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Molecular Mechanics for Weakly Interacting Assemblies of Rare Gas Atoms and Small Molecules

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Abstract: Simple, easily evaluated potentials have been found that describe the intermolecular interaction potential energy surfaces of assemblies of certain atoms and small molecules. The potentials are constructed from parameters and properties associated entirely with the individual atoms or molecules, and thus are developed in a transferable form suitable for molecular mechanics investigations of small and medium-sized clusters. The properties are electrical properties, permanent moments, and polarizabilities that have been obtained from ab initio calculation. The parameters are empirical values used in atom-atom Lennard-Jones terms. The total potential is a sum of the electrical interaction energy and the Lennard-Jones terms, which represent the nonelectrical contributions to the potential. The parameters have been found for seven species, and calculational results on over 20 clusters are reported. The key features of this model are transferability from complex to complex, inclusion of cooperative effects, and the capability to directly predict properties (induced moments) of the clusters.

The structures and properties of weakly bound clusters have become a significant problem area in molecular spectroscopy and theoretical chemistry[1] not only because of unique structural features of clusters but also because this is the connection point between isolated molecule and condensed-phase understanding. Molecular mechanics technology for weak clusters could be quite helpful if the potentials were reasonably reliable. There are both special difficulties and useful simplifications in developing such a technology. Simplifying the task is the allowable neglect of intramolecular relaxation. That is, the changes in intramolecular structural parameters upon weak interaction are most often small, and hence ignorable, at least for many structural questions. Complicating the task is the requirement for reliability of interaction potentials to persist at far separation distances. Furthermore, parametrization of bond potentials according to type or functionality is not effective for weak bonds in the way it is for chemical bonds. While one may have a set of parameters for the stretching potential of $-C{\equiv}C-$ that is taken to be appropriate whatever the surrounding chemical structure, it would be more cumbersome to have numerous *sets* of parameters for $HC{\equiv}CH$ with $-OH$, and with NH_3, and so on. Also, pairwise potentials alone will not be capable of bringing in cooperative effects that are surely important in some clusters. On top of all this, the relative energetics of interest in weak clusters tend to be small, thus making it more difficult to achieve good accuracy.

From the foundation set in place by Buckingham,[2] we know that permanent moment energetics are significant at long range. The idea that classical electrical interaction of polarizable charge distributions plays a key, and perhaps dominant, role in weak intermolecular potentials[3,4] offers a means of overcoming the difficulties for setting up molecular mechanics potentials for weak assemblies. First, the electrical interaction between two atoms or molecules is obtained from moments and polarizabilities associated with each atom or molecule. Unlike molecular mechanics descriptions of chemically bonded species, an electrical potential arises from parameters intrinsic to the interacting species A and B, not to the A-B bond. This is beneficial given the diversity of weak bonding arrangements and partners. Next, electrical interaction has a cooperative component as long as polarization is included. For instance, the polarization energy of molecule A in the presence of molecules B and C depends quadratically on the sum of the fields due to B and C. The cross term in that quadratic dependence is a three-body interaction energy term. It is not certain that polarization alone accounts for cooperative effects in weakly interacting assemblies, but there is reason to believe that it at least provides a sizable, perhaps major, share. Electrical polarization seems to be the primary electronic structure change upon weak bond formation,[4,5] and recent, critical calculations on the torsional vibrations of $(HF)_3$ have demonstrated improvement in accuracy of an electrical potential upon incorporation of polarization effects.[6]

Efficient computational algorithms, based on Applequist's polytensor organization of electrical properties,[7] have been worked out and implemented for the evaluation of the classical electrical interaction energy of a collection of molecules and atoms.[8] The procedure is open-ended with respect to the order of multipoles or to distribution of multipolar centers throughout a molecule and can completely solve the polarization and hyperpolarization equations (to any order of hyperpolarizability). To establish a full molecular mechanics capability, the remaining contributions to the potential must be developed. The most important way that these show up is in the hard walls that keep weakly attractive species at distances usually characterized by van der Waals radii. An ideal multipole representation of the charge fields of two molecules will often give rise to an interaction potential that is smoothly downhill along the separation or radial coordinate. This tends to be a correct representation of the true potential at long range, but at some close-in distance, it must be augmented so as to properly turn sharply upward.

Effects of charge penetration, exchange repulsion, dispersion, and charge transfer, if present, are the effects that are collectively represented by empirical augmenting potentials in our model for molecular mechanics potentials of weak assemblies. We choose these potentials to be based on parameters associated with individual atoms or molecules, not with the particular weak bonds, just as for the electrical interaction. The potential is a sum of the electrical interaction energy among all interacting species and the pair interactions of the augmenting potentials.

We may draw on a wealth of ideas in selecting the form of the augmenting potentials. Because of the behavior of overlap densities in a perturbative analysis of exchange repulsion, an energetic contribution that decreases exponentially with increasing distance may be an appropriate form for the wall.[9] But, it has proven

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Table I. Calculated State Energies and Average Bond Lengths with Ar–Ar Potentials[a]

	6–12 potential	exptl potential[14]
E_0 (cm^{-1})	16.73	18.17
E_1 (cm^{-1})	42.33	46.11
E_2 (cm^{-1})	61.63	66.81
$\langle R\rangle_{00} - R_e$ (Å)	0.143	0.134
$\langle R\rangle_{11} - R_e$ (Å)	0.378	0.360
$\langle R\rangle_{22} - R_e$ (Å)	0.644	0.635

[a] One way the experimentally deduced potential curve[14] was reported was as a set of energies and distances. A functional representation of these points was obtained for the numerical analysis done here so as to keep it comparable with the treatment done on the 6–12 potential. The transition frequencies so calculated here agree with measured frequencies to 2 cm^{-1}. The average bond lengths $\langle R\rangle$ for specific vibrational states were obtained numerically from the expectation value of R^{-2}.

easier to find parameters for a more slowly changing potential, and so an inverse power of the separation distance, R, is used in place of an exponential. There is likely some sacrifice in the accuracy of the potential from doing this, but it will be mainly in the highly repulsive regions, and these are not of interest for this model. As in the standard Lennard-Jones potential, an R^{-12} repulsive term is employed. Truncation of the dispersion potential at lowest order (see ref 10 and 11) gives a potential that is attractive and with a functional dependence of R^{-6}, the other part of a Lennard-Jones potential. More elaborate models of the dispersion contribution have been developed,[11,12] and it is possible that such models might be employed to further refine the procedure being used here. For now, though, it is a standard Lennard-Jones, or "6–12", potential that is used, and we choose to make it atom-centered. That is, there is a potential term for every atom in molecule A with every atom in molecule B. Finally, employing the idea behind "combining rules" that have been designed for rare gas atom potentials[13] and other potentials, the parameters for the Lennard-Jones terms are put in a product form. Thus, for a single pair of species A and B, the augmenting potential is

$$V_{\text{A-B}} = \sum_{i}^{|A|}\sum_{j}^{|B|}\left(\frac{d_i d_j}{R_{ij}^{12}} - \frac{c_i c_j}{R_{ij}^{6}}\right)$$

The sums are over centers, usually constituent atoms, in the molecules A and B. R_{ij} is the distance between these centers. The parameters needed in these potentials are the c's and d's.

The c's and d's are found empirically to reproduce structural and sometimes stability values of binary clusters, provided there is either good quality ab initio potential surface information or else spectroscopic data that have yielded structural or energetic information. The test of the approach is in its predictions on systems other than those used to find the c and d parameters. This report gives the test systems that were used to find the parameters for a small set of atoms and molecules, and gives predictions based on those parameters. Since the augmenting potentials may very well correct for errors, truncation, and deficiencies in the electrical interaction energies, the c and d parameters are associated with a specific level of electrical interaction and, to a lesser degree, with specific property values.

Rare Gas Atoms

There is no classical, electrical interaction between two rare gas atoms, and so if they are to be described within the model, the augmenting Lennard-Jones potential must give the complete atom–atom interaction. In a way, this is a useful limiting case from which to select the first c's and d's, because these values will be fully determined by known values of the well-depths, D_e, and equilibrium separations, R_e, for the homonuclear rare gas dimers. Three tests must be made, though the first is just another demonstration that a 6–12 function is realistic in form. The parameters can be set so as to precisely reproduce D_e and R_e, and ideally, the resulting function should be faithful in shape to the true potential curve. Evidence that it is faithful comes from the evaluation of vibrational state parameters, particularly transition energies and vibrational averaging of the bond lengths. Table I gives a comparison based on numerical determination of vibrational wave functions between the Ar_2 6–12 potential and the experimentally deduced potential.[14] The agreement is quite satisfactory, though it is known that 6–10 and 6–8 potentials will be about as suitable. It is a direction for further refinement of the scheme being presented to include other inverse power terms in the augmenting potential.

Table II. Parameters for Rare Gas Atoms

atom	c (au)	d (au)
He	1.4612	180.833
Ne	3.3395	479.338
Ar	10.641	2698.22

Table III. Well-Depths and Bond Lengths of Rare Gas Dimers

	R_e (Å)		D_e (cm^{-1})	
dimer	6–12 potential	expt[a]	6–12 potential	expt[a]
He_2	2.96	2.96 [15, 16]	7.65	7.65 [15, 16]
Ne_2	3.112	3.11 [15, 17]	29.7	29.7 [15, 17]
Ar_2	3.761	3.76 [14, 15]	96.6	98.7 [14, 15]
HeNe	3.036	3.21 [15, 16]	15.1	9.9 [15, 16]
HeAr	3.338	3.51 [15, 16]	27.2	16.8 [15, 16]
NeAr	3.421	3.43 [15, 17]	53.6	50.0 [15, 17]

[a] References in brackets.

The second test to be performed concerns the appropriateness of the c's and d's entering the 6–12 potential in product form, though this is by no means an unusual approach. With the rare gas atoms, this can be tested by the predictions of R_e and D_e of heteronuclear dimers. Experimental values of the well-depths and equilibrium separations for homonuclear pairs were used to select the c's and d's for He, Ne, and Ar, and these are listed in Table II. With these parameter values, potentials were generated for HeNe, HeAr, and NeAr. As shown in Table III, the calculated R_e and D_e values of the heteronuclear species do compare well with measured values.

The third test that must be made with these wall potentials is whether they are usable when a rare gas atom interacts with a polar molecule, for it is then that electrical interaction will enter the picture. This kind of test is performed in the course of parameter selection for the small molecules and in application to specific problems. The set of electrical properties used for the rare gas atoms consists of the dipole and quadrupole polarizability. For He, the quadrupole polarizability is essentially unimportant in every case examined.

Hydrogen Molecule

Parameters for the hydrogen molecule were determined in a special manner that could not be used for the determination of parameters for the other molecules. The reference complex used for the parametrization was $(H_2)_2$, and the simplicity of this four-electron dimer meant that very high level ab initio calculations could be employed in generating potential surface points. That is what was done. Results of well-correlated, large basis set ab initio calculations[18] were used for 24 potential energy surface points

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Table IV. Comparison of an ab Initio and a Model Surface of $(H_2)_2$

	ab initio energy relative to separated limit; error of model (cm^{-1})							
$R_{\text{c.o.m.}}$ (Å)	rectangular		T-shaped		colinear		twisted	
2.9	73.4	8.3	35.9	0.6	122.4	−1.5	61.4	6.8
3.0	44.9	−2.2	7.9	−4.7	74.0	−1.0	35.6	−4.3
3.2	13.1	−7.1	−19.2	−4.4	20.8	5.1	6.7	−9.0
3.4	−0.2	−5.8	−26.5	−1.6	−0.4	8.5	−4.7	−7.4
3.6	−4.9	−3.9	−25.8	0.3	−7.4	8.9	−8.2	−5.2
4.0	−5.5	−1.9	−18.6	1.4	−7.8	6.7	−7.4	−2.7

Table V. Parameters for Small Molecules

molecule	center	*c* (au)	*d* (au)	electrical properties used with
H_2	c.o.m.	3.25	722.0	Q, α, C
	H	0.155	9.8	
HF	F	6.1	1400.0	$\mu, Q, \alpha, A, C, \beta^a$
	H	0.0	0.0	
HCN	c.o.m.	0.0	1000.0	$\mu, Q, R, \alpha, A, C, \beta$
	H	0.0	7.6	
	C	6.0	2500.0	
	N	4.0	1775.0	
CO_2	C	0.0	400.0	Q, α, C
	O	5.25	850.0	

[a] The electrical properties of HF were for the ground vibrational state, whereas other molecular properties were for fixed, equilibrium structures. μ, Q, and R are first, second, and third permanent moments. α and β are the dipole polarizability and hyperpolarizability. C is the quadrupole polarizability and A is the dipole-quadrupole polarizability.

that corresponded to a rectangular, a T-shaped, a linear, and a twisted arrangement of the two hydrogen molecules. The *c* and *d* parameters were selected by iterative adjustment so as to minimize the difference between the electrical model energies and the ab initio energies. Both the root-mean-square error and the largest difference for an individual point were reduced by successive adjustment of the *c* and *d* parameters. In effect, this amounts to fitting to the Lennard-Jones terms the difference between the ab initio energies and the purely electrical energies. The pure electrical energies were obtained with the second permanent moment, and with the dipole and the quadrupole polarizabilities of equilibrium H_2 as determined from ab initio calculations.[19]

It was found that H_2 required an isotropic component of the 6-12 potential, and so the molecule's inversion (mass) center was used as a third site for the augmenting potential. Table IV shows how well the ab initio surface points are represented with the model. The maximum error for any point is less than 9 cm^{-1}, and the mean error is 5.3 cm^{-1}. Table V gives the optimum parameters obtained for H_2. Surface points with relative energies more than 150 cm^{-1} above the separated limit were not included in the parameter selection process, and so it is expected that errors in the model could be larger for sharply repulsive regions. These regions, though, are not the most important in developing a molecular mechanics capability.

With parameters for hydrogen and rare gases, the first tests of the model can be made for atom–molecule complexes. Well-depths and bond lengths for hydrogen–rare gas complexes have been extracted from spectroscopic measurements by Dunker and Gordon[20] and recently by Le Roy and Hutson.[21] Results can be compared with predictions of the model for NeH_2 and for ArH_2. As shown in Table VI, the agreement is quite good, especially for NeH_2. This is significant since no information about these atom–molecule potentials was used in setting up the model. The model potential arises from parameters intrinsic to the rare gas atoms and to hydrogen, and these were determined without consideration of the rare gas–hydrogen interactions.

There is an underestimation in the attractiveness of H_2 for Ar relative to Ne. This probably goes along with the fact that higher multipole polarizabilities and hyperpolarizabilities are more sizable for argon than for neon, and yet the truncation of the polarization expansion in the model was the same for both. It is likely that more extensive expansions are required as one moves down the periodic table, but this is a refinement in the model that should best wait for the applications needs that arise.

Diatomics and Small Molecules

For molecules with more electrons than hydrogen, the information that is available to guide selection of the empirical parameters in the model is not as complete or not as reliable. The problems of basis set superposition error, basis set completeness, and correlation effects can become more difficult in ab initio calculations of potential surfaces. If one turns to experimental information, it is best for the structural effects of zero-point motion to have been removed from the measured values, and that is usually done approximately. Generally, the available information tends to be that which partly characterizes, or is a manifestation of, the potential surfaces of binary complexes in the vicinities of equilibrium structures, rather than full surfaces. Fortunately, for a molecular mechanics capability, the equilibrium regions are of greatest interest and concern. The primary goal for the model has to be effectiveness in determining equilibrium structures and stabilities. How well it works beyond this will indicate how well the physical assumption (that the interaction is best partitioned into electrical and nonelectrical parts) holds overall.

For HF, the electrical properties that have been selected for use in the electrical part of the model potential are the dipole and quadrupole moments, the dipole polarizability, the dipole–quadrupole polarizability, the quadrupole polarizability, and the dipole hyperpolarizability. For the molecules with two heavy (nonhydrogen) atoms, the octupole moment is added to this list of properties. Tests have been performed with various truncations of the multipole and polarization expansions for certain systems. The specific truncation that has been employed has two advantages. It is accurate at long range and it is well behaved close-in. Typically, the electrical contribution to the stability of a cluster at equilibrium usually is similar to or is a major fraction of the net stability calculated with the model.

The hard-wall parameters for a molecule were selected so that the model potential would reproduce as well as possible the equilibrium structure and equilibrium stability of a particular binary complex where that diatomic is a constituent. In some cases, estimates were made to extract equilibrium values from on-average experimental values of structural parameters and from zero-point stabilities. Because of the use of largely equilibrium information, the model potentials may show increasing error upon moving away from equilibrium regions. In particular, it is not expected that the potentials will be quantitative in highly repulsive regions, those where the energy is more than 3000 cm^{-1} above the equilibrium. Accuracy in these regions might require more general functional forms for the wall potential, and then more information in order to find the parameters for those functions. This is an embellishment of the basic scheme which we may pursue later.

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Table VI. Model Calculations of Structures and Stabilities of Complexes of Atoms and Diatomics, and Comparisons

	result of the model/comparison value[a]			
complex	well-depth (cm^{-1})	$R_{c.o.m.}$ (Å)	other structural data	ref
NeH_2	22.5	3.308	linear	model
	25.3	3.306	linear	[20]
ArH_2	40.6	3.634	linear	model
	51.1	3.582	linear	[21]
$(HF)_2$	1537	2.745	θ 103.8°, −15.2°	model
	1593	2.745	θ 120.1°, −6.4°	*[22]
			112.9°, −8.6°	*[23]
		2.744	θ 118 ± 6°, −9 ± 6° [b]	[24]
		2.740	θ 121 ± 2°, −6 ± 3° [b]	[25]
$(HF)_2$ t.s.[c]	302 (ΔE)	2.792	θ 62.9°	model
	302		θ 62.4°	[28]
	379	2.675	θ 54.4°	[22]
Ar–HF	192	3.252	linear	model
	191[d]			*[29]
	214[d]			[31]
H_2–HF	256	2.932	T-shaped; HF into H_2	model
	238–306[e]	2.974	T-shaped; HF into H_2	[32]
$(HF)_3$	4983	2.687	cyclic C_{3h}, θ 30.1°	model
	4900	2.648	cyclic C_{3h}, θ 26.3°	[33]

[a] For each value, the model calculation is on the line above the comparison value. The comparison values are experimental, are from potential surfaces based on experimental measurement, or are ab initio results, and are from the references given in brackets. An asterisk designates that the comparison value was used for the determination of the 6–12 potential parameters for at least one of the species in the complex. [b] The experimentally determined R value reported in ref 24 is 2.7660. This represents the vibrationally averaged structure. A theoretical result[22] that gave the difference between the vibrationally averaged and equilibrium bond lengths as 0.022 Å was used to arrive at the comparison value of 2.744. From the experimental result in ref 25, it was concluded that because of slightly different orientation angles, the R value should be 0.004 Å shorter than the value in ref 24, and so this amount was subtracted from 2.744. The experimentally determined bond angles measured relative to the F-F axis were given in ref 24 as 63° and 10°; these have been converted to angles relative to the line connecting the HF mass centers and have been stated here so that 0° means an H-to-F orientation. The angles were reported to be 60° and 7° in ref 25, and the same adjustment was made in listing them in this table. It should be noted that an analytic representation of the HF-dimer potential surface, developed with the ab initio calculations of Michael et al.,[22] has been reported by Hancock et al.,[26] and that another high-level ab initio surface has been developed from a much larger set of grid points.[27] [c] The HF-dimer interconversion transition state (t.s.) is a symmetric structure with an inversion center, and only one angle specifies the monomer orientations. The energy listed (ΔE) is the barrier height, or the energy difference between the transition-state structure and the equilibrium. [d] The well-depth from ref 29 was obtained from functional fitting of experimental data and, as discussed therein, is similar to other determinations. A value of 125 cm^{-1} was reported as an equilibrium value with respect to radial (weak stretch) vibration. From this reported value, 4.827 cm^{-1} as subtracted to correct for the measured change[29] in the HF stretching frequency, and 70.245 cm^{-1} [29] was added for the doubly degenerate weak bend. This yielded 191 cm^{-1} for D_e which would correspond to what was calculated with the model. The second comparison value for the stability, 214 cm^{-1}, is from a model surface[31] based on spectroscopic data. The separation distance for ArHF was not used in the parameter determination because vibrational averaging effects are known to be quite large,[29] and errors could be introduced by attempting to guess the equilibrium value from vibrationally averaged values.[29,30] [e] The ab initio value of the well-depth given in ref 32 is 306 cm^{-1}. However, counterpoise corrections, of the "polarization counterpoise correction" type,[34] gave 68 cm^{-1} as the basis set superposition effect on the well-depth. This has been subtracted from the value of 306 to give the lower comparison value in this table, though it may be that 68 cm^{-1} is an overestimation of basis set superposition effect. Also, the calculated bond length was given twice in ref 32, and incorrectly stated one of those times as 2.794 instead of the correct value of 2.974.

After 6–12 parameters were selected for a molecule on the basis of one binary complex, the parameters were sometimes refined upon checking predictions for a second complex, and perhaps a third. For instance, parameters for hydrogen fluoride were first obtained so that the model potential gave reasonable values for the equilibrium structure and stability of $(HF)_2$. These parameters were then adjusted slightly so as to improve the model's description of the well-depth of Ar–HF (see Table VI), though the changes were limited to those that did not significantly affect the description of $(HF)_2$. Often, the readjustments made from using a second or third complex were small, and this adds support to the idea that the hard-wall potentials may be constructed using parameters intrinsic to the constituent molecules yet independent of *which* molecules are interacting.

Table V lists the 6–12 parameters that have been selected for the several small molecules that have been studied so far. This is a short list relative to the molecules that have been used in spectroscopic study of weak complexes. However, it is representative enough to show the power of the model because so many different types of complexes arise from this collection. There are T-shaped, linear, bent, and cyclic complexes among those arising from this set of constituents, and the bond strengths range from the very weak (under 100 cm^{-1}) to the strong (over 2000 cm^{-1}) on the stability spectrum of "weak" complexes.

Tables VI and VII show the well-depth and structural predictions of the model for various complexes. As indicated, certain of the complexes were used for the parameter selection, while other complexes are tests of the model. The comparison information includes both ab initio and experimental data, and where multiple sets of results are available, some judgment has been required to select the comparison values. For example, ab initio calculations[22] on the hydrogen fluoride dimer have given equilibrium angles which are within experimental error ranges of the vibrationally averaged values for the angles.[24–43] Other ab initio calculations[23] have given equilibrium angles that were smaller in magnitude by about 7°. These smaller angles were preferred in finding the hard-wall parameters because they resulted from use of a basis set that was more flexible in describing electrical polarization, and overall larger.[23] The model was capable of reproducing these angles to within 10° and of still yielding a good separation distance and stability.

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Table VII. Model Calculations of Structures and Stabilities of Polyatomic Complexes, and Comparisons

complex	result of the model/comparison value[a]			ref
	well-depth (cm^{-1})	$R_{c.o.m.}$ (Å)	other structural values (Å or deg)	
ArHCN	85	4.416	linear	model
		4.343	θ 30.8° (vib, av)	35, 36
HCN-H_2	117	4.042	nearly T-shaped (H_2 into CN) θ 84.6°, 9.6°	model
HCN-HF	2215	3.370	linear	model
	2182	3.345[b]	linear (vib av)	*37
$(HCN)_2$	1452	4.421	linear	model
	1540	4.444	near linear (vib av)	*38
		4.448	θ 13.6°, −9.3° (vib av)	39
HCN-HCN-HF	3973	3.354; 4.394	linear	model
		3.304; 4.379	nearly linear (vib av)	39
OCO-Ar	118	3.478	T-shaped	model
		3.493	T-shaped (θ 82.5°) (vib av)	*40
OCO-HF	820	3.980	virtually linear[c]	model
		3.954	nearly linear (vib av)	41
OCO-HCN (I)[d]	530	5.002	linear	model
	590	5.035	θ 7.7°, −12.4° (vib av)	*42
OCO-HCN (II)[d]	649	3.583	T-shaped	model
		3.592	θ 79°, 17° (T) (vib av)	*43

[a] For each value, the model calculation is on the line above the comparison value. The comparison values are both experimental and ab initio results from the references given in brackets. An asterisk designates that the comparison value was used for the determination of the 6–12 potential parameters for at least one of the species in the complex. [b] The distance was reported in ref 37 as the N-to-F distance, which was 2.796 Å. [c] The potential surface for OCO–HF shows that the coupled bending of the two monomers, with relaxation to smaller separation distance, is a pathway through the surface where the energy changes are slight (a few cm^{-1}) for angle changes of 20–30° off-linear. In fact, the global minima are found off-linear, but their energies are so very slightly less than the energy for the best linear structure. In this sense, the best characterization of the species is linear (or virtually linear) with a quite flat bending potential. [d] Two conformers of OCO–HCN have been observed.[42,43] One is linear and the other is essentially T-shaped with the nitrogen pointing into the carbon.

The calculations on the interconversion transition state of $(HF)_2$, a cyclic arrangement of the two molecules, yield a good value for the barrier height and a value for the orientation angle not too different from theoretical values that have been reported.[22,28] The model predicts the separation distance will be greater than at the equilibrium structure, whereas ab initio calculations[22] show the opposite. It is likely that the ab initio calculations suffer from some amount of basis set superposition effect that could artificially pull the molecules closer together in the transition state—more so than at equilibrium, but it is not clear how large of an effect that is. At the same time, it could be that there is more pronounced error in the model for transition state or side-on structures. Most likely this error would be in the parameters or the form of the augmenting wall potential, and as surer information about the transition state becomes available, it will be used to refine the wall potential.

A particularly challenging case is the OCO–HCN complex, because for this special pair of molecules, two different conformers have been observed spectroscopically.[42,43] One is linear, and the other is T-shaped with the nitrogen end of HCN pointing into the center of the carbon dioxide molecule. The experimental information on these two species was used in the parameter selection for carbon dioxide; the parameters for HCN had already been chosen on the basis of $(HCN)_2$ and HCN–HF. There is a difference of more than 1 Å in the separation distance of the two conformers, and this difference was successfully reproduced by the model with adjustment of just the very few parameters used in the hard-wall potential.

As already mentioned, a difficulty in using spectroscopic data for fixing hard-wall parameters in the model is the uncertain effect of vibrational averaging. It may often amount to 0.01–0.03 Å in a separation distance. Because this is the size of the desired reliability of the model, it could improve the selection of the model parameters if corrections could be made for vibrational averaging effects. In some cases (see Table VII), this has been done with the help of ab initio calculations. Unfortunately, corrections or estimates of corrections cannot be done systematically, because the vibrational averaging effects are varied and complicated. For instance, the pure weak bond stretching motion in $(HCN)_2$ will give rise to a vibrational average of the bond length that is greater than the equilibrium length. However, bending vibrations will average-in shorter lengths as shown by the contours in Figure 1. These two effects may differ from system to system and compete. In many systems, it may be fair to assume that the average separation distance is greater than the equilibrium, but this does not have to be case, and may not be where there are substantial bending effects. ArHF and Ar HCN are two cases where there is definitely large amplitude bending motion. This makes the experimental on-average separations much different from the equilibrium values, and consequently, the separation distances for these systems were not used in the selection of parameters.

Discussion

The calculations show the extent to which a molecular mechanics capability now exists for weakly interacting collections of small molecules and rare gas atoms. It appears that the lengths of weak bonds can be determined to within several hundredths of an ångstrom in most cases, that orientation angles can be determined to within 10°, and that good stabilization energies are obtained. It may be that the model can achieve a higher degree of accuracy, but testing is limited by how well equilibrium structures and energies are known for most complexes. And, as mentioned, there are a number of clear-cut possibilities for refining the scheme should that prove worth doing.

The following specific elements are what constitute this scheme and they are also the requirements for implementing it. (i) *Molecular electrical properties.* These are available as published ab initio calculational results (for instance, ref 19) or need to be obtained from measurement or high level calculations. In our implementation, these properties are collected in a database and retrieved as needed. (ii) *Wall potential parameters.* The ones that have been found in the course of this study are given in Tables II and IV. Parameters for other molecules will be developed in the course of future applications. (iii) *Electrical interaction energies.* An efficient, coded scheme for evaluation of electrical interaction energy is the central part of the technology. A detailed presentation of the special techniques and computational approaches have already been presented.[8] Augmenting electrical energies with a contribution from the wall potentials is a minor task. In our implementation, the evaluation is carried out by expressing all atomic positions in a laboratory coordinate system. (iv) *Automated potential surface generation and minima searching.* (Distribution of the coded implementation, which we name MMC, "molecular mechanics for clusters", is anticipated.)

This technology should meet an important need to predict the structures of larger complexes and their energetics. For instance,

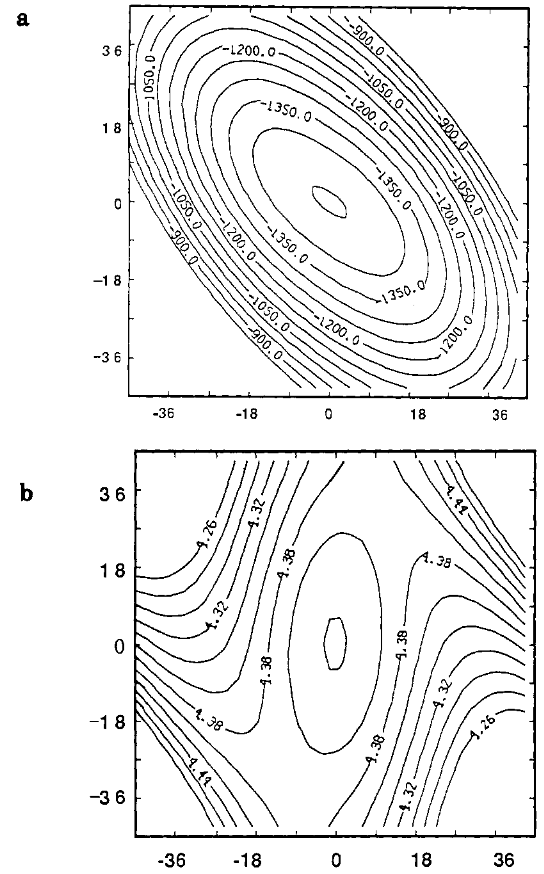

Figure 1. (a) Potential energy contours from the model for the HCN dimer as a function of the orientation angles. The horizontal axis gives the bend angle in degrees for one HCN molecule about its mass center, and the vertical axis gives the angle for the other HCN. The energy contours are in 50-cm^{-1} steps. The middle of the figure corresponds to the linear, equilibrium arrangement. The contours show that coupling of the two orientational angles in parallel is not energetically preferable to a bending motion where the head of one molecule (-N) follows the tail (H-) of the other. These energy contours correspond to the separation distance, R, being energetically optimum for every choice of orientation angles. This was accomplished by selecting a grid in the two angular coordinates, and at each grid point, the separation distance was adjusted to minimize the energy. Contours for R fixed at the equilibrium distance are similar but show a surface that is slightly steeper. (b) Contours showing the optimized separation distance in the HCN dimer as a function of the two orientation angles. The contour steps are 0.02 Å, and the central contour is at 4.42 Å. If one follows the minimum energy path for bending in (a), the optimum separation distance is seen to decrease slightly according to the model potential.

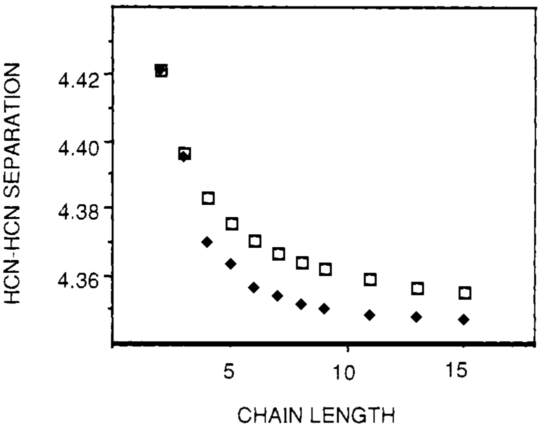

Figure 2. Intermolecular separation distance ($R_{c.o.m.}$) in ångstroms for linear chains of n (horizontal axis) HCN molecules arranged end-to-end as calculated with the model. The squares show the values for the average for all weak bonds in a given chain. The filled diamonds show the lengths of the shortest bond in each system. Naturally, the shortest bond is the most central one, and convergence in these values should be to the infinite-chain limit for $R_{c.o.m.}$. The experimental result for the vibrationally averaged separation distance for the dimer[39] is 4.448 Å, and half of the vibrationally averaged separation distance from the first to the third molecule in the trimer[48] is 4.394. The crystallographic value for the solid is 4.34 Å.[46] The asymptotic value of the central bond length from the model is under 4.35 Å.

Table VIII. Predictions of Induced Dipole Moments for Small Complexes

	dipole moment[a] (in debyes)				
	model		experimental		
complex	total	induced	total	induced	ref
Ar-OCO	0.090	0.090	0.068	0.068	40
OCO-HF	2.239	0.395	2.247	0.60	41
OCO-NCH (II)	3.455	0.417	3.207	0.36	42
HCN-HF	5.603	0.721	5.612	0.80	37
HCN-H_2	3.151	0.113			
HCN-HCN	6.700	0.623			
HCN-HCN-HF	9.385	1.435			
$(HCN)_3$ linear	10.504	1.389			

[a] The total induced moment is the magnitude of the total dipole moment of the complex less the magnitude of the dipole moment that arises from the vector sums of the permanent dipoles of the constituent species. For each complex, the calculations with the model were done at the equilibrium structure predicted by the model, and ab initio values were used for the permanent dipoles. The experimental values for induced moments were taken from the cited reports.

the model yields structures for Ar_3HF and Ar_4HF that have HF pointing into a trigonal argon face, as already established by the microwave studies of Gutowsky and co-workers,[44,45] and it predicts that the preferential binding site for HF with Ar_5 and Ar_6 clusters is also on the face, rather than an edge or vertex. It seems capable of locating different conformations, as in the OCO-HCN complex, and this is particularly useful in the spectroscopic hunt for conformers of weak complexes. It is likely that, as the number of constituent molecules in a cluster increases, the number of distinct conformations will increase. Making the model especially useful for these problems is that cooperativity effects are included via the electrical component of the total interaction. For instance, as shown in Figure 2, the model reveals a smooth decrease in the average equilibrium intermolecular separation distance as a chain of HCN molecules is extended. The separation distance in the solid phase of HCN[44] is asymptotically approached by the series of calculated values. In a study of infinite chains of HCN by Karpfen,[47] pairwise intermolecular potentials gave only a small share of the contraction in bonds from the dimer to the infinite chain, meaning that cooperative effects must be largely responsible. It cannot be established that electrical polarization is the sole source of cooperative effects in weak interactions, but this example and a recent critical study of the torsional potential of $(HF)_3$[6] suggest that it may be the major source. This is consistent with our argument that the primary electronic structure change of a monomer upon weak interaction is that change associated with simple electrical (multipole) polarization.[3-5]

The goal in developing this particular molecular mechanics capability has been to find a unifying description of interactions in binary complexes with those of large complexes and possibly condensed phases. The basis for the description is electrical interaction, with the nonelectrical contributions being represented in a very simple, pairwise form. Beginning with the established idea that interaction of permanent charge fields is crucial in weak

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interaction potentials,[2] it seems that simple electrical polarization, which may be determined while neglecting intermolecular quantum effects, is the primary electronic structure change of a constituent participating in a weak assembly of atoms and molecules.[4,5] This requires that in addition to energetics, the analysis of the MMC scheme should properly yield induced moments. Is this the case? In molecular beam electric resonance studies of many complexes, Klemperer and co-workers have reported unsatisfactory results from using electrical analysis to compute induced dipoles that they had measured (for instance, ref 41). However, we find the situation to be quite different, with the electrical analysis working nicely in predicting induced moments. Results given in Table VIII for a few systems confirm that induced dipoles arise from simple polarization. The differences between calculated, equilibrium, total dipole moments, and the vibrationally averaged values measured experimentally are small. The Klemperer group reached an opposite conclusion, probably by relying on dipole polarizabilities alone to give the polarization. Finally, reliability in computing a dipole moment, and presumably a dipole moment surface, means that this approach provides the information to obtain vibrational transition moments.[6]

That a molecular mechanics capability for weakly interacting systems should be based on electrical interaction is clear from a number of recent studies.[2,23,49-55] Buckingham and Fowler[49] have used permanent moment interactions with atom-atom infinitely hard walls to locate minima on potential surfaces of binary complexes. Stone has shown that distribution of moment centers is an effective means of representing the charge fields of large molecules.[52,53] Spackman has developed a sophisticated, yet simple-to-use scheme for generating weak interaction potentials and has examined a number of binary complexes.[54,55] A partitioning based on charge densities is used to obtain repulsive and electrostatic contributions that relate to the constituent atoms of the interacting species. Polarization or any perturbation of the constituent species is neglected in Spackman's model. The inclusion of polarization in the present model, though, is the feature that fits so many more of the puzzle pieces together. Often, it is a small energetic effect, but it brings in cooperative elements, accounts for induced moments, and makes refinements in energetics that are important for barrier heights, shapes of potential wells, and sometimes relative stabilities of different conformations.[3-6]

The evaluation of the model's interaction potentials is computationally fast relative to electronic structure calculations. And, of course, the computational expense is roughly independent of the size and form of the constituents, and it grows only quadratically with the number of constituents in a cluster. Thus, it is feasible to study a cluster with tens of constituents on a Macintosh II, for example. The evaluation of the interaction, though, is more cumbersome and slower than conventional molecular mechanics because it involves solving the electrical interaction equations with moderate-sized expansions. The cost of evaluating the Lennard-Jones terms is negligible relative to the electrical part. While it is not yet a technology that ought to be merged with conventional molecular mechanics, it seems likely that simplified representations which match the speeds of conventional molecular mechanics can be worked out without too much sacrifice in accuracy. Thus, in addition to the stand-alone usefulness of this approach, its development could lead to better weak interaction potentials for existing programs.

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Registry No. H_2, 1333-74-0; HF, 7664-39-3; HCN, 74-90-8; CO_2, 124-38-9; He, 7440-59-7; Ne, 7440-01-9; Ar, 7440-37-1.

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Evidence for the Existence of the Metastable Manganate(V) Ester Intermediate in the Permanganate Oxidation of *endo*-Dicyclopentadiene

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Abstract: It has been demonstrated that the manganese species observed during the permanganate oxidation of *endo*-dicyclopentadiene in dichloromethane by use of quaternary ammonium salts is a manganate(V) ester intermediate. Although the apparent oxidation state of manganese in the intermediate calculated from the results of iodometric titration was +4, the true oxidation state was found to be +5 because the analyses of the organic products obtained after the titration disclosed that a rapid oxidative decomposition path, which cannot be quenched by iodide, exists during the iodometry. Kinetic studies disclosed a first-order dependence of the decay of the intermediate on the concentration of the alkene. The results of the titration (apparent oxidation state and product ratio) changed with time in accordance with the decay of the intermediate. These results can be explained by a mechanism in which the detectable intermediate is a cyclic manganate(V) diester ion, which is reduced gradually to Mn(IV) via abstraction of a hydrogen atom from the alkene.

In the last decade, there has been considerable discussion concerning the nature of the "detectable intermediates" observed during the permanganate oxidation of carbon-carbon double bonds in aqueous[2-6] and nonaqueous solution.[1,7-10] Although it was