Nonadditive Interactions in Trimers Containing H₂, N₂, and O₂

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A study comparing the magnitudes of the second-order nonadditive induction energy and the nonadditive triple-dipole dispersion energy for interactions in trimers containing the linear homonuclear molecules H₂, N₂, and O₂ has been undertaken. The configurations are a linear, symmetric and an equilateral triangle arrangement of the trimers: H₂−H₂−H₂, N₂−N₂−N₂, O₂−O₂−O₂, N₂−N₂−O₂, and O₂−N₂−H₂. The observed trends are discussed.

I. INTRODUCTION

Explicit equations for the second-order nonadditive induction energy for long-range interactions involving three linear homonuclear molecules were derived recently using the MAPLE symbolic computational language[1,2] and involve the permanent quadrupole moments and dipole polarizabilities of the interacting molecules.

In this previous study the nonadditive induction energy ($E_{\text{ind,non}}$) was compared with the third-order triple-dipole dispersion energy (DDD) for a system consisting of three hydrogen molecules in two different configurations. The DDD is considered to be a significant term in the multipole expansion of the nonadditive part of the many-body long-range potential for molecules and is the leading term for interactions involving only atoms, where there is no induction at all.

However, it was found in the previous work that the nonadditive induction energy at second-order was as important as the DDD (for a range of different molecular orientations).[1] In some cases it was found that both nonadditive energies had the same sign, in others opposite signs. However, in all cases they were found to have similar orders of magnitude.

For systems consisting only of nonpolar linear molecules the lowest nonvanishing permanent multipole moment is the quadrupole moment (i.e., there is no induction energy arising from permanent dipole moments). This quadrupole moment can induce dipole moments in neighboring molecules and give rise to a second-order nonadditive induction energy in molecular trimers varying as R^{-8}, whereas the corresponding DDD varies as R^{-9} (with R representing intermolecular separation). This suggests that this induction energy term may be as significant a contribution to the nonadditive long-range intermolecular potential as the DDD, and this is clearly the case for the H₂ trimer.[1]

In this present study these long-range nonadditive energies are compared for several trimers containing H₂, N₂, and O₂. The "exact" triple-dipole energy is computed using analytic expressions derived previously.[3] The trimers studied here involve only the same species as well as mixtures of different molecules, namely H₂−H₂−H₂, N₂−N₂−N₂, O₂−O₂−O₂, N₂−N₂−O₂, O₂−N₂−H₂. The similarities and differences

between the different three-body interactions are examined by comparing the values of the nonadditive energies for two different configurations as well as their relative magnitudes. In addition, the distance-independent part of the nonadditive induction energy expression is computed for each trimer.

II. THEORY AND RESULTS

The long-range intermolecular interaction energies are adequately calculated by the use of Rayleigh−Schrodinger perturbation theory, with a multipole expansion of the interaction potential usually employed to describe the long-range interactions (where electron exchange and charge overlap effects are considered to be negligible). The DDD arises from the third-order perturbation theory and for trimers consisting of only rare-gas atoms may be described by the well-known Axilrod-Teller term[4]

$$\text{DDD} = [(1 + 3\cos\theta_A\cos\theta_B\cos\theta_C)C_9(a,b,c)]R_{ab}^{-3}R_{ac}^{-3}R_{bc}^{-3} \tag{1}$$

where C_9 is the triple-dipole dispersion energy coefficient, R_{ab}, R_{ac}, and R_{bc} are interatomic distances, and θ_A, θ_B, and θ_C are the internal angles of the triangle formed by the atoms a, b, and c. The higher-order dispersion terms which involve quadrupoles, octupoles, and higher multipoles are expected to be smaller in magnitude (due to their larger $1/R$ dependence).

However, the DDD for systems containing linear Σ-state molecules has been recently derived.[3] This is a very complicated expression involving coefficients which depend on the oscillator strengths and excitation energies of the constituent molecules as well as functions which depend on the intermolecular configuration and spatial orientations of the molecules. The explicit expression for the DDD is given in ref 3 and will not be reproduced here.

The general expression for the long-range nonadditive induction energy was obtained by MAPLE (as detailed in ref 1) from the standard second-order perturbation theory expression. This complicated expression is simplified by considering only the leading term (which involves the interaction of the permanent quadrupole moments of the two
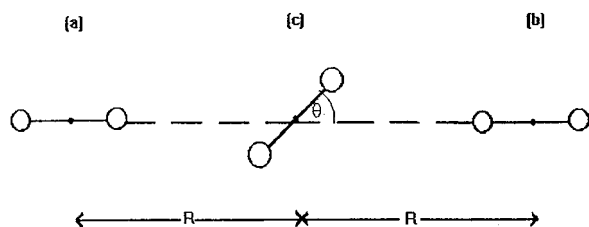
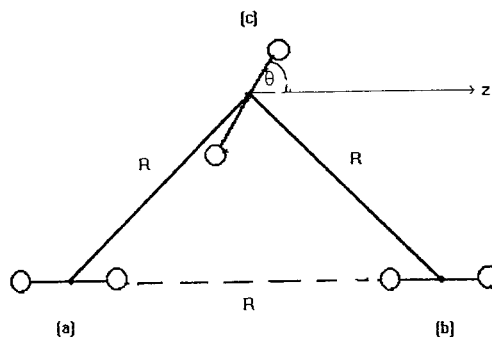**Figure 1.** The linear, symmetric configuration for the trimer system.

Figure 2. The equilateral triangle configuration for the trimer system.

molecules with the third molecule through its dipole polarizability). So in this study the lead term of the $E_{\text{ind,non}}$ expression was calculated and compared with the corresponding DDD given by the expression in ref 3.

The two configurations of the trimer systems studied are shown in Figures 1 and 2, with the intermolecular distance R representing the separation of the centers of mass of a pair of molecules. In both configurations the molecule denoted as c (i.e., the central molecule in the linear configuration and the molecule at the apex in the triangular configuration) is allowed to rotate through an angle θ in the plane containing all three molecules, with molecules a and b kept fixed as shown. The individual terms contributing to $E_{\text{ind,non}}$ may be readily examined from the analytic expressions obtained using the MAPLE program, since the results for each orientation of molecule c may be generated and visually displayed. For example, for the linear configuration (Figure 1) with $\theta = 0°$ we obtain

$$E_{\text{ind,non}} = 9R^{-8}(16\Theta_{zz}(a)\Theta_{zz}(b)\alpha_c^{\|} - \Theta_{zz}(b)\Theta_{zz}(c)\alpha_a^{\|} - \\ \Theta_{zz}(a)\Theta_{zz}(c)\alpha_b^{\|})/16 \quad (2)$$

and for the equilateral triangle configuration (Figure 2) with $\theta = 0°$ we obtain

$$E_{\text{ind,non}} = 9R^{-8}(3584\Theta_{zz}(a)\Theta_{zz}(c)\alpha_b^{\|} + \\ 3584\Theta_{zz}(b)\Theta_{zz}(c)\alpha_a^{\|} + 1568\Theta_{zz}(a)\,\Theta_{zz}(b)\alpha_c^{\|} - \\ 96\Theta_{zz}(a)\Theta_{zz}(b)\alpha_c^{\perp})/8192 \quad (3)$$

A FORTRAN program was written to compute the DDD values, and numerical values for the dipole polarizabilities of H₂, N₂, and O₂ are also computed by this program from dipole oscillator strength data, which along with the quadrupole moments are used as input to the MAPLE code. For the quadrupole moment of H₂ an experimental value of 0.466 atomic units was used in the calculations,[5] as in the previous work on the H₂ trimer.[1] The quadrupole moments of N₂

Table 1. Triple-Dipole Dispersion Energy (DDD) and Second-Order Nonadditive Induction Energy ($E_{\text{ind,non}}$) for the Linear, Symmetric Configuration and the Equilateral Triangle Configuration of the Trimers (a−b−c)[a]

trimer (a−b−c)	DDD (linear)	$E_{\text{ind,non}}$ (linear)	DDD (triangle)	$E_{\text{ind,non}}$ (triangle)
H₂−H₂−H₂	-1.36×10^{-5}	2.97×10^{-5}	0.71×10^{-7}	1.40×10^{-7}
N₂−N₂−N₂	-1.81×10^{-4}	4.72×10^{-4}	0.92×10^{-6}	2.23×10^{-6}
O₂−O₂−O₂	-1.67×10^{-4}	0.37×10^{-4}	0.70×10^{-6}	0.18×10^{-6}
N₂−N₂−O₂	-1.76×10^{-4}	5.38×10^{-4}	0.75×10^{-6}	0.91×10^{-6}
O₂−N₂−H₂	-7.39×10^{-5}	8.48×10^{-5}	3.85×10^{-7}	-3.98×10^{-7}

[a] Refer to Figures 1 and 2 for the geometrical arrangement of the trimers. $\theta = 0°$, $R = 5$ au (linear) and $R = 10$ au (equilateral triangle). All energies in atomic units.

Table 2. Coefficients of R^{-8} in the Nonadditive Induction Energy Expressions Given by Eq 2 (Linear Configuration, $\theta = 0°$) and Eq 3 (Equilateral Triangle Configuration, $\theta = 0°$) for the Trimers Studied[a]

trimer (a−b−c)	coeff (linear)	coeff (triangle)
H₂−H₂−H₂	11.6	14
N₂−N₂−N₂	184	223
O₂−O₂−O₂	14.5	18
N₂−N₂−O₂	210	91.2
O₂−N₂−H₂	33.1	−39.8

[a] Refer to Figures 1 and 2 for the definition of the appropriate configurations. All quantities are in atomic units.

Table 3. Ratio of the Magnitudes of the DDD and $E_{\text{ind,non}}$ for the Linear Configuration of the Trimer Systems (Ratio = |DDD/$E_{\text{ind,non}}$|) with $R = 5$ au[a]

trimer (a−b−c)	ratio ($\theta = 0°$)	ratio ($\theta = 90°$)
H₂−H₂−H₂	0.46	0.36
N₂−N₂−N₂	0.38	0.3
O₂−O₂−O₂	4.5	3.9
N₂−N₂−O₂	0.33	0.33
O₂−N₂−H₂	0.87	1.3

[a] Refer to Figure 1 for the definition of the geometrical parameters for this configuration.

and O₂ were determined (at the experimental equilibrium bond length) by MP2 ab initio calculations with [5s4p3d] basis sets for the atoms using the CADPAC suite of programs,[6] giving values of −1.257 atomic units for N₂ and −0.348 atomic units for O₂.

The results of this comparative study are shown in Tables 1−3. For each trimer system shown in Table 1 numerical values of $E_{\text{ind,non}}$ and DDD are compared for both configurations with $\theta = 0°$. In Table 2 the molecular property coefficients of R^{-8} in eqs 2 and 3 are contrasted, and Table 3 shows the relative magnitudes of the triple-dipole dispersion energy and the nonadditive induction energy for the linear, symmetric configuration (with $R = 5$ au). These results are discussed in the next section.

III. DISCUSSION OF RESULTS

Table 1 shows that the triple-dipole dispersion energy is always attractive for the linear configuration and repulsive for the equilateral triangle arrangement at $\theta = 0°$. This is also the case for all orientations of molecule c. However, it should be noted that the nonadditive induction energy is always repulsive for the linear configuration (for all angles

θ) but changes sign for the equilateral triangle configuration (i.e., it goes from repulsive to attractive or vice versa as θ varies from 0° to 90°). For example, for $H_2-H_2-H_2$, $N_2-N_2-N_2$, and $O_2-O_2-O_2$ the induction energy is repulsive at $\theta = 0°$ (see Table 1) and changes sign between 40° and 50° for the triangular arrangement (i.e., it becomes zero (negligible) between $\theta = 40°$ and 50° and consequently the DDD dominates the overall nonadditive energy within this range of orientations).

The triple-dipole dispersion energy for the trimer systems studied are strongly anisotropic (angle-dependent) as is evident from the fact that the values given in Table 1 (for $\theta = 0°$, linear configuration) decrease by between 30 and 44% for all the trimers as molecule c is rotated to $\theta = 90°$. For the triangular geometry, the DDD increases by between 53 and 94% for the same rotation.

The dependence of the nonadditive induction energy upon the molecular property coefficients (i.e., the sums of the products of the molecular quadrupole moments and dipole polarizabilities) is shown in Table 2. It should be noted that these coefficients have their maximum value at $\theta = 0°$ (shown in the table) and decreases to a minimum at $\theta = 90°$ by 13%, 14%, 32%, 42%, and 53% for $H_2-H_2-H_2$, $N_2-N_2-N_2$, $O_2-O_2-O_2$, $N_2-N_2-O_2$, and $O_2-N_2-H_2$, respectively, for the linear configuration.

Table 2 also shows that, for the linear configuration, the H_2 trimer has the smallest property coefficient (primarily because of the relatively small dipole polarizability of H_2), and the $N_2-N_2-N_2$ and $N_2-N_2-O_2$ complexes have much larger values of roughly similar magnitude (primarily because of the large N_2 quadrupole moment).

The property coefficients increase by about a factor of 1.2 in going from the linear to the triangular configuration for all the trimers, except $N_2-N_2-O_2$. In this configuration the central molecule is displaced from the line joining the centers of mass of all three molecules, thereby allowing for the polarization of its charge cloud in the direction perpendicular to its bond axis. For $N_2-N_2-O_2$ there is a decrease in the property coefficient by a factor of 2.3 in going from the linear to the triangular geometry. We find a similar decrease in the property coefficient (for the triangular arrangement) in going from $N_2-N_2-N_2$ to $N_2-N_2-O_2$. In this configuration the dominant repulsive contribution to $E_{ind,non}$ mainly arises from the quadrupole of the molecule occupying the apical position (i.e., molecule c) and the quadrupole of one of the N_2 molecules interacting with the other N_2 molecule through its parallel dipole polarizability (see eq 3). Therefore, the decrease in the property coefficient is readily understood by noting that O_2 replaces N_2 in the apical position in the $N_2-N_2-O_2$ system, thereby leading to a decrease in the dominant repulsive contribution to the nonadditive induction energy (since the O_2 quadrupole moment is less polarizing than the N_2 quadrupole moment).

Since the quadrupole moment of H_2 is opposite in sign to that of N_2 and O_2, and there is only one H_2 molecule in the $O_2-N_2-H_2$ complex, it is possible for the attractive terms

in the nonadditive induction energy expression to dominate, and this is clearly the case for the equilateral triangle configuration (see column 3 of Table 2).

Table 3 shows the relative magnitudes of the DDD and $E_{ind,non}$ for the linear configuration (with $R = 5$ au). The induction energy is larger in magnitude for all trimers except $O_2-O_2-O_2$, with the induction energy being more than 3 times larger than the corresponding DDD for $N_2-N_2-O_2$. For the O_2 trimer the DDD is 4.5 times larger than $E_{ind,non}$. This trend can be understood for the trimers containing only the same molecules by first assuming that the magnitude of the DDD is roughly twice that of the Axilrod−Teller term[4] (i.e., $C_9R^{-9}/2$). This is not an unreasonable assumption as we wish to show a qualitative trend, and for the worst case this approximation recovers at least 70% of the "exact" DDD. For these trimers the expression for $E_{ind,non}$ given by eq 3 reduces to $63\Theta_{zz}2\alpha^{\parallel}R^{-8}/8$, so that for $R = 5$ au, the ratio $|DDD/E_{ind,non}|$ may be roughly approximated by $4C_9/(315\Theta_{zz}2\alpha^{\parallel})$. Using this rough formula we obtain values of 0.42, 0.34, and 3.11 for the trimers $H_2-H_2-H_2$, $N_2-N_2-N_2$, and $O_2-O_2-O_2$, respectively. These values follow the same qualitative trend shown in Table 3. Apparently, the dominance of the DDD in the $O_2-O_2-O_2$ interaction is due to the relatively small quadrupole moment of O_2 (which appears in the denominator of our rough formula).

Another interesting observation is that for the like−like−like interactions there is a decrease in the DDD to $E_{ind,non}$ ratio from the $\theta = 0°$ orientation to the $\theta = 90°$ orientation; the ratio for $N_2-N_2-O_2$ remains unchanged, and there is an increase for $O_2-N_2-H_2$. This indicates that for the H_2 trimer, N_2 trimer, and O_2 trimer, the magnitude of the DDD decreases faster than for $E_{ind,non}$, for $N_2-N_2-O_2$ both decrease to about the same extent, and $E_{ind,non}$ decreases to a greater extent than the DDD for $O_2-N_2-H_2$.

Clearly, both long-range nonadditive energies are competitive in the trimers that were studied, with their relative magnitudes varying from complex to complex as discussed above. The MAPLE program for the evaluation of the nonadditive induction energy and the FORTRAN routine for the calculation of the triple-dipole dispersion energy are available from the author on request.

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