Molecular Modeling Exercises and Experiments

Structural and Thermodynamic Properties of the Argon Dimer

A Computational Chemistry Exercise in Quantum and Statistical Mechanics

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One of the overall objectives in teaching physical chemistry is to make students aware of the grand sweep of knowledge contained in that subject and how one can apply first-principles analyses to a vast range of seemingly different topics. In this context, one would logically like to begin with the microscopic understanding of matter and its characteristics (quantum chemistry and statistical mechanics) and extend this knowledge to the macroscopic domain to predict measurable bulk properties (e.g., thermodynamic and kinetic) of systems.

This article describes an opportunity for students to explore the domains of statistical mechanics and thermodynamics by utilizing a quantum chemical approach to the study of interatomic interactions. The focus of this exercise is the argon dimer, Ar_2, which is a paradigmatic example of a van der Waals complex that is a manifestation of dispersion, or induced dipole–induced dipole interactions. While any of the rare gas dimers could be used in this study, Ar_2 is chosen because its structure and binding energy are well-known experimentally, as are its thermodynamic properties. It is also amenable to a rigorous quantum computational investigation because its binding energy is sufficiently large (i.e., 100 cm^{-1}) so as to override more subtle effects, the number of electrons is not excessive, and the nuclei are not too massive to warrant the consideration of relativistic effects.

The project described here can be carried out by undergraduates taking physical chemistry or a computational chemistry course, by graduate students, or by students working on a directed-study project. It can be undertaken by a single student or by a group in which individuals take on different responsibilities while working on the components of the project. The results are wide ranging enough to make it possible for each of the students in a group to present a portion of the work individually.

Before the details of the study are described, the schematic outline of the project is presented. One begins by constructing the interatomic, or pair potential of Ar_2, $V(r)$, where r is the internuclear separation, by carrying out high-level ab initio quantum chemical calculations. *This potential forms the basis of all the other results obtained in the study*. Students will be impressed to learn that this potential is the key that can be used to unlock so many of the properties of the argon dimer. They will see that it provides the connection between the microscopic and macroscopic domains.

Once $V(r)$ is obtained, the fundamental molecular constants, including the "bond length" and dissociation energy, are extracted. Then the second virial coefficient, B_2, is calculated using a relationship obtained from statistical mechanics. Also, from the molecular constants, the entropies and partition functions of the argon atom and dimer can be computed, and from this information the standard thermodynamic functions of dimer formation (and the equilibrium constant) can be determined.

Calculation of the Pair Potential

The argon dimer potential energy surface (PES) is obtained by calculating the energy of a pair of Ar atoms as a function of their internuclear separation. The computational approach suggested here employs the coupled-cluster method *(1)* with single, double, and perturbative triple excitations, CCSD(T) *(2)*, along with a family of augmented correlation-consistent basis sets, aug-cc-pVXZ (where X denotes double, triple, and quadruple-ζ: D, T, Q). This method, which can be readily employed by students using the Gaussian 03 suite of programs (for Windows or Unix) *(3)*, represents a satisfactory compromise between rigor and practicality. This high-level method is needed to properly take into account electron correlation effects that are important in the type of nonbonded interactions in the argon dimer and thus represent the shape of the PES reasonably accurately. Because the calculations employing the quadruple-ζ basis sets take considerably more time, the points used to construct $V(r)$ must be chosen judiciously. To achieve the highest level of computational rigor within the limitations of the available computing resources, students will obtain three $V(r)$ surfaces for the argon dimer using basis sets of increasing size and then extrapolate these surfaces to obtain $V(r)$ in the "complete basis set" (CBS) limit *(4)*. The details of acquiring these scans, examples of input files, the method used to obtain the CBS energies, as well as a table of all energies obtained in the calculations, are provided in the supporting material.

As a compromise between computational precision (which would require a higher point density) and computational cost (i.e., total run times), the $V(r)$ surface was constructed from 35 points representing different Ar–Ar separations between 2.5 Å and 6.7 Å. The results are illustrated in Figure 1, which shows 31 of the 35 ab initio calculated points. The four points not included are those between 2.5 and 3.5 Å. They represent the highly repulsive portion of the PES and are used in the determination of the second virial coefficient, B_2, to be discussed later.
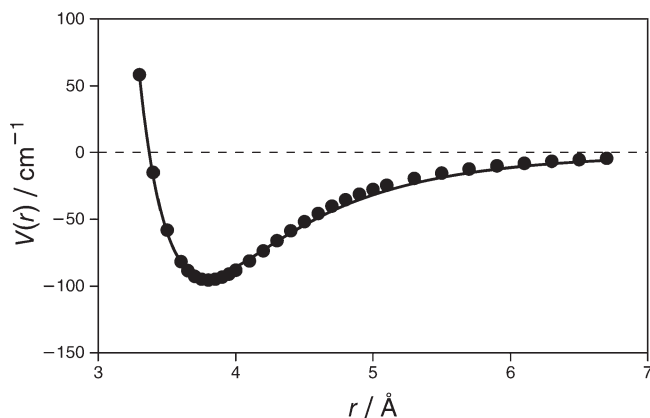
Figure 1. Argon dimer interatomic potential energy surface, $V(r)$, obtained from CCSD(T)/CBS calculations at selected interatomic separations, r: • calculated points and — regression fit to eq 1.

Figure 2. Portion of the ab initio potential energy, $V(r)$: • calculated points and — regression fit to eq 2.

Because the Lennard−Jones 6−12 potential

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad (1)$$

where ε and σ are the well depth and the value of r where $V(r) = 0$, is frequently used to represent pairwise interactions, it is instructive to compare the ab initio PES with the 6−12 potential. A regression analysis of the data yields ε and σ values of 93.2(7) cm^{-1} and 3.372(2) Å, respectively. These results compare with 86.1 cm^{-1} and 3.418 Å as reported by Hirschfelder, presumably from gas imperfection measurements. Evidently, the ab initio and 6−12 potentials do not map onto each other in great detail. The CCSD(T)/CBS ab initio well depth and minimum obtained with the method described in this work, however, compare well with those from other ab initio calculations *(5)*.

Molecular Constants

Once the points (in cm^{-1} units) along the Ar_2 PES are obtained, 14 data points along $V(r)$ near the bottom of the well (from 3.5 Å to 4.4 Å) are fit to a seven-parameter power series *(6)*

$$V(r) = a_0 + a_2(r - r_e)^2 + a_3(r - r_e)^3 + a_4(r - r_e)^4$$
$$+ a_5(r - r_e)^5 + a_6(r - r_e)^6 \quad (2)$$

where a_0 is the energy at the bottom of the well where $r = r_e$, the equilibrium internuclear separation. The parameter a_0 is negative because zero energy is reached asymptotically at infinite separation. The well depth, D_e, is equal to $-a_0$. The parameter a_2 accounts for the harmonic property of the potential, and the remaining constants are used to capture its anharmonic property. Fitting details are found in the supporting information. The result of fitting eq 2 to the 14 data points is shown in Figure 2. The standard deviation of regression is 0.00256, and the seven regression parameters are $a_0 = -95.430(1)$, $a_2 = 248.4(1)$, $a_3 = -410.8(5)$, $a_4 = 433.1(7)$, $a_5 = -3501(4)$, $a_6 = 151(4)$, and $r_e = 3.79793(3)$ Å. The units of a_n are cm^{-1} Å^{-n}.

Using these parameters, the rotational constant, B_e, can be expressed as *(7)*

$$B_e = \frac{h}{8\pi^2 c \mu r_e^2} \quad (3)$$

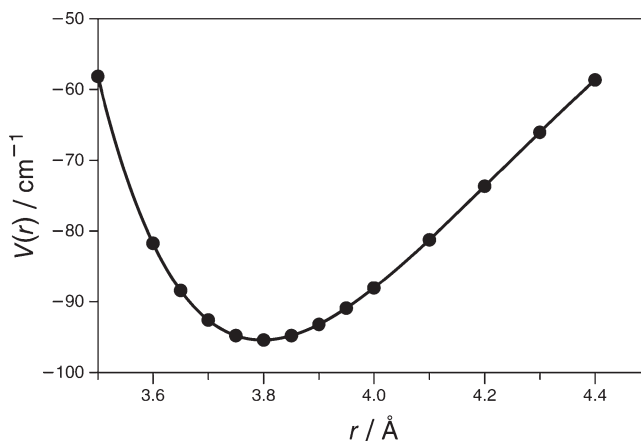**Table 1. Values of the Molecular Constants of the Ar Dimer**

Spectroscopic Constant	This Work[a]	Experimental Value[b]
r_e/Å	3.7978	3.761(3)
D_e/cm^{-1}	95.430(1)	99.2
B_e/cm^{-1}	0.05851	0.05965(8)
$\tilde{\nu}_e$/cm^{-1}	28.96	30.68(3)
α_e/cm^{-1}	0.00375	0.00364(10)
D/cm^{-1}	9.55×10^{-7}	
$\tilde{\nu}_e\chi_e$/cm^{-1}	2.12	2.42(5)

[a] Data obtained from 14 ab initio $V(r)$ points between 3.5 and 4.4 Å and eqs 2−7. [b] Data from ref *8*.

in which h and c are Planck's constant and the speed of light, respectively, and μ is the reduced mass (one-half the mass of the Ar atom). The harmonic frequency ($\tilde{\nu}_e$, in cm^{-1}) is, as expected, extracted from an expression containing a_2

$$\tilde{\nu}_e = \frac{1}{2\pi c}\sqrt{\frac{2a_2}{\mu}} \quad (4)$$

The rotational vibrational coupling constant, α_e, is given by

$$\alpha_e = -\frac{6B_e^2}{\tilde{\nu}_e}\left(\frac{a_3 r_e}{a_2} + 1\right) \quad (5)$$

and the centrifugal distortion constant, D (not to be confused with D_e), by

$$D = \frac{4B_e^3}{\tilde{\nu}_e^2} \quad (6)$$

Finally, the anharmonicity constant, $\tilde{\nu}_e\chi_e$, is calculated from the expression

$$\tilde{\nu}_e\chi_e = \frac{B_e}{8}\left[15\left(1 + \frac{\alpha_e\tilde{\nu}_e}{6B_e^2}\right)^2 - \frac{12a_4 r_e^2}{a_2}\right] \quad (7)$$

The results provided by these calculations are summarized in Table 1 along with experimental data obtained from vacuum ultraviolet laser spectroscopy.

Students will be encouraged by seeing how well their calculations agree with the experimental results for the argon dimer.

The uncertainties in the molecular constants can be obtained from propagation-of-errors analyses of eqs 3−7 and the respective standard deviations of the parameters represented in eq 2. (Students may find some of these tasks challenging.)

For an optional exercise in this project, students can spline their ab initio potential, including the portion extrapolated to 20 Å (see the discussion in the following section) to an array of equally spaced points and use a utility such as FINDIF *(9)* to diagonalize the potential, thereby obtaining the eigenvalues. They will find that their potential supports nine bound states. Using this information they can determine the harmonic and anharmonic constants. Such an analysis gives $\tilde{\nu}_e = 23.4(4)$ cm^{-1} and $\tilde{\nu}_e \chi_e = 1.43(6)$ cm^{-1}. Details are provided in the supporting material. These values differ from the ones obtained from the analysis of the $V(r)$ surface using eq 2 (Table 1) because the latter analysis also takes into account the other molecular constants listed in Table 1.

The Second Virial Coefficient

Students can now proceed to obtain the second virial coefficient, B_2, defined through the familiar power series expression for an imperfect gas

$$PV_m = RT \left(1 + \frac{B_2}{V_m} + \cdots \right) \qquad (8)$$

where P, T, and V_m are the pressure, absolute temperature, and molar volume, respectively, and R is the gas constant. From statistical mechanics, the second virial coefficient can be expressed in terms of $V(r)$ through

$$B_2 = 2\pi N_A \int_0^\infty [1 - e^{-V(r)/(kT)}] r^2 \mathrm{d}r \qquad (9)$$

where N_A and k are Avogadro's number and the Boltzmann constant, respectively *(10)*. The integration limits in eq 9 require that $V(r)$ be evaluated not only for small values of r, but for large ones as well. This is the reason that four values of $V(r)$ have been obtained at small r (i.e., 2.5, 2.7, 2.9, and 3.1 Å), points well onto the repulsive wall of the potential. The integration of eq 9 can be readily carried out numerically (see the supporting material). Students will see that the integrand in eq 9 is equivalent to r^2 for $r = 2.5$ Å (because $V(r) \gg kT$), so they can confidently represent it by r^2 for an arbitrary number of values down to $r = 0$.

As for the upper limit of the integration, it is necessary to obtain values of $V(r)$ well beyond the 6.7 Å high end of the calculation range to obtain a satisfactory value of B_2. To accomplish this objective, students can learn that for the argon dimer, $V(r)$ at large values of r is dominated by the attractive forces between the atoms, which can be approximated in the induced dipole–induced dipole model (i.e., involving dispersion, London, or van der Waals forces) by a simple expression containing a single term in r^{-6}, viz.

$$V(r) \approx -\frac{C}{r^6} \qquad (10)$$

where C is a constant *(11)*. This expression is used to extrapolate $V(r)$ out to 20 Å, a point at which the integral in eq 9 reasonably converges. To obtain C, students can fit the last three data points [i.e., $V(r)$ for $r = 6.3$, 6.5, and 6.7 Å] to eq 10, which is known as the London formula. The value of C obtained in this way, $4.148(23) \times 10^5$ cm^{-1} Å^6, is not very precise, but when used in

Table 2. Ar Atom Polarazibility and Second Virial Coefficient

Property	This Work	Literature Value
$\alpha'/\text{Å}^3$	2.09	1.85 [a]
B_2/cm^3	−15.9	−15.1 [b]

[a] Data from ref *13*. [b] Data from ref *14*.

eq 10 nevertheless provides a suitable way to improve on the accuracy of B_2 without having to carry out additional ab initio calculations.

Because eq 10 attempts to account for the dispersion attraction between two argon atoms, it is interesting to consider the constant C in the London equation in the context of classical electrostatics, that is

$$C = \frac{3}{4} \alpha'^2 I \qquad (11)$$

where α' is the polarizability volume and I is the ionization energy of the argon atom *(12)*. Students can use eq 11 to check the reasonableness of the value of C obtained from their ab initio calculations. Thus using the ionization energy of Ar (1.2709×10^5 cm^{-1}), they find $\alpha' = 2.086(6)$ Å^3, which is in qualitative agreement with a reported value of 1.85 Å^3 *(13)*.

Now in possession of a pair potential that spans from 0 to 20 Å, students can proceed to determine B_2 by carrying out a numerical integration of eq 9. In doing so for $T = 300$ K, they will obtain, after conversion to cm units, a value of −15.9 cm^3, which is in good agreement with −15.1 cm^3 that is obtained from a meta analysis of gas imperfection data *(14)*. The results obtained in this section are summarized in Table 2.

Students might wonder why it is recommended that they extrapolate their potential from 6.7 Å (the largest internuclear separation in their calculations) to 20 Å. If they examine their potential graphically it might seem that at 6.7 Å it is close enough to the limiting value of zero (the potential has a value of about −4 cm^{-1} at that point). However, if they were to evaluate the integral in eq 9 with an upper limit of 6.7 Å, they will find that B_2 is about −7.1 cm^3, a value that significantly underestimates the attractive pair interactions between argon atoms. Students should be encouraged to examine the integrand, $I(r)$, of eq 9 (not to be confused with I in eq 11). They will see that this function is positive when $V(r) > 0$ (accounting for repulsive interactions) and negative when $V(r) < 0$ (accounting for attractive interactions); thus underrepresenting $V(r)$ for larger values of r correspondingly causes the calculated value of B_2 to be too large (not negative enough).

This situation can provide students with a learning experience in computational work by their calculating B_2 from eq 9 using only their data up to 6.7 Å and being asked to determine why their value is too positive. If they then graph $I(r)$ in eq 9, they will realize that a significant portion of the true integrand (the portion for which $I(r) < 0$) is unaccounted for by their calculations. A plot of $I(r)$ versus r is presented in the supporting material. This discovery will lead to suggestions for carrying out additional calculations or for appropriately extrapolating $V(r)$.

Thermodynamic Properties of the Argon Dimer

Thus far students have used their ab initio argon pair potential to find the molecular constants of the dimer, an estimate of the polarizability volume of the argon atom, and

the argon second virial coefficient. But they can confront an additional challenge as they consider using their results to obtain the standard thermodynamic quantities of dimer formation, that is, $\Delta_r U^\circ$, $\Delta_r H^\circ$, $\Delta_r S^\circ$, and K_P° for

$$2Ar \rightleftharpoons Ar_2 \tag{12}$$
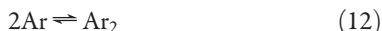
Once $\Delta_r H^\circ$, $\Delta_r S^\circ$ are found, $\Delta_r G^\circ$ and the equilibrium constant K_P° can be found from the Gibbs equation $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ and from $K_P^\circ = \exp(-\Delta_r G^\circ / RT)$. (In this section, energy units of kJ mol^{-1} are implicit. Details of the calculations are provided in the supporting material).

This task begins by expressing $\Delta_r U^\circ$ as the difference between the thermally populated dimer (including its zero-point energy) and two thermally populated Ar atoms at an absolute temperature T (300 K is used in this work), that is,

$$\Delta_r U^\circ = E_{elec,D} + E_{zpe,D} + E_{trans,D} + E_{rot,D} + E_{vib,D} - 2(E_{elec,M} + E_{trans,M}) \tag{13}$$

where $E_{elec,D}$ and $E_{elec,M}$ are the electronic energies of the dimer and monomer, $E_{zpe,D}$ is the zero-point energy of the dimer, and $E_{X,D(M)}$, is the thermal population of the dimer (monomer) for the X degree of freedom (i.e., translation, rotation, and vibration). Because the dimer well depth, D_e, obtained from the pair potential, is equal to $-(E_{elec,D} - 2E_{elec,M})$, eq 13 can be rewritten as

$$\Delta_r U^\circ = -D_e + E_{zpe} + E_{trans,D} + E_{rot,D} + E_{vib,D} - 2E_{trans,M} \tag{14}$$

In the harmonic oscillator approximation, $E_{zpe} = (1/2)hc\tilde{\nu}_e$, and the equilibrium translational, rotational, and vibrational energies of dimer and monomer are obtained from the expressions for a diatomic rigid rotator perfect gas in the canonical ensemble (15). The results are $E_{trans,D} = E_{trans,M} = (3/2)RT$, $E_{rot,D} = RT$, and

$$E_{vib,D} = R\Theta_{vib}\frac{1}{e^{\Theta_{vib}/T} - 1} \tag{15}$$

where Θ_{vib} is the vibrational temperature, $hc\tilde{\nu}_e/k$. At this point some students might become suspicious if they remember that eq 15 is valid for $(\Theta_{vib}/T) < 1$; for the argon dimer, this quotient is about 0.14. They will also realize from their $V(r)$ curve that the dimer is clearly not a harmonic oscillator.

Now $\Delta_r H^\circ$ can be obtained from the definition $H \equiv U + PV$ and its application to a perfect gas in eq 12, that is, $\Delta_r H^\circ = \Delta_r U^\circ - RT$. To find $\Delta_r G^\circ$, students will have to calculate $\Delta_r S^\circ$ for dimer formation. Again they will turn to the results of a statistical mechanics treatment of the diatomic harmonic oscillator–rigid rotator and use the following expressions for the translational, rotational, and vibrational entropies, S_{trans}, S_{rot}, and S_{vib} (the electronic entropies of the argon atom and dimer are both equal to zero because each is a singlet state):

$$S_{trans} = \frac{5}{2}R + R\ln\left[\frac{(2\pi m)^{3/2}}{h^3}\frac{(kT)^{5/2}}{P^\circ}\right] \tag{16}$$

where m is the molecular mass (dimer or monomer) and P° is the standard pressure, 10^5 Pa (1 bar). The dimer rotational entropy is calculated from

$$S_{rot} = R + R\ln\frac{T}{\sigma\Theta_{rot}} \tag{17}$$

Table 3. Values of the Thermodynamic Quantities for the Reaction $2Ar \rightleftharpoons Ar_2$ at 298.15 K

Quantity/Unit	Value[a]
$\Delta_r U^\circ/(kJ\ mol^{-1})$	0.1096
$\Delta_r H^\circ/(kJ\ mol^{-1})$	−2.385
$\Delta_r S^\circ/(kJ\ mol^{-1}\ K^{-1})$	−0.05104
$\Delta_r G^\circ/(kJ\ mol^{-1})$	12.89
$K_P^\circ/(bar^{-1})$	0.005611
$K_c^\circ/(cm^3\ mol^{-1})$	139.1

[a] Data based on the calculations described in this work.

in which σ and Θ_{rot} are the rotational symmetry number (2 for the argon dimer) and Θ_{rot} the rotational temperature, $B_e hc/k$, respectively. The vibrational entropy is found from

$$S_{vib} = R\frac{\Theta_{vib}}{T}(e^{\Theta_{vib}/T} - 1)^{-1/2} - R\ln(1 - e^{\Theta_{vib}/T}) \tag{18}$$

The results obtained in this section are summarized in Table 3. Values of the monomer and dimer energies, entropies, and other quantities used in eqs 14–18 are listed in the supporting material.

Students can be given the option of obtaining the concentration-based equilibrium constant, K_c°, using an alternate (but fundamentally equivalent) approach that utilizes the Ar and Ar$_2$ partition coefficients. In this way they will use the relation

$$K_c^\circ = \frac{q_D}{q_M^2}e^{-\Delta_r U_0^\circ/(RT)} \tag{19}$$

where q_D and q_M are the argon dimer and atom partition functions and $\Delta_r U_0^\circ$ is the negative of the argon dimer well depth to the zero-point energy. Expressed in terms of the calculated quantities, $\Delta_r U_0^\circ = -D_{e-} 1/2hc\tilde{\nu}_e$. The dimer partition function is the product of those for the degrees of freedom, that is, $q_D = q_{D,trans}q_{D,rot}q_{D,vib}$. For the monomer, $q_M = q_{M,trans}$. The partition functions (again, in the canonical ensemble, and in the harmonic oscillator–rigid rotator approximation, HORR) are

$$q_{D,trans} = \left(\frac{2\pi m_D kT}{h^2}\right)^{3/2}V \tag{20}$$

$$q_{D,rot} \approx \frac{T}{\sigma\Theta_{rot}} \tag{21}$$

$$q_{D,vib} \approx (1 - e^{-\Theta_{vib}/T})^{-1} \tag{22}$$

where m_D is the molecular mass of the dimer (eq 20 can also express the partition coefficient for the monomer, by using m_M, the mass of the monomer). It is important to remind students that the translational partition function has units of volume, and in eq 20 V is customarily equal to the SI value of 1 m^3, but for this work it is more convenient to set $V = 10^{-6}$ m^3 (i.e., 1 cm^3).

If students successfully navigate the treacherous waters involved in performing these calculations (being ever mindful of units), they should obtain a value of K_c° that is nearly identical to that found using eqs 14–18, that is, 140 cm^3 mol^{-1} for $T = 300$ K. Seeing this agreement will reinforce the fundamental applicability of statistical mechanics to their project.

However, if students expect as good an agreement between their thermodynamic calculations and the experimental data and

as they found with the molecular constants, they are in for a surprise. This is because the value of K_c for the argon dimerization at 300 K, obtained from mass spectrometric studies, place this value at about 18.7 cm³ mol⁻¹ *(16)*. Detailed statistical mechanical calculations provide a value of 21.9 cm³ mol⁻¹ *(17)*. The reason that the statistical mechanical calculations described earlier overestimate K_c is that the HORR model approximation does not hold in this application. This should not, of course, come as a surprise to the students. Furthermore, they can be guided into reasoning why this model *overestimates* K_c. The problem lies with the calculation of the argon dimer entropy (or equivalently, the rovibrational partition function). It can be pointed out that entropy of a system is an indication of its capacity to dissipate energy among energy levels. The HORR model assumes that there are an infinite number of accessible rovibrational states that can be populated according to its degeneracy and energy level. This can be seen in the fundamental expression of the rovibrational partition function, q_{rv} (for a nondegenerate vibrational mode), viz.

$$q_{rv} = \sum_{J,n} g_J e^{-E_{j,n}/(kT)} \qquad (23)$$

where J and n are the rotational and vibrational quantum numbers, g_J is the rotational degeneracy $(2J + 1)$, and $E_{J,n}$ is the rovibrational energy relative to the zero-point energy. The number of accessible levels in the argon dimer is considerably less than those implicit in the HORR model. This discrepancy can be directly traced to the value of q_{rv}, which from eqs 21 and 22 is calculated to be 1.37×10^4, whereas the empirical value of q_{rv}, obtained from eq 19, and the experimental value of K_c, and $\Delta_r U_0$ from this work, is 1.74×10^2.

Curious students will wonder how one can cast aside the HORR model and obtain a more realistic value of q_{rv}. One approach would be to diagonalize the ab initio pair potential (obtain the anharmonic vibrational eigenvalues), then add to each energy level the appropriate number of rotational levels such that the total energy does not exceed the dimer dissociation energy and then carry out the sum over states indicated in eq 23. But even this approach, although an improvement, is not complete because the *effective* rovibrational potential contains, in addition to the "bound" states (those with energies less than D_e), "quasibound" states that have energies greater than D_e. This situation arises as a consequence of Newton's third law. For a rotating molecule, the centrifugal force is counterbalanced by the restoring force, which is accounted for by $V_0'(r)$, the derivative of the potential energy curve for the rotationless molecule ($J = 0$). The centrifugal force is equal to $L^2/\mu r^3$, where L is the angular momentum and μ is the reduced mass. Further treatment *(17)* gives the result

$$V(r) = V_0(r) + \frac{L^2}{2\mu r^2} \qquad (24)$$

where $V(r)$ is the potential energy of the rotating molecule ($J > 0$). The $L^2/\mu r^2$ term represents the classical rotational kinetic energy. Students will recognize that the quantum mechanical treatment of a rotator gives the rotational energy as $J(J + 1)/8\pi^2\mu r^2$. We can therefore express the effective pair potential for a rotating molecule as

$$V_J(r) = V_0(r) + J(J + 1)\frac{h}{8\pi^2 c\mu r^2} \qquad (25)$$
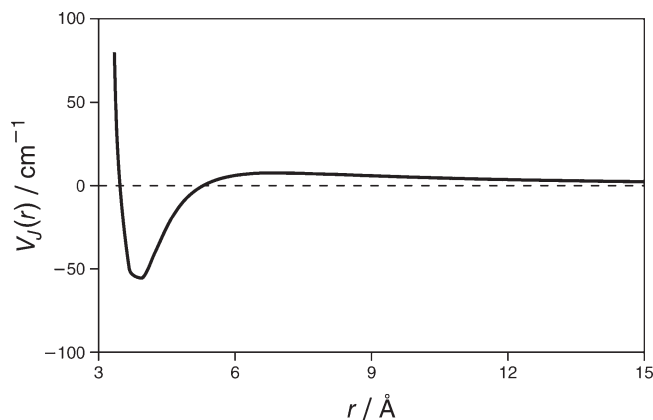

Figure 3. Plot of the effective potential $V_J(r)$ for the argon dimer for $J = 30$ obtained from eq 25 and based on the ab initio potential calculated in this work.

where $V_0(r)$ corresponds to the ab initio potential calculated in this work. An example of the impact of molecular rotation on the PES is shown in Figure 3, which presents $V_J(r)$ for $J = 30$. Note that although the well depth of this high rotational state is about 55 cm⁻¹, which compares with 95.2 cm⁻¹ for the $J = 0$ state, the potential curve shows a maximum value of about 13 cm⁻¹ (at ca. 6 Å) above the dissociation limit, and thus gives rise to a quasibound, or metastable state, that contributes to the entropy of the dimer.

A complete accounting of *all* rovibrational states, bound and quasibound, requires the diagonalization of all $V_J(r)$ potentials, that is, eq 25, for all values of J. This undertaking is beyond the scope envisioned for this project.

Summary

By working on and completing this project, students will gain first-hand experience in seeing how, from first principles and the application of quantum chemical techniques, they can obtain a wealth of information about a diatomic molecule (the argon dimer) that can be tested by experimentation. This information includes the molecular structure and constants, the second virial coefficient, the polarizability volume, and the standard thermodynamic functions of formation (and the equilibrium constant). The project affords students the opportunity to verify the interrelationship among quantum chemistry, statistical thermodynamics, and equilibrium thermodynamics.

Acknowledgment

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Supporting Information Available

The details of acquiring these scans, examples of input files, the method used to obtain the CBS energies, as well as a table of all energies obtained in the calculations. This material is available via the Internet at http://pubs.acs.org.