of a finite system is a well-

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defined quantity. For a neutral molecule with N atoms, both the electrical dipole moment $\vec{p}$ and the derivative of the dipole moment with respect to the ith atomic position $\vec{u}_i$ are well defined. Only the latter quantity is uniquely defined for a charged molecule. These derivatives may be expressed as a $3 \times 3N$ tensor $\mathbf{Z}$ which has units of charge and is written

$$Z_{\alpha,i\mu} = \partial p_\alpha / \partial u_{i\mu} \tag{1}$$

This tensor is also sometimes called the "polar tensor"[9], and it is used for the calculation of the infrared intensity.[9-11] The infrared intensities are also related to the vibrational component of the *dc* molecular polarizability,[12] and a simple proof of this is included below.

By vibrational polarizability, we refer to the following physics. When a molecule is placed in a static electric field, it can lower its energy through several mechanisms. First, the electronic clouds rearrange themselves in response to the field which leads to an induced electronic dipole moment given by $p_{el,x} = \sum_y \alpha_{el,xy} E_y$. This is usually the largest linear effect. Second, this induced dipole moment is further modified since the atomic positions rearrange themselves in response to the forces caused by the direct application of a field and the subsequent electronic rearrangement. The tensor that describes the portion of the induced dipole moment due to atomic rearrangement is what we refer to as the double harmonic vibrational polarizability.

To concentrate on effects due to vibrational polarizability, we ignore molecular rotation and assume the molecule to be oriented in the lab frame. Equivalently, we work in a frame which is tied to the molecule, so that there is a fixed dipole moment. The polarizability α is then a 3×3 tensor which reduces to a scalar for symmetrical molecules such as CH_4 or SF_6. The molecular vibrations within the harmonic approximation correspond to the classical normal modes of a coupled system of oscillators

$$M_i \frac{d^2 u_{i\mu}}{dt^2} = -\sum_{j\nu} K_{i\mu,j\nu} u_{j\nu} \tag{2}$$

where the $3N \times 3N$ force constant tensor K is defined as

$$K_{i\mu,j\nu} = \frac{\partial^2 \mathscr{E}}{\partial u_{i\mu} \partial u_{j,\nu}} \tag{3}$$

and $\mathscr{E}$ is the total energy of the molecule at zero field.

The dipole moment $\vec{p}$ is a first derivative of the energy ($\mathscr{E}$), and the dynamical charge tensor and the electronic polarizability tensor are second partial derivatives given by

$$p_\alpha = -\partial \mathscr{E} / \partial E_\alpha \tag{4}$$

$$Z_{\alpha,i\mu} = -\partial^2 \mathscr{E} / \partial E_\alpha \partial u_{i\mu} = \partial F_{i\mu} / \partial E_\alpha \tag{5}$$

$$\alpha_{el,\alpha\beta} = -\partial^2 \mathscr{E} / \partial E_\alpha \partial E_\beta \tag{6}$$

In eqs 4−6, the electronic degrees of freedom must be relaxed in response to changes in the independent variables $(\vec{E}, \vec{u}_1, ..., \vec{u}_N)$, and the derivatives are evaluated at zero field and displacement ($\vec{E} = \vec{u}_i = 0$). Equation 5 also shows that the dynamical charge tensor determines how the Hellmann−

Feynman force ($F_{i\mu} = -\partial \mathscr{E} / \partial u_{i\mu}$) changes due to the application of an external electric field. As discussed in ref 11, the relationship between the dynamic effective charge tensor and the derivative of the Hellmann−Feynman force is both instructive and optimal for efficient determination of infrared and Raman intensities.

Now the total energy of the molecule may be expanded as a Taylor series in powers of both the atomic displacements and applied electric fields according to

$$\mathscr{E} = \mathscr{E}_0 - \vec{p} \cdot \vec{E} - \frac{1}{2} \vec{E} \cdot \alpha_{el} \cdot \vec{E} - \vec{E} \cdot Z \cdot \mathbf{u} + \frac{1}{2} \mathbf{u} \cdot K \cdot \mathbf{u} \tag{7}$$

In the above equation $\vec{p}$ and α are the zero-field values of the dipole moment and polarizability, respectively. The tensor notation is fairly obvious except perhaps for the asymmetrical tensor Z whose transpose Z^T is defined by

$$\vec{E} \cdot Z \cdot \mathbf{u} = \mathbf{u} \cdot Z^T \cdot \vec{E} \tag{8}$$

Now if a static external field $\vec{E}$ is applied, the atomic coordinates $\mathbf{u}$ will relax to new positions to minimize the energy according to

$$\mathbf{u} = K^{-1} \cdot Z^T \cdot \vec{E} \tag{9}$$

The force-constant matrix K operates in the $3N$-dimensional displacement space, which can be divided into two subspaces: the null space (spanned by the translational and rotational degrees of freedom ($L = 6$ in general $L = 5$ for a linear molecule) and the $3N-L$ dimension space that is orthogonal to it. The 3-vector $Z \cdot \mathbf{u}$ is the displacive electrical dipole caused by the displacement $\mathbf{u}$. It clearly vanishes when $\mathbf{u}$ lies in the null space. Taking the gradient of eq 9 by $\mathbf{u}$, the new equilibrium displacement in an external field is given by $K \cdot \mathbf{u} - Z^T \cdot \mathbf{u} = 0$. This $3N$-vector lies in the $3N-L$-dimensional positive space, and the force constant matrix can be inverted in this space, giving for the induced displacement the $3N-L$-vector. The corresponding energy of the relaxed molecule is then determined to be

$$\mathscr{E} = \mathscr{E}_0 - \vec{p} \cdot \vec{E} - \frac{1}{2} \vec{E} \cdot [\alpha_{el} + \alpha_{vib}] \cdot \vec{E} \tag{10}$$

In the above, the vibrational part of the polarizability is given by

$$\alpha_{vib} = Z \cdot K^{-1} \cdot Z^T \tag{11}$$

In fully indexed Cartesian form, the polarizability matrix is

$$\alpha_{vib,\alpha\beta} = \sum_{i\mu,j\nu} Z_{\alpha,i\mu} (K^{-1})_{i\mu,j\nu} Z^T_{j\nu,\beta} \tag{12}$$

While the above expression clearly exhibits the isotopic independence of this part of the polarizability tensor, a simpler expression, directly comparable to experimental observables, is possible by rewriting this energy in terms of the normal modes of vibration. Let $|v\rangle$ denote the eigenvector and ω_v the corresponding eigenfrequency, which satisfies the Newtonian equations

$$K |v\rangle = \omega_v^2 M |v\rangle \tag{13}$$

where M is the mass tensor which in the atom displacement basis $(i\mu)$ is

$$M_{i\mu,j\nu} = M_i \delta_{ij} \delta_{\mu\nu} \qquad (14)$$

The orthogonality and completeness relations are

$$\langle v|\mathrm{M}|v'\rangle = \delta_{vv'} \qquad (15)$$

$$\sum_v |v\rangle\langle v| = \mathrm{M}^{-1} \qquad (16)$$

The force constant matrix can be written as

$$\mathrm{K} = \sum_v \mathrm{M}|v\rangle \, \omega_v^2 \, \langle v|\mathrm{M} \qquad (17)$$

$$\mathrm{K}^{-1} = \sum_v |v\rangle \, \omega_v^{-2} \, \langle v| \qquad (18)$$

The effective charge tensor can now be written in the eigenvector basis as the charge vector for each normal mode

$$Z_{\beta,v} = \hat{\beta}\cdot\mathrm{Z}|v\rangle \qquad (19)$$

Then the vibrational polarizability can be written as a sum of contributions from the normal modes

$$\alpha_{\mathrm{vib},\alpha\beta} = \sum_v Z_{\alpha,v} \omega_v^{-2} Z_{v,\beta}^{\mathrm{T}} \qquad (20)$$

The above expression is easier to work with than eq 12 since it is clear that the five or six zero-frequency modes are to be excluded in the sum. While both eqs 12 and 20 give the same answer, it is necessary to invert within a $3N-L$ dimensional subspace when working with eq 12. However, it is also worthwhile noting that, in principle, eq 20 allows one to determine the double-harmonic vibrational polarizability from *measured* infrared spectra. Equation 12 is not directly useful for extracting second-harmonic vibrational polarizabilities from an experiment.

This equation is a generalization of a known relation[12] between infrared intensities and static polarizability. In the past, this equation has been used to determine vibrational polarizabilities from experimental IR data and from calculations.[13] We include our derivation here because it appears to be rather simple in comparison to previous derivations that appear in the literature. Equation 20 follows immediately from eq 17.29 of Born and Huang.[14] It has also been derived by Flytzanis.[15] Probably the earliest modern discussion of vibrational polarizabilities using quantum-mechanical derivations can be found in refs 16 and 17 where applications to $CHCl_3$ and CHF_3 are discussed and the above formula is derived within a sum over states method within the clamped nucleus approximation. Equations 1 and A5 of ref 16b lead to our eq 20. However, as noted in refs 16 and 17, one of the earliest discussions dates back to 1924.[18]

In addition to the interaction discussed above, there are other smaller vibrational effects that modify the polarizability of a molecule. The presence of the field modifies the spring constant matrix which changes the zero-point energy of the molecule. Also, the occurrence of anharmonicity, both diagonal and off-diagonal, leads to further corrections. We are unaware of discussions on the role of off-diagonal anharmonicity, but discussion of the zero-point effect and diagonal anharmonicity may be found in ref 19. In the notation of the work of Marti and Bishop, the above term is equivalent to $[\mu^2]^{0,0}$ in their paper.

II. Computational Details

The calculations presented below have been performed using the NRLMOL suite of density-functional-based cluster codes.[20] The Perdew-Burke-Ernzerhof (PBE) energy functional has been used in all calculations.[21] The Kohn−Sham equations are solved self-consistently for each electron in the problem. Then the HF forces are calculated, and the geometries are updated using standard force optimization methods. Geometries were considered converged when the force on each atom fell below 0.001 Hartree/Bohr. However, for the Na and H_2O clusters we used a tighter force convergence criteria of 0.0001 Hartree/Bohr. The numerical integration mesh was also significantly more dense for our calculations on the water molecules. The method for generating the basis sets used for these calculations is discussed in ref 22. These basis sets have been specifically optimized for the PBE-GGA functional using a total-energy minimization criteria for the isolated atoms. A unique feature of these basis sets is that they satisfy a theorem, proved in ref 22, that the shortest-range Gaussian function must scale as $Z^{10/3}$ in order to have the same uniform accuracy in the total energy as a function of atomic charge. This feature aids in eliminating basis-set superposition error between weakly interacting atoms.[23] For an entirely typical example we discuss fluorine in some detail. For the fluorine atom we use 14-single Gaussian exponents that range between 1.2317422×10^5 and 0.11818616 Bohr^{-2}. These are contracted to 5 s-type functions, 4 p-type functions, and 3 d-type functions. In addition the r^2 s-types derived from the d-functions are also used in the basis set. This leads to a total of 35 basis functions on the fluorine atom. Two of the contracted s-states and one of the contracted p-states are chosen so the energy of the spin-unpolarized atom is the same as the result obtained from a calculation using 14 single Gaussian for the s and p manifolds. Basis sets and the unpublished geometries are available upon request. For further discussion about how the basis-set construction method used here performs relative to large single-Gaussian basis sets, the interested reader is referred to ref 11 which discusses the calculation of electronic polarizabilities, dipole moments, and vibrational frequencies, and infrared and Raman intensities for CH_4, H_2O, C_2H_2, C_2H_4, and C_2H_6. Once the optimized geometries[24−26] are obtained, the vibrational frequencies, eigenvectors, and dynamical charge tensors ($Z_{\alpha,i\mu}$) are determined using the method discussed in ref 11. We then use eq 20 to determine the vibrational component of the polarizability. As discussed in ref 11, the infrared and Raman spectra showed some sensitivity to the inclusion of longer range polarization functions. We have used such polarization functions for the calculations displayed in Table. 1.

For a few cases where agreement between PBE-GGA, Hartree−Fock (HF), and/or experiment seems uncharacteristic, we have performed Hartree−Fock calculations using

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Table 1: Calculated and Experimental Vibrational Polarizabilities (Å³) for Molecules[d]

molecule	vibrational		electronic	
	theory	expt	theory	expt
H_2O	0.04	0.04	1.57	1.45
$(H_2O)_2$	23.30		3.19	
$(H_2O)_3$	13.50		4.82	
$(H_2O)_5$	14.52		8.13	
NF_3	1.15	0.70	3.07	2.81
HCCH	0.48	0.45	3.56	3.40
CH_4	0.04	0.03	2.63	2.60
$TiCl_4$	2.04	>1.68	15.03	15.0
SF_6	2.29	2.29	5.15	4.49
SiF_4	2.09	1.75	3.72	3.32
HCN	0.21	0.14	2.62	2.59
H_3CNC	0.07		4.87	
H_3CCN	0.03	0.04	4.59	4.28
C_{60}@Kr[a]	0.55		83.3	
C_{60}	0.58	2.0	82.9	79 ± 4
Na_2	0.00		35.91	37.91−40.0[*]
Na_3	1.72		60.89	69.8[*]
Na_8	0.63		116.2	133.5[*]
NaF	0.29		2.71	
$(NaF)_2$	9.08		3.94	20.7 ± 3.1[*]
$(NaCl)_2$	8.94		13.06	23.4 ± 2.5[*]
Ti_8C_{12} [b]	3.72		56.40	
As@Ni_{12}@As_{20} [c]	4.56		140.86	

[a] Reference 24. [b] Reference 25. [c] Reference 26. [d] This is one-third of the trace of the polarizability tensor. Unless otherwise stated the experimental values are taken from ref 12. Experimental data for C_{60} is from refs 28−31 and references therein. For the pure sodium clusters, the experimental values are total polarizabilities (denoted with an *) which have been taken from refs 51, 52, and 54.

a new exact-exchange option that we have implemented into the NRLMOL code. Unless stated otherwise, these calculations have been performed using the default PBE-GGA basis sets at the PBE-GGA geometry. We have performed these calculations to eliminate the possibility that the deviation between the methods is due to an underlying numerical, geometrical, or basis-set completeness issue. For the Hartree−Fock calculations discussed here we have converged the total energy to 10^{-9} Hartree and used the same finite field approach as for the case of the PBE-GGA calculations.

III. Results

Table 1 presents calculations on several molecular systems which include both covalent, ionic bonding, and hydrogen bonding. It also include calculations on systems with both loosely and tightly bound electrons. We have calculated both the electronic and vibrational contributions to the polarizability tensor. Agreement is generally good.

Fullerene Molecule. The polarizability of the Fullerene molecules has been well studied both theoretically and experimentally.[27−31] Here we calculate the electronic polarizability to be 82.9 Å³ which is in good agreement with one of the earliest density-functional calculations[27] of 83.5 Å³. This earlier calculation used the same code, a slightly different version of DFT, slightly smaller basis sets, and geometries that were not as well converged.[27] The good agreement between the early and most recent calculations

indicate that the electronic part of the neutral fullerene polarizability is rather robust, and the experimental polarizability[28−31] is known to be very close to this number as shown in Table 1 (79 ± 4). Within HF, Fowler, Lazzeretti, and Zanasi have calculated the electronic polarizability of the fullerene molecule to be 65.6 Å³. Their method is an iterative AO-based version of the coupled HF procedure due to McWeeny and Diercksen.[33] Fowler et al. point out that their result (65.6 Å³) is protected by the Hylleraas variation principle and is guaranteed to be a *lower bound* to the coupled HF value provided the unperturbed wave function is close enough to the HF ground state. More recently Perpete, Champagne, and Kirtman[34] have improved upon the earlier HF calculation by including vibrational contributions within the double-harmonic and "infinite optical frequency" (e.g. static field) approximation. Their vibrational contributions used DFT-based normal coordinates. In this work they find an electronic polarizability of 63.4 Å³. Their calculated vibrational polarizability (0.78 Å³) is in reasonably good agreement with the value obtained here (0.58 Å³.) Most importantly, the uncertainty in calculated linear polarizabilities is at least as large as these numbers. Whitehouse and Buckingham[35] have also calculated the static polarizability of the C_{60} molecule as a function of basis set with the Hartree−Fock approximation. They have confirmed the earlier results showing a polarizability of 65.5 Å³ for their largest basis sets. It appears that there are definitely deviations between HF and PBE-GGA for the linear polarizability of the C_{60} molecule.

Based on experiments, it has also been suggested that the polarizability due to lattice relaxation is 2 Å³ (see ref 28) which is small but still four times larger than the value calculated here. In a recent letter Munn et al.[36] have suggested that the polarizability per fullerene molecule in a lattice may exhibit further enhancements over the isolated fullerene molecule and that the total polarizability associated with a fullerene molecule in a lattice is deduced to be closer to 89.9 Å³. In ref 27 it has been shown that the polarizability of an anion would indeed increase relative to the neutral which lends some support to the their discussion.

The deviation could also be due to the lower T_h symmetry that occurs when the icosahedral C_{60} molecules are placed on a cubic lattice. Such a symmetry lowering would cause some of the optically silent G_u and H_u modes to split and partially fall into the IR active T_{1u} manifold which in turn could lead to additional vibrational polarizability. There will also be weak IR activity due to weak intermolecular vibrations activated by weakly broken translational symmetry.[37] Also included in Table 1 are the electronic and vibrational polarizabilities of a C_{60} molecule with an endohedral Kr atom. The addition of the Kr atom adds another infrared mode due to a rattling motion of Kr inside the C_{60} cage. The low-frequency Kr rattling mode is found to be at 88 cm^{-1}, but the IR intensity associated with this mode is 1000 times smaller than the four T_{1u} modes associated with the fullerene cage. Because of this the vibrational polarizabilities are unchanged due to the addition of an inert endohedral atom. More interesting, albeit beyond double-harmonic, polarization effects do appear in alkali-doped

fullerene molecules which have been shown to relax off-center,[38] create the potential for Jahn−Teller distortions,[38,39] and exhibit interesting polarization effects, within the molecule and when exposed to an external field. Temperature-dependent model calculations, based upon HF-based energetics of the rattling ion, of this effect have been investigated by Whitehouse and Buckingham.[35]

Acetylene. The acetylene molecule provides an interesting test case because the anisotropy of the polarizability tensor is reversed significantly by the inclusion of the vibrational terms. For example, in $Å^3$ the electronic and vibrational polarizability tensors have been measured to be (2.43, 2.43, 5.12) and (0.667, 0.667, 0.027), respectively. Density functional theory yields (2.96, 2.96, 4.78) and (0.71, 0.71, 0.030) $Å^3$ which is in reasonably good agreement with experiment. In ref 7, careful studies on the acetylene molecule have been performed as a function of basis set and level of correlation. They point out that their calculated vibrational polarizabilities are not very sensitive to either basis set choice or level of correlation. Russell and Spackman find an average vibrational polarizability of 0.41 $Å^3$ which is slightly less than the experimental polarizability of Gussoni (0.45 $Å^3$ and the PBE-GGA values of 0.48 $Å^3$ reported here.

Halogen Containing Ionic Molecules. Halogen containing compounds are known to exhibit high vibrational polarizabilities as would be expected since they make very good ionic systems.[16,17] We have performed calculations on NaF, Na_2F_2, Na_2Cl_2, SF_6, SiF_4, and $TiCl_4$. Of the molecules in this size regime listed in the large database of Gussoni, the latter three stand out as having very large vibrational contributions. The agreement between theory and experiment is in the neighborhood of 15% for these systems.

In a recent letter, Andrade et al.[40] have calculated the vibrational polarizability for NaF with HF. The calculated double-harmonic vibrational polarizability (labeled nuclear relaxation term in their work) is 0.35 $Å^3$ (HF) and in relatively good agreement with our PBE-GGA calculation of 0.29 $Å^3$. Andrade et al. find that higher levels of theory do not change their result significantly. However, agreement between HF and PBE-GGA is not good for the electronic polarizibility. They find an average electronic polarizability of 1.34 $Å^3$ which is in good agreement with the work of Pluta[41] (1.32 $Å^3$) but roughly half the size of what we have calculated for NaF. To eliminate the possibility that this deviation is due to the basis set employed here, we have repeated our PBE-GGA calculation (bond length is 1.950 Å) for NaF using a very large basis set. For fluorine, we have used 14-single s-Gaussians ($1.232 \times 10^5 \leq \alpha_i \leq 0.118$), 14-single p-Gaussians ($1.232 \times 10^5 \leq \alpha_i \leq 0.118$), and 6-single d-Gaussians ($10.03 \leq \alpha_i \leq 0.118$). For sodium, we have 14-single s-Gaussians ($2.515 \times 10^5 \leq \alpha_i \leq 0.0269$), 14-single p-Gaussians ($2.515 \times 10^5 \leq \alpha_i \leq 0.0269$), and 6-single d-Gaussians ($3.998 \leq \alpha_i \leq 0.0.0269$). We find transverse and longitudinal polarizabilities of 2.379 and 3.298 $Å^3$ leading to an isotropic electronic polarizability of 2.685 in good agreement with the answer obtained from our default-DFT basis sets in Table 1. We have also repeated a HF calculation for NaF using the same default-DFT basis set and for applied electric fields of 0.0001, 0.0002, 0.0004,

0.0008, and 0.0016 atomic units. We find longitudinal and transverse polarizabilities of 1.30 and 1.24 $Å^3$, respectively, leading to an average polarizability of 1.26 $Å^3$ which is slightly smaller than that of Pluta and Andrade and once again significantly smaller than our PBE-GGA result. Thus it appears that there is, again, a real difference between PBE-GGA and Hartree−Fock for the case of the NaF molecule.

While we have been unable to find experimental work on the NaF monomer, Guella et al.[42] have measured the polarizability for many alkali-halide dimers so we have performed calculations on some of these structures to make contact with experiment. Our calculated total values for $(NaF)_2$ and $(NaCl)_2$ polarizabilities are 13.12 and 22 $Å^3$ respectively. While the $(NaCl)_2$ is in good agreement with the $T = 1030$ K experimental value (23.4 $\pm$ 2.5 $Å^3$) a significantly large deviation is observed for the seemingly simpler case of $(NaF)_2$ which has a $T = 1221$ K experimental value of 20.7 $\pm$ 3.4 $Å^3$.

Isomeric Dependencies. Acetonitrile (CH_3CN) and methylisonitrile (CH_3NC) have the same chemical composition. However, the former has the two carbon atoms bound to one another, while the latter has the nitrogen bound to the methyl radical. This causes a 5% difference in the electronic polarizability and a factor of 2 difference in the vibrational polarizability. The source of the deviation in the vibrational polarizability is clearly due to changes in the spring constant matrix since eq 11 shows that changes of mass cannot perturb the vibrational contributions within the double harmonic approximation.[4] There is a 1-fold mode at 2269 cm^{-1} for acetonitrile that is reduced to 2149 cm^{-1} for methylisonitrile. In addition to a reduction in the vibrational frequency, the infrared intensity of the methylisonitrile is 2.57 compared to 0.227 in the case of acetonitrile. This mode accounts for about 75% of the difference in the vibrational polarizability. The large change in infrared intensity in this frequency range should be a clear indicator of methylisonitrile isomerization to acetonitrile at higher temperatures.

Sodium Clusters. In two recent papers[43] Blundell, Guet, and Zope and Kronik, Vasiliev, and Chelikowsky[44] have calculated the temperature dependence of polarizabilities in sodium clusters. They show that temperature effects enhance the apparent polarizability at 300 K. This temperature enhancement appears to account for most of the difference between experiment and the calculated electronic polarizabilities from many different theoretical calculations.[45−50] Our results show that the vibrational contribution to the polarizability is indeed small for the sodium clusters which supports the assertion that temperature effects are important in these systems.

To make contact with other works we note that Maroulis[6] has performed benchmark calculations on the Na_2 as a function of basis set and level of correlation. For Hartree−Fock (HF) his results are essentially converged as a function of basis set, and an average value of 40.35 $Å^3$ has been found. As noted by Maroulis, this value is larger than the DFT value of 35.91 $Å^3$. The experimental values range between 37.91[51,52] and 40.00[53,54] with the larger value corresponding to the more recent experimental work. According to the CRC, the small and large values are low- and high-temperature

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values, respectively.[55] To ensure that the deviation is indeed a HF vs GGA-PBE we have repeated the HF calculation for the Na_2 polarizability with NRLMOL. Using default DFT basis sets and the PBE-GGA bond length, we find transverse and longitudinal polarizabilities of 32.8 $Å^3$ and 52.2 $Å^3$ at the PBE-GGA geometry in very good agreement with the large-basis-set calculations of Maroulis (34.07 $Å^3$ and 52.92 $Å^3$, respectively).

Weakly Bound Molecules. As mentioned in our discussion of fullerene molecules the vibrational polarizability between two weakly bound molecules could be enhanced if the weak intermolecular vibrations are IR active. As discussed in ref 56 the water dimer represents an extreme example of this case. As shown in Table 1, we find the electronic polarizability of this molecule (3.19 $Å^3$) to be approximately twice that of a water monomer. The electronic polarizabilities obtained for the water trimer and pentamer also show a linear scaling as a function of the number of molecules. This result is in good agreement with the work of Maroulis[5] (2.90 $Å^3$) and Eckart et al. (2.48 $Å^3$).[56] Maroulis[5] have carefully studied the electronic polarizability as a function of both basis set and level of correlation. The uncertainties due to these effects are at most 12.5% indicating that large deviations from these values must be due to other effects. Our calculated double-harmonic vibrational polarizability of 23.30 $Å^3$ is indeed a factor of 7 times larger than the electronic polarizability. Eckart et al. find this term to be even larger (39.2 $Å^3$) and further demonstrate that anharmonic corrections enhance the vibrational component of the dimer by an additional factor of 3. The large vibrational enhancement in polarizability in going from the monomer to dimer is indeed interesting. In particular, the scaling of this term as a function of system size is impossible to guess based upon the results of the monomer and dimer. It is reasonable to expect that this large result should be an upper limit since a dielectric medium that is coupled to an IR active mode should counteract the IR activity and thus the vibrational polarizability. So the presence of more water molecules should lead to a vibrational polarizability that is eventually sublinear in the total number of molecules. To partially address this point we have performed additional calculations on the trimer and pentamer. Our results show a decrease in the total vibrational polarizability in going from the dimer to the trimer and a flattening of the total vibrational polarizability for the pentamer. For the pentamer the ratio of the vibrational to electronic polarizability has decreased significantly from seven for the dimer to slightly less than two for the pentamer. Overall, these results show that weak intermolecular vibrations can enhance the vibrational polarizability over what is determined from intramolecular vibrations.

IV. Summary

We have used the PBE-GGA functional to calculate electronic polarizabilities and vibrational polarizabilities using a finite-field method and NRLMOL on a relatively large collection of small to intermediate size clusters and molecules. The double-harmonic approximation has been employed here which allows, in principle, direct comparison

to experiment through accurate measurements of infrared spectra. We have compared our electronic and vibrational polarizabilities to experiment and other theoretical calculations. For the most part, the PBE-GGA vibrational polarizabilities are in good agreement with both experiment and the work here suggests that DFT will be a good computational tool for the study of vibrational polarizabilities of clusters and molecules especially for systems where where the vibrational polarizability is known to be large.

However, there are a few notable exceptions where the results exhibit rather large dependencies upon method. For the fullerene molecule, the vibrational polarizabilities, as calculated here and elsewhere within Hartree−Fock, are in relatively close agreement with one another but are a factor of 3−4 smaller than experiment. For the electronic polarizability, where experiment and PBE-GGA agree quite well, the HF result is significantly smaller. For NaF, Hartree−Fock (three different calculations) and PBE-GGA differ by a factor of 2 on the electronic polarizability but are within 17% for the vibrational polarizability. An experimental value for the electronic polarizability of NaF is unavailable. The combined PBE-GGA electronic and vibrational polarizability values for $(NaF)_2$ is significantly smaller than the experimental result; however, agreement between experiment and PBE-GGA returns for the isoelectronic $(NaCl)_2$ molecule.

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