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Vibrational dependence of the H_2-H_2 C_6 dispersion coefficients

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We use the sum-over-states formalism to compute the imaginary-frequency dipole polarizabilities for H_2, 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 C_6 dispersion coefficients for a pair of H_2 molecules as functions of the two molecules' bond lengths. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1873512]

The parahydrogen dimer $(pH_2)_2$ formed by two $j=0$ H_2 molecules is the molecular analog of the He_2 van der Waals dimer. Because the pH_2-pH_2 interaction is relatively weak and the H_2-H_2 reduced mass is small, the dimer formed between two $v=0$ pH_2 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 H_2-H_2 potential given in Ref. 2, for example, fully 30% of the $(pH_2)_2$ dimer's probability density is located in the classically forbidden region $R \geqslant 10\ a_0$, where the pH_2-pH_2 potential is dominated by dispersion interactions. In this paper, we compute R^{-6} dispersion coefficients for H_2-H_2, H_2-D_2, and D_2-D_2 dimers in which one of the monomers is in the $v=1$ level; these coefficients provide constraints on the shape of the H_2-H_2 potential in the classically forbidden large R region, and hence on the binding energies of near-threshold states of these van der Waals dimers.

We begin by computing the H_2 dipole polarizabilities α_{xx} and α_{zz} at imaginary frequencies using the sum-over-states formalism,

$$\alpha_{qq}(i\omega) = 2\sum_{n\neq 0} \frac{(E_n - E_0)|\langle 0|\hat{\mu}_q|n\rangle|^2}{(E_n - E_0)^2 + \hbar^2\omega^2}, \tag{1}$$

where $\hat{\mu}$ 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 H_2 bond defines the molecule-fixed z axis. The ground state electronic wave function $|0\rangle$ and excited state electronic wave functions $|n\rangle$, their energies E_0 and E_n, and the dipole moment matrix elements $\langle 0|\hat{\mu}_q|n\rangle$ are obtained from full configuration interaction (CI) electronic structure calculations employing a cc-pVQZ atom-centered Gaussian basis set for hydrogen[3] that has been doubly augmented[4,5] (denoted d-aug-cc-pVQZ) with diffuse functions that facilitate the accurate *ab initio* computation of dipole polarizabilities.[6]

These electronic structure calculations are performed at H_2 bond lengths r ranging from 0.9 a_0 to 2.1 a_0 in steps of 0.1 a_0, and also at $r_{avg}=1.449\ a_0$, which is close to the $v=0$ vibrationally averaged H_2 bond length. Calculations at $r=0.9\ a_0$, $r=1.449\ a_0$, and $r=2.1\ a_0$ 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

$$\sum_{n\neq 0} |\langle 0|\hat{\mu}_x|n\rangle|^2, \quad \sum_{n\neq 0} |\langle 0|\hat{\mu}_z|n\rangle|^2, \tag{2}$$

which should give the ground state expectation values $\langle 0|\hat{\mu}_x^2|0\rangle$ and $\langle 0|\hat{\mu}_z^2|0\rangle$ 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 H_2 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 H_2 polarizabilities computed in Ref. 10.

Equipped with the polarizabilities defined by Eq. (1), we next compute the isotropic polarizability $\alpha=(2\alpha_{xx}+\alpha_{zz})/3$ and the polarizability anisotropy $\Delta\alpha=\alpha_{zz}-\alpha_{xx}$. Using these quantities and one-dimensional quadrature, we then obtain the C_6 dispersion coefficient for a pair of $j=0$ H_2 molecules with bond lengths r_1 and r_2,

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

and the anisotropic dispersion coefficients $C_{6,02}$, $C_{6,20}$, and $C_{6,22}$ defined by[11]

$$C_{6,ab}(r_1,r_2) = \frac{\hbar}{\pi(4\pi\epsilon_0)^2}\int_0^\infty f_a(i\omega,r_1)f_b(i\omega,r_2)d\omega. \tag{4}$$

In Eq. (4), $f_0(i\omega)=\alpha(i\omega)$ while $f_2(i\omega)=\Delta\alpha(i\omega)$.

For each pair of H_2 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 $0\leqslant\omega\leqslant 50$ 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-

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TABLE I. Vibrational matrix elements $\langle v|(r-r_0)^n|v'\rangle$ for $j=0$ H_2 and D_2 molecules. These integrals are based on vibrational wave functions computed from the potential curve in Ref. 9 using the Numerov–Cooley (Ref. 13) method.

Molecule	v	v'	$n=1$ (a_0)	$n=2$ (a_0^2)
H_2	0	0	0.048 34	0.030 53
H_2	0	1	0.166 39	0.026 74
H_2	1	1	0.144 95	0.106 87
D_2	0	0	0.034 35	0.020 90
D_2	0	1	0.139 52	0.015 84
D_2	1	1	0.101 93	0.070 15

grals to include larger values of ω.) At $r_1=r_2=r_{\text{avg}}$ 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[12] using a similar computational approach (but a different basis set for describing the electronic wave functions): $C_6=12.058\,168$ 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

$$P(r_1,r_2)=\sum_{b=0}^{2}\sum_{c=0}^{2}A_{bc}(r_1-r_0)^b(r_2-r_0)^c, \tag{5}$$

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.

TABLE II. Vibrationally averaged C_6 dispersion coefficients (in atomic units) for various molecular pairs.

Pair		C_6	$C_{6,20}$	$C_{6,02}$	$C_{6,22}$
H_2 (v_1,v_1')	H_2 (v_2,v_2')				
(0, 0)	(0, 0)	12.077	1.246	1.246	0.408
(0, 0)	(1, 1)	12.799	1.327	1.450	0.479
(0, 1)	(1, 0)	0.137	0.035	0.035	0.027
H_2 (v_1,v_1')	D_2 (v_2,v_2')				
(0, 0)	(0, 0)	11.972	1.234	1.217	0.398
(0, 0)	(1, 1)	12.477	1.291	1.358	0.447
(1, 1)	(0, 0)	12.687	1.437	1.296	0.467
D_2 (v_1,v_1')	D_2 (v_2,v_2')				
(0, 0)	(0, 0)	11.869	1.205	1.205	0.388
(0, 0)	(1, 1)	12.368	1.260	1.345	0.435
(0, 1)	(1, 0)	0.096	0.024	0.024	0.018

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