Comparison of vibrational and electronic contributions to van der Waals interactions

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The van der Waals interaction can be caused by either ionic vibrations or instantaneous electronic motion relative to the atomic center. In this study, the vibrational contribution to the van der Waals interaction is formulated by considering the interaction between induced dipoles caused by the infrared-active normal modes of a neutral molecule. Using the derived formula, the contribution is quantified, within the density-functional theory formalism, using a *screened*, i.e., self-consistent, vibrational polarizability. Applications for several neutral nonpolar dimers are presented. It is found that the vibrational contributions for the dimers are substantially smaller than their electronic contributions. The ratio of the vibrational to electronic contributions depends strongly on the ratio of the screened vibrational to electronic polarizabilities and on the ratio of the frequency of the strongest infrared-active mode to an ionization energy.

I. INTRODUCTION

Chemical and biological molecules ranging from rare-gas diatomic molecules to proteins, DNA, RNA, and fullerenes (C_{60}) are held together by noncovalent weak interactions such as van der Waals (vdW) interactions and/or hydrogen bonds.[1–8] The vdW attraction between fullerene molecules plays a crucial role in characterizing their physical, chemical, and mechanical properties.[3] The vdW forces acting on proteins are partly responsible for their structure and flexibility.[4] The strength of the vdW interaction for small molecules is typically on the order of $5-20$ meV. Quantum mechanically, electrons localized around nuclei can move instantaneously, which causes a fluctuating dipole moment within an atom. This induces dipole moments in neighboring atoms. The interaction between the fluctuating dipole moment and the induced dipole moments is attractive and is called the dispersion or vdW interaction. For a collection of neutral atoms and molecules that do not have permanent dipole moments, the vdW interaction plays a major role in binding.

As a simple model for the vdW interaction, Drude described an atom in terms of positive and negative charges, representing the nucleus and electrons, that are joined by a spring. From this ansatz it follows that the total zero-point energy of two neutral atoms is decreased by a term that scales as $1/R^6$.[9–13] This Drude model has been modified and generalized to understand intermolecular interactions between small molecules such as hydrogen molecules, rare-gas dimers, and alkali dimers at long distances.[14–16] In addition, the vdW interactions for the small molecules have been extensively studied by improving calculations of dynamic and static polarizabilities using coupled multiconfiguration[17] or configuration interaction methods.[18,19] Additional strategies have been to theoretically determine upper and lower bounds of the vdW coefficients based on the Padé approximation and sum rules applied to the calculations of the polarizabilities.[20–25]

Density-functional theory (DFT) has been greatly successful in describing many physical and chemical properties in various many-electron systems. Rapcewicz and Ashcroft[26] have formulated the fluctuations in the electronic charge density as response or correlation density functions and obtained the attractive interaction in the asymptotic limit using an effective density $\rho_{eff} = \sqrt{\rho(\vec{r}_1)\rho(\vec{r}_2)}$, where $\rho(\vec{r}_1)$ and $\rho(\vec{r}_2)$ are the densities of electrons at positions $\vec{r}_1$ and $\vec{r}_2$ in two separate atoms. Their calculated vdW coefficients for rare-gas atoms were in good agreement with experiment. Starting with the work of Rapcewicz and Ashcroft,[26] Andersson *et al.*[27] have developed the approximations to the vdW interactions for dimers of various atoms. In this work, dynamic atomic polarizabilities were determined using the DFT-calculated ground-state charge densities and a spatial cutoff in the response frequency. Dobson and collaborators[28] have derived a vdW interaction from density-density response functions that satisfy charge conservation and reciprocity. Van Gisbergen *et al.*[29] and Misquitta *et al.*[30] have respectively used time dependent DFT and symmetry-adapted perturbation theory with Kohn-Sham orbitals to calculate the vdW interactions for polyatomic molecules from dynamic atomic polarizabilities.

Fluctuations in electronic charge density can also be induced by vibrations of atoms within a molecule. To distinguish this attractive term from the effect due to instantaneous electronic motion, this is hereafter referred to as a vibrational contribution to the vdW interaction. The vibrational vdW interaction can be calculated using DFT because it only requires the computation of vibrational normal modes and the corresponding frequencies for each monomer participating in the vdW bonding. It has been known that the electronic dispersion energy scales with the square of an atomic polarizability,[10–13] which leads to the fact that the binding energy increases quadratically with increasing molecular weight. For some molecules, vibrational polarizabilities have been experimentally determined to be on the same order as their electronic polarizabilities.[31] This observation motivated us to investigate the vibrational vdW interaction as a function

of molecular weight and to compare it to the electronic contribution.

In this paper, the vibrational vdW interaction is formulated using an analogy of the Drude model.[9–13,16] The vibrational vdW is quantified for nine different nonpolar dimers using an all-electron Gaussian-orbital-based DFT code, NR-LMOL (Naval Research Laboratory Molecular Orbital Library),[32] within the generalized gradient approximation (GGA).[33] Then, to lowest order, the electronic contributions are estimated using (i) Kohn-Sham orbitals and orbital energies and (ii) approximate London's formula.[10–13] The calculated vibrational contribution (using a *screened* vibrational polarizability) is compared to the empirical electronic one for the examined dimers. The dependence of the vdW interactions on atomic number is discussed and an upper limit for the ratio of the vibrational to electronic contributions is offered.

II. FORMALISM

A. Drude model

In the one-dimensional Drude model,[9–13,16] an atom with a fluctuating dipole moment is described by a linear harmonic oscillator in which positive and negative charges are joined by a spring with force constant k. We consider two identical neutral atoms with a separation, R, that is much larger than the separations between charges, $|x_1|$ and $|x_2|$, on the two atoms. Under these conditions, the lowest-order Coulomb interaction between the two atoms (oscillators) becomes a dipole-dipole interaction. Thus, the total Hamiltonian of the system is written as

$$\mathcal{H}_e = \frac{m\dot{x}_1^2}{2} + \frac{kx_1^2}{2} + \frac{m\dot{x}_2^2}{2} + \frac{kx_2^2}{2} - \frac{2e^2 x_1 x_2}{R^3}. \quad (1)$$

If the coupled oscillators are decoupled using a normal-mode transformation, the zero-point energy of the system is reduced from that of the sum of the two uncoupled oscillators, $\hbar\omega_0$, where $\omega_0 = \sqrt{k/m}$, by

$$\Delta U_e = - \hbar \omega_0 \frac{1}{8}\left(\frac{2e^2}{kR^3}\right)^2. \quad (2)$$

This energy difference, which is inversely proportional to the sixth power of the separation of the two oscillators, is the vdW interaction energy.

B. Vibrational contribution

While the Drude model was originally used to qualitatively explain the electronic vdW interaction, it also points to the fact that other mechanisms such as infrared vibrational modes can yield a vdW interaction as well. To calculate the vibrational vdW interaction energy, we generalize the one-dimensional Drude model to a system of many three-dimensional harmonic oscillators. Suppose that a system consists of N_m molecules, each of which comprises N atoms. The N three-dimensional coupled harmonic oscillators corresponding to individual atoms in a molecule can be transformed to $3N$ one-dimensional uncoupled harmonic oscilla-

tors in normal-mode coordinates. Among the $3N$ normal modes, only N_{IR} infrared (IR) active modes contribute to the vibrational vdW interaction. Thus, similar to Eq. (1), the total Hamiltonian, in terms of the normal-mode coordinates $Q_{i\nu}$ and momenta $P_{i\nu}$, becomes

$$\mathcal{H}_v = \sum_{\nu=1}^{N_m}\sum_{i=1}^{N_{IR}}\left(\frac{P_{i\nu}^2}{2m_{i\nu}} + \frac{1}{2}m_{i\nu}\omega_{i\nu}^2 Q_{i\nu}^2\right) + \sum_{\nu>\nu'}^{N_m}\sum_{\nu'=1}^{N_m} V_d(\nu,\nu'),$$

$$(3)$$

$$V_d(\nu,\nu') = \sum_{ij}\frac{\vec{\mu}_{i\nu}\cdot\vec{\mu}_{j\nu'} - 3(\vec{\mu}_{i\nu}\cdot\hat{R}_{\nu\nu'})(\vec{\mu}_{j\nu'}\cdot\hat{R}_{\nu\nu'})}{R_{\nu\nu'}^3}, \quad (4)$$

where V_d is the dipole-dipole interaction, $\omega_{i\nu}$ is the frequency of the ith IR-active normal mode for the νth molecule with the effective mass of $m_{i\nu}$, $\vec{\mu}_{i\nu}$ is a dynamic dipole moment induced by a displacement along the corresponding normal-mode direction, and $R_{\nu\nu'}$ is a separation between a pair of molecules (ν,ν'). Here the summations of the last term in Eq. (3) run over all pairs of the molecules and the summation in Eq. (4) runs over all IR active modes. The dynamic dipole moment is expanded according to

$$\vec{\mu}_{i\nu}(Q_{i\nu}) = \vec{\mu}_{i\nu}(Q_{i\nu}=0) + Q_{i\nu}\frac{\partial\vec{\mu}}{\partial Q_{i\nu}} + \cdots, \quad (5)$$

where $\vec{\mu}_{i\nu}(Q_{i\nu}=0)=0$ because the molecules considered do not carry permanent dipole moments. The x component of the dynamic dipole moment of the first molecule can be rewritten as

$$\mu_{i1}^x = Q_{i1}\frac{\partial\mu_x}{\partial Q_{i1}} = Q_{i1}\sum_{k=1}^{3N}\frac{\partial\mu_x}{\partial R_k}\frac{\partial R_k}{\partial Q_{i1}} = Q_{i1}\sum_{k=1}^{3N}\frac{\partial F_k}{\partial E_x}\frac{\partial R_k}{\partial Q_{i1}} \equiv Q_{i1}A_i^x,$$

$$(6)$$

where the sum is over atoms and Cartesian coordinates, R_k is an atomic coordinate, F_k is a component of the force on an atom, E_x is the x component of an applied electric field, A_i^x represents an effective charge, and $\partial R_k/\partial Q_{i1}$ is the kth element of the ith eigenvector (normal mode). The induced dipole-dipole interaction between the νth and ν'th molecules can be written, in terms of the normal-mode coordinates and effective charges, as

$$V_d(\nu,\nu') = \sum_{ij} Q_{i\nu}Q_{j\nu'}[A_i^x A_j^x(\cos\theta_1\cos\theta_2\cos\phi$$

$$- 2\sin\theta_1\sin\theta_2) + A_i^y A_j^y\cos\phi$$

$$+ A_i^z A_j^z(\sin\theta_1\sin\theta_2\cos\phi - 2\cos\theta_1\cos\theta_2)$$

$$+ A_i^x A_j^y\cos\theta_1\sin\phi + A_i^y A_j^x\cos\theta_2\sin\phi$$

$$+ A_i^x A_j^z(\cos\theta_1\sin\theta_2\cos\phi + 2\sin\theta_1\cos\theta_2)$$

$$+ A_i^z A_j^x(\sin\theta_1\cos\theta_2\cos\phi + 2\cos\theta_1\sin\theta_2)$$

$$+ A_i^y A_j^z\sin\theta_2\sin\phi - A_i^z A_j^y\sin\theta_1\sin\phi]/R_{\nu\nu'}^3$$

$$\equiv \sum_{ij}\frac{Q_{i\nu}Q_{j\nu'}K_{ij}(\theta_1,\theta_2,\phi)}{R_{\nu\nu'}^3}, \quad (7)$$

where the summation on $i(j)$ runs over all IR modes for the νth (ν'th) molecule. Here we used the coordinate systems following van der Merwe.[34] θ_1 and θ_2 are the angles between the separation vector $\vec{R}_{\nu\nu'}$ and the z axes of molecule ν and ν'. x_ν ($x_{\nu'}$) is coplanar with $\vec{R}_{\nu\nu'}$ and z_ν ($z_{\nu'}$). ϕ is the angle between the projected vectors of z_ν and $z_{\nu'}$ onto a plane perpendicular to $\vec{R}_{\nu\nu'}$. $K_{ij}(\theta_1, \theta_2, \phi)$ has units of the square of charge. As shown in Eq. (7), the vibrational vdW interaction can be anisotropic. For example, the vibrational vdW interactions for two NCCN molecules and two benzene molecules are highly anisotropic. To obtain an analytical expression for the vibrational contribution, we consider V_d as a small perturbation to the unperturbed system [uncoupled harmonic oscillators, Eq. (3) without V_d] in which the normalized ground-state eigenvector is $\Psi_0 \equiv |0_\nu, 0_{\nu'}\rangle$. The first-order term in V_d vanishes because $\langle \Psi_0 | V_d | \Psi_0 \rangle = \langle 0_\nu | Q_{i\nu} | 0_\nu \rangle \langle 0_{\nu'} | Q_{j\nu'} | 0_{\nu'} \rangle = 0$. Thus, the zero-point energy difference is, to lowest order,

$$\Delta U_v = \sum_k \frac{|\langle \Psi_0 | V_d | \Psi_k \rangle|^2}{\epsilon_0 - \epsilon_k} = -\sum_{ij} \frac{|\langle 0 | Q_i | 1 \rangle \langle 0 | Q_j | 1 \rangle K_{ij}|^2}{R^6 \, \hbar \, (\omega_i + \omega_j)} \tag{8}$$

$$= -\sum_{ij} \frac{K_{ij}^2 \hbar}{4(\omega_i + \omega_j) m_i \omega_i m_j \omega_j R^6} \equiv -\frac{C_6^v}{R^6}, \tag{9}$$

where ϵ_0 is the zero-point energy of the unperturbed system, ϵ_k is an excited energy of the unperturbed system, $|1\rangle$ is the first-excited state of one molecule, and ω_i is the angular frequency of the ith normal mode with an effective mass of m_i. $\langle 0 | Q_i | 1 \rangle = \sqrt{\hbar} / \sqrt{2 m_i \omega_i}$ is derived using the ground and excited states of harmonic oscillators in standard quantum mechanics. ΔU_v is proportional to the square of the IR absorption intensity.

C. Electronic contribution

The electronic contribution is calculated using two methods: (i) Kohn-Sham orbitals and orbital energies and (ii) the approximate London's formula.[13,35] Using second-order perturbation theory, the electronic vdW interaction is written as

$$\Delta U_e^{(2)} = \sum_{\alpha \neq 0, \beta \neq 0} \frac{|\langle \Phi_0^A \Phi_0^B | V_{AB} | \Phi_\alpha^A \Phi_\alpha^B \rangle|^2}{\mathcal{E}_0^A + \mathcal{E}_0^B - \mathcal{E}_\alpha^A - \mathcal{E}_\beta^B}, \tag{10}$$

where V_{AB} is the Coulomb interaction between electrons within two molecules, $\mathcal{E}_0^A$ and $\mathcal{E}_0^B$ are eigenvalues of the ground states Φ_0^A and Φ_0^B for molecule A and molecule B, and $\mathcal{E}_\alpha^A$ and $\mathcal{E}_\beta^B$ are eigenvalues of their excited states Φ_α^A and Φ_β^B. If we consider only the lowest-order term of V_{AB}, which is a dipole-dipole interaction, then Eq. (10) is approximated to

$$\Delta U_e^{(2)} = \frac{4}{R^6} \sum_{i=1}^{n_o/2} \sum_{j=(n_o/2)+1}^{\infty} \sum_{k=1}^{n_o/2} \sum_{l=(n_o/2)+1}^{\infty} \frac{[\langle \phi_i^A | \vec{r} | \phi_j^A \rangle \langle \phi_k^B | \vec{r} | \phi_l^B \rangle - 3 \langle \phi_i^A | \vec{r} \cdot \hat{R} | \phi_j^A \rangle \langle \phi_k^B | \vec{r} \cdot \hat{R} | \phi_l^B \rangle]^2}{\epsilon_i^A - \epsilon_j^A + \epsilon_k^B - \epsilon_l^B}, \tag{11}$$

$$\equiv -\frac{C_6^e[\text{cal}]}{R^6}, \tag{12}$$

using occupied (unoccupied) Kohn-Sham orbitals ϕ_i^A and ϕ_k^B (ϕ_j^A and ϕ_l^B) and orbital energies ϵ_i^A and ϵ_k^B (ϵ_j^A and ϵ_l^B). Here n_0 is the total number of electrons in a molecule and $\hat{R}$ is a unit vector along the separation between the two molecules considered. Kohn-Sham orbitals and orbital energies are obtained using all-electron Gaussian basis sets within the GGA. A factor of 4 arises from spin indices. The expression for $C_6^e[\text{cal}]$ is similar to that used in Refs. 36 and 37. Before continuing, we review how Eq. (11) can be simplified to the approximate London's formula.[13,35] The xx component of a static atomic polarizability tensor *neglecting screening*, hereafter referred to as the bare polarizability tensor, is defined as

$$\alpha_{e,xx}^{\text{bare}} = 2 \sum_{\alpha \neq 0} \frac{|\langle \Phi_0 | \hat{x} \cdot \vec{r} | \Phi_\alpha \rangle|^2}{\mathcal{E}_\alpha - \mathcal{E}_0} = 4 \sum_{i=1}^{n_o/2} \sum_{j=n_o/2+1}^{\infty} \frac{|\langle \phi_i | \hat{x} \cdot \vec{r} | \phi_j \rangle|^2}{\epsilon_j - \epsilon_i}. \tag{13}$$

Assume that there is only a single dominant dipole matrix element, that the vdW interaction is isotropic, and that the denominator in Eq. (13) is dominated by an ionization energy I. Then the electronic contribution, Eq. (11), becomes

$$\Delta U_e^{(2)} \approx -\frac{3}{4R^6} (\alpha_e^{\text{bare}})^2 I. \tag{14}$$

If a bare polarizability α_e^{bare} in Eq. (14) is replaced by a screened polarizability α_e^{scr}, then this becomes identical to the approximate London's formula.

TABLE I. The atomic number Z, calculated static vibrational polarizability α_v^{cal}, and bare and screened electronic polarizability $\alpha_{e,\text{bare}}^{\text{cal}}$ and $\alpha_{e,\text{scr}}^{\text{cal}}$ are presented along with values[31] obtained from infrared absorption and dielectric measurements (α_v^{exp}) and from optical measurements (α_e^{exp}), respectively, in units of Å^3. Here ω_h indicates the wave number of the strongest IR active normal mode (could be degenerate) and I denotes a calculated ionization energy. Notice that $1~\text{cm}^{-1} = 1.2375 \times 10^{-4}$ eV.

	Z	α_v^{cal}	α_v^{exp}	$\alpha_{e,\text{bare}}^{\text{cal}}$	$\alpha_{e,\text{scr}}^{\text{cal}}$	α_e^{exp}	ω_h (1/cm)	I (eV)
CH_4	10	0.039	0.03, 0.03	3.59	2.63	2.60	3071	14.04
NCCN	26	0.94	0.91, 3.30	11.62	5.15	4.71	233	13.09
C_6H_6	42	0.35	0.29, 0.75	19.94	10.5	9.96	659	9.27
SiF_4	50	2.07	1.75, 2.14	5.08	3.73	3.32	969	14.4
SF_6	70	2.30	2.29, 2.06	8.18	5.15	4.49	846	13.77
CCl_4	74	1.41	0.84, 0.95	20.26	11.0	10.24	711	10.56
$SnCl_4$	118	4.35	6.36, 4.09	26.6	14.7	13.97	380	10.84
$SnBr_4$	190	3.98	3.23, 3.49	38.4	20.2	18.57	266	9.92
SnI_4	262	3.94	none, 5.75	73.96	30.3	26.19	208	8.91

III. RESULTS AND COMPARISON OF VIBRATIONAL TO ELECTRONIC CONTRIBUTIONS

We now present the calculation of coefficients of the vibrational contribution C_6^v for nine different nonpolar dimers: CH_4-CH_4, NCCN-NCCN, C_6H_6-C_6H_6, SiF_4-SiF_4, SF_6-SF_6, CCl_4-CCl_4, $SnCl_4$-$SnCl_4$, $SnBr_4$-$SnBr_4$, and SnI_4-SnI_4. The geometry of each monomer is optimized using all-electron Gaussian-orbital-based NRLMOL within the GGA. Then all atoms in a monomer are displaced from the equilibrium positions along the $\pm x$, $\pm y$, and $\pm z$ axes, which leads to $6N$ displaced geometries for systems without any symmetry. The energies of the displaced geometries are calculated self-consistently using NRLMOL. For small displacements, one can calculate, within the harmonic-oscillator approximation, normal modes and their corresponding frequencies and effective masses by solving eigenvalue problems.[38] The IR absorption intensity of the ith normal mode is, to first order, proportional to $|d\vec{\mu}/dQ_i|^2$, where $\vec{\mu}$ is an electric dipole moment. An external electric field is applied to the optimized geometry along various directions to compute the IR intensity using the relationship $\partial\mu_i/\partial R_k = \partial F_k/\partial E_i$. The energies and forces of the geometries in the presence of an external electric field are calculated self-consistently. We determine IR active modes as well as the dynamic dipole moments [effective charges $A_i^{x,y,z}$ or $K_{ij}(\theta_1, \theta_2, \phi)$] for each IR mode. The vibrational polarizability tensor is calculated as a sum of the square of all effective charges weighted by vibrational frequencies of all normal modes,[40]

$$\alpha_{v,\mu\nu} = \sum_i A_i^{\mu} \omega_i^{-2} (A_i^{\nu})^T, \qquad (15)$$

where the summation runs over all normal modes with frequency ω_i, and μ, $\nu = x$, y, and z. This is a *screened* vibrational polarizability tensor. In most cases, the calculated mean values of the polarizability are in good agreement with the two sets of experimental values obtained from infrared absorption and dielectric measurements[31] (Table I). The values of C_6^v calculated for the nine dimers using Eq. (9)

are shown in Table II. The vdW interactions are isotropic for all of the molecules examined except for linear NCCN and planar C_6H_6 molecules in which the interactions are calculated at $\theta_1 = \theta_2 = 0$ and $\phi = 0$. (The reason that the anisotropy of the vdW interaction is not pursued will be provided later in this section.) The value of C_6^v increases by three orders of magnitude as molecular weight increases by a factor of 30 (Table II and Fig. 1) despite apparent fluctuations.

The calculated value of C_6^e[cal] increases substantially with increasing molecular weight (Table II and Fig. 2) as expected. The values of C_6^e[cal] for the nine dimers are much greater (by a factor of 2 or 3) than the corresponding theoretical[39] and empirical values, C_6^e[emp], calculated from construction of dipole oscillator strength distributions (DOSD)[23,24,41,42] and from the approximate London's formula [same as Eq. (14) but α_e^{bare} is now replaced by α_e^{scr}]. This discrepancy is due to the absence of screening of electronic charges in Eq. (11). A screened atomic polarizability tensor $\alpha_{e,\mu\nu}^{\text{scr}}$ is defined as

$$\alpha_{e,\mu\nu}^{\text{scr}} = -\frac{\partial}{\partial E_\nu}\frac{\partial \mathcal{E}}{\partial E_\mu}, \qquad (16)$$

where $\mathcal{E}$ is the total energy of the system and E_μ is the μ component of an external electric field. The screened atomic polarizabilities, $\alpha_{e,\text{scr}}^{\text{cal}}$, calculated using Eq. (16) agree well with the experimental values, α_e^{exp} (Ref. 31), as shown in Table I. But the values of $\alpha_{e,scr}^{\text{cal}}$ are much smaller than those of $\alpha_{e,\text{bare}}^{\text{cal}}$ for the nine dimers. When the same formula, Eq. (11), is applied to rare-gas dimers such as He–He, Ne–Ne, and Ar–Ar, the values of C_6^e[cal] agree with experimental (not shown), empirical (Ref. 25), and other theoretical values (Refs. 27 and 29) for light atoms such as He but not for heavy atoms (Table III). This observation is consistent with the results reported by Refs.36 and 37 even when an exact exchange (EXX) or exchange only (x-only) functional was used. Our calculated C_6^e[cal] values for the rare-gas dimers are outside of the theoretical upper and lower bounds obtained from the Padé approximation and the sum rules.[20–22]

TABLE II. The atomic number Z, calculated values of C_6^v [using Eq. (9)], empirical values of C_6^e from Refs. 23, 24, 39, 41, and 42, and Eq. (14) (with $\alpha_{e,\text{scr}}^{\text{cal}}$), and calculated values of C_6^e [using Eq. (12)] in units of (hartree $\cdot a_B^6$), and their ratios, are shown for nine different dimers of the same nuclear species.

	Z	C_6^v	C_6^e[emp]	C_6^e[cal]	C_6^e[cal]$(\alpha_{e,\text{scr}}^{\text{cal}}/\alpha_{e,\text{bare}}^{\text{cal}})^2$	C_6^v/C_6^e[emp][a]
CH_4	10	0.00036	158.4[b]	121.9*	223.6	120.0	2×10^{-6}
NCCN	26	0.0603		435.8*	1204	375	1×10^{-4}
C_6H_6	42	0.0043	1723[c]	1284*	4354	1207.3	2×10^{-6}
			1163[d]				
SiF_4	50	0.37	330.2[e]	251.5*	598.7	322.8	1×10^{-3}
SF_6	70	0.67	585.8[f]	458.5*	1434	568.4	1×10^{-3}
CCl_4	74	0.22		1604*	5565	1640.5	1×10^{-4}
$SnCl_4$	118	0.54		2941*	8263	2523.5	2×10^{-4}
$SnBr_4$	190	0.40		5081*	14873	4115.7	8×10^{-5}
SnI_4	262	0.37		10268*	38383	6442.1	4×10^{-5}

[a]The values of C_6^e[emp] were taken from the empirical results using dipole oscillator distribution[23,24,41,42] when they are available. Otherwise, they were estimated from $3I(\alpha_{e,\text{scr}}^{\text{cal}})^2/4$. Those values are marked by $\star$.
[b]Reference 23.
[c]Reference 41.
[d]Reference 39.
[e]Reference 42.
[f]Reference 24.

This is expected because a bare atomic polarizability was used in our calculation instead of a screened static polariz-ability as discussed in Sec. II. C. The bare polarizability tends to be greater than the screened polarizability for heavy atoms. This is further supported by the observation that weighting C_6^e[cal] by $(\alpha_{e,\text{scr}}^{\text{cal}}/\alpha_{e,\text{bare}}^{\text{cal}})^2$ yields values closer to C_6^e[emp] (Tables I and II).

For a dimer consisting of like monomers, $C_6^v \approx 0.5\hbar\omega_h\alpha_v^2$ when a single IR active mode of frequency ω_h is dominant, where α_v is a vibrational polarizability, and $C_6^e \approx 3I\alpha_e^2/4$ when a single optical absorption of energy I is dominant. So the ratio is

$$\frac{C_6^v}{C_6^e} \approx \frac{2}{3}\frac{\hbar\omega_h}{I}\left(\frac{\alpha_v}{\alpha_e}\right)^2, \qquad (17)$$

where I is approximated by an ionization energy. In the cal-culation of C_6^e[cal], a bare atomic polarizability was consid-ered, while in C_6^v a screened vibrational polarizability was included. Therefore, to obtain a proper ratio with screening, the values of C_6^e[emp] and C_6^v are used. The values of C_6^e[emp] do not seem to be correlated with the values of C_6^v. For example, we compare the values of C_6^e[emp] and C_6^v for C_6H_6 to those for SF_6. For the two covalent molecules in-vestigated (CH_4 and benzene), the ratio C_6^v/C_6^e[emp] is in the range of 10^{-6}. For the ionic molecules studied, such as SiF_4,
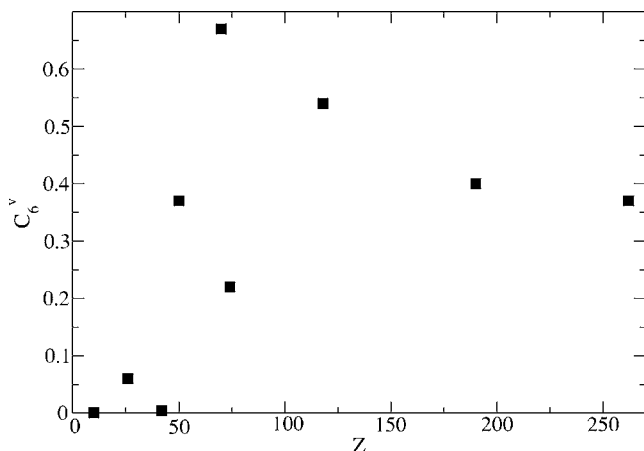

FIG. 1. Vibrational dispersion coefficient C_6^v (in units of hartree $\cdot a_B^6$)) vs atomic number Z for the nine dimers of the same kind considered in Table II.
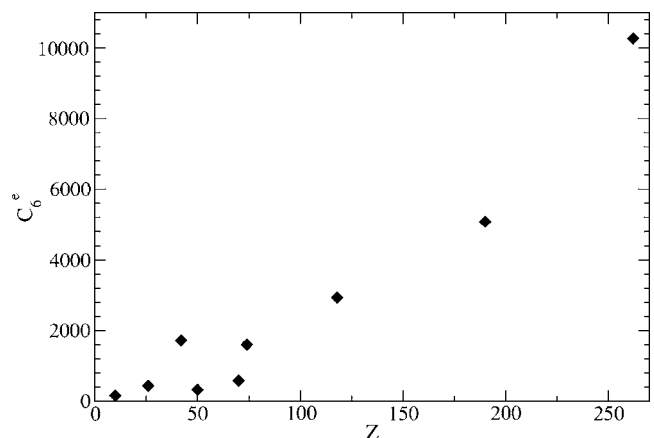

FIG. 2. Empirical electronic dispersion coefficient C_6^e[emp] (in units of hartree $\cdot a_B^6$)) vs atomic number Z for the nine dimers of the same kind considered in Table II.

TABLE III. Calculated and empirical coefficients for the electronic contribution to vdW interaction for three rare-gas dimers in units of (hartree $\cdot a_B^6$), using Eq. (11), Kohn-Sham orbital, and orbital energies with exchange-only (x-only) functional and exact exchange (EXX) functional, time-dependent density functional theory (TDDFT), and distributions in dipole oscillator strength (DDOS).

	C_6^e [Eq. (11)]	C_6^e (x-only, Ref. 36)	C_6^e (EXX, Ref.37)	C_6^e (TDDFT, Ref.29)	C_6^e[emp] (DDOS, Ref.25)
He-He	1.565	1.664	1.72	1.82	1.458
Ne-Ne	8.40	7.447	7.92	7.26	6.383
Ar-Ar	108.9	128.5	131.86	69.9	64.30

F_6, CCl_4, $SnCl_4$, $SnBr_4$, and SnI_4, the ratio is 10^{-5}–10^{-3}. Since the ratio is so small, it may not be interesting to further investigate an anisotropic aspect of the vdW interaction. The ratio increases by three orders of magnitude from CH_4 to SiF_4 and SF_6, but after that it decreases slightly as molecular weight increases according to Table II (Fig. 3). Therefore, the results shown in Table II are not sufficient to determine whether the ratio increases consistently with increasing molecular weight or if a correlation with molecular weight exists. It is, however, presumed that the ratio may not be significantly influenced by molecular weight because the crucial factor in the ratio is α_v/α_e. Among the nine molecules examined, vibrations of SiF_4 and SF_6 molecules contribute to the vdW interaction most. In these cases the value of α_v is half that of α_e, while the frequencies of the dominant IR modes for the two dimers are about 1% of an ionization energy I. So the value of C_6^v is approximately 0.1% of that of C_6^e[emp]. Typical frequencies of strong IR modes for small molecules fall in the range of 200–3000 cm^{-1} ($\approx$0.025–0.37 eV), while the ionization energies are typically in the range of 10 eV. Considering this, we find that the upper limit in C_6^v/C_6^e[emp] is approximately 1% even when $\alpha_v \approx \alpha_e$. That the purely vibrational contribution is substantially smaller than the electronic one for ionic molecules can also be understood as follows. If there exists a single dominant IR mode with a frequency of ω_h for a monomer, then the electronic contribution for the dimer is on the order of

$$\Delta U_e^{(2)} \approx -\frac{\hbar^4 e^4}{m^2(\hbar\omega)^3 R^6} \approx -\frac{1^4\hbar^4}{1^2 \times (10 \text{ eV})^3 R^6} = -\frac{\hbar^4}{R^6}10^{-3}.$$
(18)

The vibrational contribution for the dimer is

$$\Delta U_v \approx -\frac{1^4\hbar^4}{(10\times 2\times 10^3)^2(0.1 \text{ eV})^3 R^6} = -\frac{\hbar^4}{R^6}10^{-6}.$$
(19)

For nonionic dimers, the electronic part does not seem to change much but the vibrational part decreases by two or three orders of magnitude because both effective charges and effective masses decrease by one or two orders of magnitude in comparison to ionic dimers.

IV. CONCLUSION

In conclusion, we have considered an interaction between induced dipole moments caused by vibrations of atoms (or nuclei) in a molecule and compared it to an induced dipole-dipole interaction caused by fluctuations of electrons within an atom. Using second-order perturbation theory, we derived formulas for the vibrational and electronic contributions to the vdW interaction and calculated the contributions for several dimers using DFT. The calculated vibrational vdW interaction is proportional to the square of a screened vibrational polarizability. The calculated electronic part using the Kohn-Sham orbital and orbital energies is overestimated for heavy atoms due to neglect of screening of the electronic charges created by a local field. We find that the vibrational contribution is substantially smaller compared to the empirical electronic contribution (calculated using distributions in the dipole oscillator strength and the approximate London's formula) and that the upper bound could be 1% of the electronic part. Further investigation is needed to determine whether the ratio of the vibrational and electronic part could scale differently with molecular weight. According to our estimates, vibrations of atoms would play a more significant role in the vdW interaction for high-symmetry molecules with large vibrational polarizabilities and hard (high-energy) IR modes, or for low-symmetry molecules with ultrasoft IR modes and corresponding small effective masses.
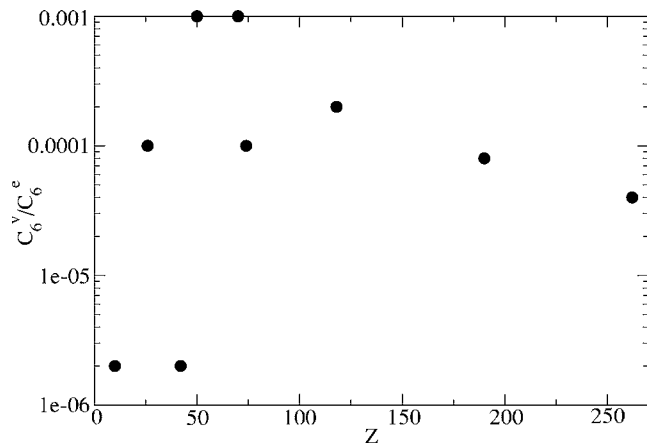

FIG. 3. Ratio C_6^v/C_6^e[emp] (logarithmic scale) vs Z for the nine dimers of the same kind considered in Table II.

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