Density-Functional-Based Determination of Vibrational Polarizabilities in Molecules

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We develop a direct derivation for the primary contribution to the vibrational polarizability for molecules, clusters and other finite systems. The vibrational polarizability is then 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 quantitative accuracy.

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I. INTRODUCTION

Materials with high dielectric constants have many important technological applications. For molecular assembled materials, the Clausius-Mossotti relation tells us that the dielectric constant is related in a simple way to the molecular polarizability and points to critical densities at which this relation is expected to diverge. 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 generally accepted to be 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. 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 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. However, the lowest nonzero moment of a finite system is a well 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 $i$th atomic position $\frac{\partial \vec{p}}{\partial u_i}$ are well defined. Only the latter quantity is uniquely defined for a charged molecule. These derivatives may be expressed as a $3\times 3$ tensor $Z$ which has units of charge, and is written

$$ Z_{\alpha,i\mu} = \frac{\partial p_\alpha}{\partial u_{i\mu}}. $$

(1)

This tensor is also sometimes called the “polar tensor” and it is used for the calculation of the infrared intensity. The infrared intensities are also related to the vibrational component of the dc molecular polarizability, 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 $p_{el,i} = \Sigma_x \alpha_{el,xy} E_y$. This is generally 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 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 $\alpha$ is then a $3 \times 3$ 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

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

(2)

where the $3N \times 3N$ force constant tensor $K$ is defined as...
\[ K_{i\mu,j\nu} = \frac{\partial^2 E}{\partial u_{i\mu} \partial u_{j\nu}} \quad (3) \]

and \( E \) is the total energy of the molecule at zero field.

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

\[ p_\alpha = -\frac{\partial E}{\partial E_\alpha}, \quad (4) \]

\[ Z_{\alpha,i\mu} = -\frac{\partial^2 E}{\partial E_\alpha \partial u_{i\mu}} = \partial F_{i\mu} / \partial E_\alpha, \quad (5) \]

\[ \alpha_{\text{el},\alpha\beta} = -\frac{\partial^2 E}{\partial E_\alpha \partial E_\beta}. \quad (6) \]

In Eqs. (4-6), the electronic degrees of freedom must be relaxed in response to changes of the independent variables \( (\vec{E}, \vec{u}_1, \ldots, \vec{u}_N) \) and the derivatives are evaluated at zero field and displacement \( (\vec{E} = \vec{u}_i = 0) \). Eq. 6 also shows that the dynamical charge tensor determines how the Hellmann-Feynman (HF) force \( (F_{i\mu} = -\partial E / \partial u_{i\mu}) \) changes due to the application of an external electric field. As discussed in Ref. 6, the relationship between the dynamic effective charge tensor and the derivative of the HF 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

\[ E = E_0 - \vec{p} \cdot \vec{E} - \frac{1}{2} \vec{E} \cdot \alpha_{\text{el}} \cdot \vec{E} - \vec{E} \cdot Z \cdot \vec{u} + \frac{1}{2} \vec{u} \cdot K \cdot \vec{u}. \quad (7) \]

In the above equation \( \vec{p} \) and \( \alpha \) 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

\[ \vec{E} \cdot Z \cdot \vec{u} = \vec{u} \cdot Z^T \cdot \vec{E}. \quad (8) \]

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

\[ \vec{u} = K^{-1} \cdot Z^T \cdot \vec{E}, \quad (9) \]

and the corresponding energy of the relaxed molecule is

\[ E = E_0 - \vec{p} \cdot \vec{E} - \frac{1}{2} \vec{E} \cdot \alpha_{\text{el}} + \alpha_{\text{vib}} \cdot \vec{E} \quad (10) \]

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

\[ \alpha_{\text{vib}} = Z \cdot K^{-1} \cdot Z^T. \quad (11) \]

In fully indexed Cartesian form, the polarizability matrix is

\[ \alpha_{\text{vib},\alpha\beta} = \sum_{i\mu,j\nu} Z_{\alpha,i\mu}(K^{-1})_{i\mu,j\nu} Z_{j\nu,\beta}^T. \quad (12) \]

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 \( |v> \) denote the eigenvector and \( \omega_v \) the corresponding eigenfrequency, which satisfies the Newtonian equations

\[ K|v> = \omega_v^2 M|v>, \quad (13) \]

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

\[ M_{i\mu,j\nu} = M_{ij} \delta_{\nu\mu}. \quad (14) \]

The orthogonality and completeness relations are

\[ <v|M|v' >= \delta_{vv'}. \quad (15) \]

\[ \sum_v |v> <v| = M^{-1} \quad (16) \]

The force constant matrix can be written as

\[ K = \sum_v M|v> \omega_v^2 <v|M \quad (17) \]

\[ K^{-1} = \sum_v |v> \omega_v^{-2} <v|. \quad (18) \]

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

\[ Z_{\beta,v} = \hat{\beta} \cdot Z|v>. \quad (19) \]

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

\[ \alpha_{\text{vib},\alpha\beta} = \sum_v Z_{\alpha,v} \omega_v^{-2} Z_{v,\beta}^T. \quad (20) \]

This equation is a generalization of a known relation 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. We include our derivation here because it appears to be rather simple in comparison to previous derivations that appear in the literature. Eq. (20) follows immediately from Eq. (17,29) of Born and Huang. It has also been derived by Flytzanis. Probably the earliest modern discussion of vibrational polarizabilities using quantum-mechanical derivations can be found in Ref. 68, 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. Eq. (1) and A5 of Ref. 7 lead to our Eq. (20). However, as noted in Refs. 7 and 8, one of the earliest discussions dates back to 1924.\textsuperscript{2}

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. 13. 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.\textsuperscript{14} The Perdew-Burke-Ernzerhof (PBE) energy functional has been used in all calculations.\textsuperscript{15} 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$_2$O 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. 16. Basis sets and the unpublished geometries are available upon request. Once the optimized geometries,\textsuperscript{17,18,19} the vibrational frequencies, eigenvectors, and dynamical charge tensors ($Z_{\nu,m}$) are determined using the method discussed in Ref. 7. We then use Eqn. (20) to determine the vibrational component of the polarizability. As discussed in Ref. 5, 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 I.

III. RESULTS

Table I 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.\textsuperscript{20-21,22,23,24} Here we calculate the electronic polarizability to be 82.9 $\AA^3$ which is in good agreement with one of the earliest density-functional calculations\textsuperscript{22} of 83.5 $\AA^3$. 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.\textsuperscript{20} 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\textsuperscript{21,22,23,24} is known to be very close to this number as shown in Table I. Based on experiments, it has also been suggested that the polarizability due to lattice relaxation is 2 $\AA^3$ which is small but still four times larger than the value calculated here. The deviation may 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, and H, 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.\textsuperscript{25} Also included in Table I 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.

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 $\AA^3$ 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 $(0.71, 0.71, 0.030)\ \AA^3$ which is in reasonably good agreement with experiment.

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.\textsuperscript{26} We have performed calculations on NaF, SiF$_6$, 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 percent for these systems.

Isomeric dependencies: Acetonitrile (CH$_3$CN) and methylisocyanide (CH$_3$NC) 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 five percent difference in the electronic polarizability and a factor of two 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.

There is a one-fold mode at 2269 \text{ cm}^{-1} for acetonitrile that is reduced to 2149 \text{ 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 percent 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, Blundell, Guet and Zope and Kronik, Vasiliev and Chelikowsky have calculated the temperature dependence of polarizabilities in sodium clusters. They show that temperature effects enhance the apparent polarizability at 300K. This temperature enhancement appears to account for most of the difference between experiment and the calculated electronic polarizabilities from many different theoretical calculations. 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.

**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. the water dimer represents an extreme example of this case. As shown in Table I, we find the electronic polarizability of this molecule (3.19 \text{ \AA}^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 et al. and Eckart et al. Maroulis et al. 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 percent indicating that large deviations from these values must be due to other effects. Our calculated double-harmonic vibrational polarizability of 23.30 \text{ \AA}^3 is indeed a factor of seven times larger than the electronic polarizability. Eckart et al. find this term to be even larger (39.2 \text{ \AA}^3) and further demonstrate that anharmonic corrections enhance the vibrational component of the dimer by an additional factor of three. 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 presented a straightforward derivation for the vibrational polarizability of a molecule. We have used the generalized-gradient approximation to the density functional theory to evaluate both the electronic polarizability and this vibrational correction. In accord with experiment, our results show that this term can be important in smaller ionic molecules and weakly bound systems, but that it is smaller in covalent systems or where the frontier electrons are delocalized.

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TABLE I: Calculated and experimental vibrational polarizabilities (Å^3) for molecules. This is one third of the trace of the polarizability tensor. Unless otherwise stated the experimental values are taken from Ref. 21. Theoretical data for C_{60} is from Refs. 22-24 and references therein. For the pure sodium clusters, the experimental values are total polarizabilities (denoted with a *) which have been taken from Refs. 26, 27.

| Molecule          | Vibrational | Electronic |
|-------------------|-------------|------------|
|                   | Theory      | Expt.      | Theory      | Expt.      |
| H$_2$O            | 0.04        | 0.04       | 1.57        | 1.45       |
| (H$_2$O)$_2$      | 23.30       |            | 3.19        |            |
| (H$_2$O)$_3$      | 13.50       |            | 4.82        |            |
| (H$_2$O)$_5$      | 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$_6$            | 2.95        | 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$_3$CNC          | 0.07        |            | 4.87        |            |
| H$_3$CCN          | 0.03        | 0.04       | 4.59        | 4.28       |
| C$_{60}^*$@Kr$^+$ | 0.55        |            | 83.3        |            |
| C$_{60}$          | 0.58        | 2.0        | 82.9        | 83         |
| Na$_2$            | 0.00        |            | 35.91       | 37.91[*]  |
| Na$_3$            | 1.72        |            | 60.89       | 69.8[*]   |
| Na$_8$            | 0.63        |            | 116.2       | 133.5[*]  |
| NaF               | 0.29        |            | 2.71        |            |
| Ti$_3$C$_{12}^+$  | 3.72        |            | 56.40       |            |
| As@Ni$_{12}@As_{60}^*$ | 4.56 |            | 140.86     |            |

*Ref. 15, 16, 18 respectively