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Robert Hinde, University of Tennessee

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Vibrational dependence of the H2–H2 C6 dispersion coefficients

Robert J. Hinde
Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

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We use the sum-over-states formalism to compute the imaginary-frequency dipole polarizabilities for H2, as a function of the H–H bond length, at the full configuration interaction level of theory using atom-centered d-aug-cc-pVQZ basis sets. From these polarizabilities, we obtain isotropic and anisotropic C6 dispersion coefficients for a pair of H2 molecules as functions of the two molecules’ bond lengths. © 2005 American Institute of Physics. [DOI: 10.1063/1.1873512]

The parahydrogen dimer (pH2)2 formed by two j=0 H2 molecules is the molecular analog of the He2 van der Waals dimer. Because the pH2–pH2 interaction is relatively weak and the H2–H2 reduced mass is small, the dimer formed between two v=0 pH2 molecules has just a single bound state,1 one which is characterized by an intermolecular vibrational wave function that spans a wide range of intermolecular distances R. In the ground state of the empirical H2–H2 potential given in Ref. 2, for example, fully 30% of the (pH2)2 dimer’s probability density is located in the classically forbidden region R=10 a0, where the pH2–pH2 potential is dominated by dispersion interactions. In this paper, we compute R3 dispersion coefficients for H2–H2, H2–D2, and D2–D2 dimers in which one of the monomers is in the v=1 level; these coefficients provide constraints on the shape of the H2–H2 potential in the classically forbidden large R region, and hence on the binding energies of near-threshold excited states of these van der Waals dimers.

We begin by computing the H2 dipole polarizabilities αxx and αzz at imaginary frequencies using the sum-over-states formalism,

\[ \alpha_{qq}(\omega) = 2 \sum_{n \neq 0} \left( \frac{E_n - E_0}{(E_n - E_0)^2 + \hbar^2 \omega^2} \right)^2 \mu_n^2, \]

where \( \mu \) is the dipole moment operator and q represents a Cartesian coordinate (in this case, either x or z) in the molecule-fixed frame of reference; the H2 bond defines the molecule-fixed z axis. The ground state electronic wave function \( \psi_0 \) and excited state electronic wave functions \( \psi_n \), their energies \( E_0 \) and \( E_n \), and the dipole moment matrix elements \( \langle 0 | \mu_q | n \rangle \) are obtained from full configuration interaction (CI) electronic structure calculations employing a cc-pVQZ atom-centered Gaussian basis set for hydrogen3 that has been doubly augmented4,5 (denoted d-aug-cc-pVQZ) with diffuse functions that facilitate the accurate \textit{ab initio} computation of dipole polarizabilities.6

These electronic structure computations are performed at H2 bond lengths r ranging from 0.9 a0 to 2.1 a0 in steps of 0.1 a0, and also at r=1.449 a0, which is close to the v=0 vibrationally averaged H2 bond length. Calculations at \( r=0.9 \text{ a}_0 \), \( r=1.449 \text{ a}_0 \), and \( r=2.1 \text{ a}_0 \) are also performed using the smaller d-aug-cc-pVTZ atom-centered Gaussian basis set for hydrogen. All electronic structure calculations are performed using the 22 November 2004 R1 version of GAMESS.7

At each value of r, the sum in Eq. (1) is evaluated over the entire set of excited electronic states obtained from the full CI calculations. The relevant electronic state energies and dipole moment matrix elements may be downloaded from the EPAPS depository.8

As a check on the completeness of our electronic basis set, we use our d-aug-cc-pVQZ dipole moment matrix elements to evaluate the sums

\[ \sum_{n \neq 0} |\langle 0 | \mu_x | n \rangle|^2, \quad \sum_{n \neq 0} |\langle 0 | \mu_z | n \rangle|^2, \]

which should give the ground state expectation values \( \langle 0 | \mu_x^2 | 0 \rangle \) and \( \langle 0 | \mu_z^2 | 0 \rangle \) in the limit of a complete basis set. We then compare these quantities with the corresponding ones computed directly from the electronic second moments for H2 given in Table V of Ref. 9. At the bond lengths where this comparison can be made, our results differ from those obtained from Ref. 9 by 0.2% or less. The static dipole polarizabilities given by Eq. (1) at \( \omega=0 \) are in similarly good agreement with the H2 polarizabilities computed in Ref. 10.

Equipped with the polarizabilities defined by Eq. (1), we next compute the isotropic polarizability \( \alpha = \frac{(2 \alpha_{xx} + \alpha_{zz})}{3} \) and the polarizability anisotropy \( \Delta \alpha = \alpha_{zz} - \alpha_{xx} \). Using these quantities and one-dimensional quadrature, we then obtain the C6 dispersion coefficient for a pair of \( j=0 \) H2 molecules with bond lengths \( r_1 \) and \( r_2 \),

\[ C_6(r_1, r_2) = \frac{3 \hbar}{\pi(4 \pi \epsilon_0)^2} \int_0^\infty \alpha(\omega, r_1) \alpha(\omega, r_2) d\omega, \]

and the anisotropic dispersion coefficients \( C_{6,02} \), \( C_{6,20} \), and \( C_{6,22} \) defined by\[ ^1 \]

\[ C_{6,ab}(r_1, r_2) = \frac{\hbar}{(4 \pi \epsilon_0)^2} \int_0^\infty f_d(\omega, r_1) f_d(\omega, r_2) d\omega. \]

In Eq. (4), \( f_d(\omega) = \alpha(\omega) \) while \( f_d(\omega) = \Delta \alpha(\omega) \).

For each pair of H2 bond lengths \( (r_1, r_2) \), we evaluate Eqs. (3) and (4) using trapezoid rule quadrature with a step size of \( \Delta \omega = 0.1 \) a.u. over the range \( 0 \leq \omega \leq 50 \) a.u. (We find that the values of the integrals do not change significantly when we use smaller step sizes or when we extend the inte-
grals to include larger values of $\omega$.) At $r_1=r_2=r_{\text{av}}$, we obtain $C_6=12.0571$ a.u., $C_{6,20}=C_{6,02}=1.2256$ a.u., and $C_{6,22}=0.3941$ a.u. These values are in good agreement with those obtained by Bishop and Pipin\textsuperscript{12} using a similar computational approach (but a different basis set for describing the electronic wave functions): $C_6=12.05816$ a.u., $C_{6,20}=C_{6,02}=1.2194$ a.u., and $C_{6,22}=0.3898$ a.u. Dispersion coefficients computed using the d-aug-cc-pVTZ basis set differ from the d-aug-cc-pVQZ values by 0.7% or less, indicating that the d-aug-cc-pVTZ dispersion coefficients are already nearly converged with respect to basis set. We therefore expect that further expansion of the atomic basis set beyond the d-aug-cc-pVQZ level will provide only minor improvements in the accuracy of the dispersion coefficients presented here.

We fit our computed dispersion coefficients to polynomials of the form

$$P(r_1, r_2) = \sum_{b=0}^{2} \sum_{c=0}^{2} A_{bc}(r_1 - r_0)^b(r_2 - r_0)^c,$$

where $r_0=1.4 \ a_0$. We then use the $H_2$ and $D_2$ vibrational matrix elements given in Table I to integrate these polynomial fits over specific $H_2$ and $D_2$ vibrational wave functions, thereby obtaining vibrationally averaged dispersion coefficients with the general form $\langle v_1, v_2 | P(r_1, r_2) | v_1', v_2' \rangle$ for a pair of $j=0$ molecules; these are listed in Table II. We find that, as expected, dispersion interactions are slightly stronger in $v=0+v=1$ molecular pairs than in $v=0+v=0$ pairs. We also find that off-diagonal terms of the form $\langle v_1=0, v_2=1 | P(r_1, r_2) | v_1'=1, v_2'=0 \rangle$ are small but non-negligible; the $C_6$ coefficient for $H_2(v=0)+H_2(v=1)$ pairs, for example, changes by about 2% depending on whether the vibrational excitation is delocalized across the pair of molecules in a symmetric or antisymmetric fashion.

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6The basis sets used in this work were obtained from the 02/25/04 version of the Extensible Computational Chemistry Environment Basis Set Database, located at (http://www.emsl.pnl.gov/forms/basisform.html).
8See EPAPS Document No. E-JCPSA6-122-307515 for text files containing these energies and dipole moment matrix elements. A direct link to this document may be found in the online article’s HTML reference section. The document may also be reached through the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.