

A Model Equation for the Analysis of Noncovalent Intermolecular Interactions

John E. Douglas and Peter A. Kollman*

Contribution from the Department of Pharmaceutical Chemistry, School of Pharmacy, University of California, San Francisco, California 94143. Received August 11, 1978

Abstract: We present the development of an empirical equation for the analysis of noncovalent intermolecular interactions. Our equation is based on perturbation theory expansions for the intermolecular interaction as well as explicit quantum-mechanical calculations. The equation includes the electrostatic potentials, polarizabilities, ionization potentials, and electron affinities of the molecules which make up the complex, as well as some completely empirical parameters. Using this equation, we are able to calculate the intermolecular interaction energies for a wide variety of complexes, including proton affinities, hydrogen bonds, Li^+ affinities, and "charge-transfer" complexes. The results of the model calculations are in reasonable agreement with quantum mechanically calculated interaction energies.

I. Introduction

The theoretical predictions of the strength of noncovalent intermolecular interactions have been of much interest in the last 25 years. The first quantum-mechanical calculations on the energy components of the hydrogen bond between water molecules were carried out in 1954.^{1,2} In the late 1960s Murrell and van Duijneveldt^{3,4} used perturbation theory to estimate the magnitude of the energy components in a perturbation theory expansion. In the early 1970s Morokuma,⁵ Dreyfus and Pullman,⁶ and Kollman and Allen,⁷ all suggested ways in which the intermolecular interaction energy involving molecules could be broken down into energy components, with the Morokuma decomposition the most complete. Subsequently, there have been many specific applications of these component-analysis calculations to intermolecular interactions, including proton affinities,⁸ Li^+ affinities,^{9,10} hydrogen bonds,^{11,12} dative bonds,¹³ and "charge-transfer" complexes.¹⁴

For the purpose of this paper, we focus on those components from the Morokuma analysis:⁵ (1) electrostatic, (2) polarization, (3) charge transfer, and (4) exchange repulsion.¹⁵ Subsequent studies have separated charge transfer into "charge transfer and mixing" but for the purpose of this paper we attempt to lump these components together.

From a survey of a wide variety of small intermolecular interactions, Kollman¹² concluded that the single most important component is the electrostatic term and developed an empirical relation between the electrostatic potential of the monomers and the intermolecular interaction energy. However, he¹⁶ and others have documented cases where a consideration of only the electrostatic energy fails to reproduce important chemical trends. Thus there is a clear need for a more general empirical equation encompassing all the passing components.

Parallel to the development of the detailed theoretical approaches to analyzing noncovalent complexes have been qualitative approaches such as the concept of "hard and soft Lewis acids and bases"¹⁷ and the empirical approach of Drago and co-workers.¹⁸ The latter approach has clearly demonstrated that to reproduce enthalpies of association of Lewis acids and bases in nonpolar solvents at least a two-parameter equation is required: $\Delta H = E_a E_b + C_a C_b$. E_a and C_a are described as the electrostatic and covalent properties of the Lewis acid and E_b and C_b the corresponding properties of the Lewis base. Marks and Drago¹⁹ later showed that the functional form of the equation is consistent with the Klopman perturbation method of describing chemical reactivity. In view of the usefulness of the Drago equation and the need to develop an empirical equation which had both strong theoretical underpinning and a predictive capability, we decided to use the large

number of available Morokuma component analysis calculations to develop such an equation.

We set the following criteria for the equation: (1) it should be based on and directly related to direct quantum-mechanical calculations; (2) it should be based on molecular properties, so that a nontheoretician could apply it in a simple way given the monomers that make up the complex; (3) it should be as generally applicable as possible. We often had to find a reasonable compromise among the criteria of theoretical rigor, simplicity, and generality in the development of the equation.

II. Functional Form of the Model Equation

In this section we describe the functional forms for the various energy terms that we use in the empirical equation. We have tried to base the parametrization on a consistent set of atomic and group properties which are readily obtainable from experiment or ab initio calculations. Our calculations on SO_2 complexes^{12,20} showed that $\text{SO}_2\text{-NH}_3$ would work well as a prototype system. Much of the final parametrization is based on this system. To specify the location of an electron pair in a bond (ELPR) we follow the method we have used before²¹ to model the charge distribution in molecules. We identify the location of a lone pair electron distribution around a donor atom in terms of lone-pair extents as given by Allen.²² This is the radial distance which encloses 98% of the charge as calculated with a 431G basis.

Electrostatic Term. The electrostatic energy is represented as in ref 12 to be a term of the form.

$$E_{\text{ES}} = K_{\text{ES}} \times (\text{POTA}) \times (\text{POTB}) \quad (1)$$

where POTA is the electrostatic potential in atomic units (au) of the acid A at a reference position^{12,23} (2.0 Å for protonic acids) and POTB is the same for the base B (2.12 Å for first-row bases and 2.65 Å for second row). K_{ES} is an empirical constant evaluated from 431G calculations^{24,25} which has dimensions of distance and has the units of $\text{kcal mol}^{-1} \text{au}^{-2}$, when the electrostatic energy is in kcal/mol and the electrostatic potentials are in atomic units.

A complete representation of the electrostatic energy would include not only the interactions of various multipoles on the molecules but also a penetration term.²⁶ We have represented these several electrostatic interactions with a single electrostatic potential term since it is obtainable easily from either ab initio calculations or from a simple charge distribution model.²¹ In the case of proton affinities, the electrostatic energy obtained from ab initio calculations is identical with the electrostatic potential for a given proton location.

Almost all the results presented in this paper use the ab initio

Table I. Distance Dependence of Electrostatic Potential of Hydride Bases

base	distance range, Å	<i>n</i>
H ₃ N	1.33–2.12	1.8
	3.0–5.0	
H ₃ P	1.85–3.17	2.38
	3.17–3.97	1.89
H ₂ S	1.85–3.17	2.13
	3.17–3.97	2.35
HCl	1.85–3.17	1.75
	3.17–3.97	2.02

calculated electrostatic energy at the minimum energy distance to compare with the E_{ES} of the model. In the long run, it would be useful to know the distance dependence of the electrostatic potential and the electrostatic energy on molecule–molecule separation, in order to predict geometries of complex formation.

Classically, the electrostatic potential falls off with the second power of the distance for a dipole and with the third power of the distance for a quadrupole. Other multipoles and the penetration term will have other distance dependencies. Beyond the van der Waals radius the distance dependence of the *electrostatic potential* for the hydrides NH₃, PH₃, H₂S, and HCl dies off as $1/R^2$, where R is the distance from the heteroatom in the “lone pair” direction (Table I). Similarly, the distance dependence of the *electrostatic energy* was obtained for a number of intermolecular complexes, taking data from ours and other work (Table II). For neutral intermolecular complexes we found a distance dependence of the energy to be approximately the inverse fifth power; for ion–neutral interactions, in which only one electrostatic potential factor appears, the electrostatic energy died off as $1/R^{2.5}$.

We thus decided to estimate the distance dependence of the electrostatic energy using the equation

$$E_{ES} = K_{ES} \times (\text{POTA}) \times (\text{POTB}) \times [(R_0/(R_0 + \Delta R))^{n_{ES}}] \quad (2)$$

where the first four terms are as in eq 1, R_0 is the reference distance for the electrostatic potential (see Appendix for numerical values), ΔR is the difference between the actual intermolecular separation and the reference distance, and $n_{ES} = 5$ for neutral complexes and 2.5 for ion–neutral complexes.

The scaling factor K_{ES} was initially taken as 6530 kcal mol⁻¹ au⁻² from a plot of (POTA/POTB) vs. the 431G calculated H-bond electrostatic energies (1 kcal/mol = 4.18 kJ/mol). Later, after experience with SO₂ complexes, we decided to use the NH₃–SO₂ complex as the prototype from which to scale other systems. Remarkably, K_{ES} turns out to be 6530 kcal mol⁻¹ au⁻² on this basis also and this value has been adopted in the final model.

Polarization Term. The polarization energy in kcal/mol is represented as

$$E_{PL} = K_{PL} \times (\text{POTA} \times \alpha_B + \text{POTB} \times \alpha_A)/(R_{AB})^{n_{PL}} \quad (3)$$

where the α 's are polarizabilities (units Å³), R_{AB} is an internuclear separation (Å), and the electrostatic potentials are as defined in eq 1 and are in atomic units. For interactions of the H⁺ and Li⁺ ions with bases the second term was omitted because α_A is either zero or very small. For ion–induced dipole interactions n_{PL} is 4; for dipole–induced dipole interactions it is 6. Other multipole–induced dipole interactions may be present as well. But following the approach used with the electrostatic energy we have employed a simple form for the

Table II. Values of Distance Scaling Parameters as Found from ab Initio Calculations^a

base	acid	n_{ES}	n_{PL}	b_{CT}	γ_{EX}	ref
NH ₃	HF	4.6	6.0	1.1	4.4	14
NH ₃	F ₂	6.0	5.6	1.2	4.7	14
NH ₃	BH ₃	4.1	7.5	1.6	3.4	13
NH ₃	SO ₂	5.8	6.3	1.4	3.6	20
MMA	SO ₂	5.8	7.8	1.4	3.5	20
TMA	SO ₂	6.2	8.0	1.4	3.6	20
NH ₃	H ⁺	1.2	1.9	0.4		20
NH ₃	Li ⁺	2.2	3.8	<i>b</i>	4.2	9
NH ₃	K ⁺	2.7	4.5	<i>b</i>	2.4	33
H ₂ S	HNCO	4.0	2.5	0.7	4.3	20
H ₂ S	SO ₂	5.2	6.3	0.9	3.6	20
H ₂ S	H ₂ S	4.6	4.6	0.6	3.6	20
H ₂ S	H ⁺	2.3	1.8	0.6		20
H ₂ S	Li ⁺	2.5	3.7	<i>b</i>	4.5	20
H ₂ S	K ⁺	2.6	3.8	<i>b</i>	4.9	20
PH ₃	BH ₃	4.6	10.1	0.6	3.2	20
PH ₃	H ⁺	2.4	1.5	0.4		20
H ₂ O	H ₂ O	5.3	5.4	0.81	4.1	11
HF	HF	4.6	6.4	0.65	4.5	11
CO	BH ₃	5.0	8.7	1.6	3.9	13

^a Parameter values are quite distance dependent in many cases. The number given here is an estimate of the value of the minimum energy distance of the base–acid complex. The parameter n_{ES} refers to the exponent in eq 2, n_{PL} refers to the exponent in eq 3, b_{CT} refers to the exponent in eq 7 and γ_{EX} refers to the exponent in eq 8. ^b Charge-transfer components could not be meaningfully extracted from the other components because of mixing of terms.

term and have determined the exponent, n_{PL} , from the distance dependence of the ab initio polarization energy for a number of molecular complexes (Table II). It can be seen that, although there is some variability, $n_{PL} \sim 4$ for ion–molecular interactions and $n_{PL} \sim 6$ for neutral molecule–molecule interactions.

For simple hydrides and oxides, polarizabilities were calculated from Lefevre's compilation of atom and group refractions.²⁸ For those molecules with substituents this procedure led to energies which were too large, leading us to introduce a distance-dependence correction for the substituent groups. An inverse fourth power dependence was used in accordance with the classical form for an ion–induced dipole interaction. The distance was measured from the center of the bond to the substituent group (see Appendix).

The constant K_{PL} was first chosen for neutral complexes by fitting eq 3 to the NH₃–SO₂ polarization energy,²⁹ and using the units described above has the numerical value of –470.9 with dimensions charge distance.³

In the case of proton affinities, the polarization energy was referenced to the ab initio polarization energy in polarization of NH₃¹⁰ by the relationship

$$E_{PL} = E_{PL}^0(\alpha/\alpha_0)(R_0/R)^4 \quad (4)$$

where E_{PL} is the polarization energy found in the proton-affinity calculations on NH₃, α_0 is the polarizability of NH₃, and $R_0 = 1.16$ Å, the minimum electrostatic potential in the lone-pair region of ammonia. This can be written as

$$E_{PL} = K_{PL}(\alpha/R^4) \quad (5)$$

where α is the polarizability corrected for substituent groups as described above when appropriate and R is the minimum energy distance for addition of the proton.³⁰ In this case K_{PL} has units of charge, and has the numerical value 4.43, where E_{PL} is in kcal/mol, α in Å³, and R in Å.

Charge-Transfer Term. For the charge-transfer energy we have used the equation

$$E_{CT} = \Delta - \sqrt{\Delta^2 + 4\beta^2} \quad (6)$$

where Δ is the energy difference between the highest occupied molecular orbital of the donor and the highest occupied molecular orbital of the acceptor. We evaluate Δ as the difference between the ionization potential³¹ of the base and the electron affinity of the acid.³²

This equation is a straightforward result from simple LCAO-MO theory. The derivation, with the results cast in a slightly different form, is given by Herndon.³³ Making the common assumption that the matrix element β is proportional to the overlap integral between the two orbitals,³⁴ we expect it to show an approximate distance dependence of the form

$$\beta = \beta^0 e^{-b\sigma R} \quad (7)$$

R is the difference between the electron pair location on donor and acceptor. In the case of hydrogen bonds electron pairs are positioned following the method in ref 21, based on relative electronegativities. Lone-pair electrons are placed at the lone pair extent distance of Allen.²² For other cases R is established in a manner appropriate to the system while retaining this fundamental idea. For proton affinities β is taken as β^0 with no distance correction. For Li^+ and K^+ affinities R is the difference between $\text{M}^+\cdots\text{B}$ and the corresponding $\text{H}^+\cdots\text{B}$ distance. For SO_2 as the Lewis acid a factor of 0.8 is applied to the exponent.²⁰ For complexes of SO_2 , R is established as the internuclear distance minus half the lone-pair extent of the S atom and the base atom.

Since the charge-transfer energies for proton affinities are particularly large, we first evaluated β^0 from the ab initio charge transfer energies for these systems. However, the electron affinity (EA) of the proton (13.6 eV) is larger than the ionization potential of some of the bases we have studied, and thus the direct straightforward computation of Δ as the difference between the experimental ionization potential and electron affinities would give unreasonable results. Therefore we treated the electron affinity of the proton as an additional parameter in the model which we adjusted to get a reasonable result. In order to establish a value for this parameter, we assumed several hypothetical values for the electron affinity of the proton and then calculated β from eq 7, utilizing the ab initio charge transfer contribution to the proton affinities calculated at the minimum energy distance.¹⁰ Hypothetical electron affinities of 4, 5, and 7 eV were used, leading to β values from 63 (H_2O , EA = 7 eV) to 101 kcal (H_3P , EA = 4 eV). A β^0 of 83 kcal was chosen, reflecting the mean value found for an effective electron affinity of 5 eV. This number was used also for hydrogen bond charge transfer energies. Later we calculated β^0 for our prototype system $\text{SO}_2\text{-NH}_3$. Remarkably, we found β^0 to be 84.6 kcal/mol at 2.7 Å and 82.0 kcal/mol at 2.63 Å. We have retained 83 kcal/mol in the final model.³⁵

Exchange Repulsion. Since this term is often proportional to the square of the overlap of occupied orbitals, it should show an approximate exponential distance dependence.³⁶

$$E_{\text{EX}} = K_{\text{EX}} e^{-\gamma_{\text{EX}} R} \quad (8)$$

The distance dependence of the exchange energy E_{EX} was examined for a number of complexes by plotting its logarithm as a function of molecule separation R (Table II). We chose γ_{EX} to be 3.6 since this was the value for our prototype $\text{NH}_3\text{-SO}_2$ system and also fit the other systems quite well. Using this exponent, K_{EX} was obtained for the $\text{NH}_3\text{-HF}$ system and this was found to be 132.1 kcal/mol.

The choice of R for systems other than hydrogen bonds was established in a manner appropriate to each system, while retaining the fundamental basis of a distance between the lone-pair extent of the base and the electron-pair position on the acid. For example, in the case of SO_2 complexes, we assume that the major part of the exchange repulsion comes from the

three valence electron pairs around the sulfur, two pairs in the direction of the two oxygen atoms and a lone pair, all lying in a plane perpendicular to the bond axis of the complex. We then define R simply as the distance from the lone-pair extent of the base to the sulfur atom; e.g., the nitrogen lone pair extent is 1.77 Å and $R(\text{N-S}) = 2.63$ Å for the minimum-energy structure of $\text{NH}_3\text{-SO}_2$; thus $R = 0.84$ Å. The energy calculated in this way from eq 8 is multiplied by three to give the correct total exchange repulsion energy since there are three electron pairs involved.

In the case of Li^+ and K^+ affinities, after exploring several parametrizations, we adopted the following approach. R is taken as the distance from the lone-pair extent of the base to the center of the metal ion, analogously to our choice of R in $\text{H}_3\text{N-SO}_2$; i.e., R in eq 8 is $R(\text{M-B}) - R(\text{lp})$ where $R(\text{M-B})$ is the metal-base distance. This is consistent with our choice of R in other systems where R is measured from the lone-pair extent of the base to a point representing the center of the electron distribution on the acid.³⁷

III. Results

Hydrogen Bonds. The results obtained by applying the model to the 20 hydride hydrogen bonds¹² are shown in Table III along with the corresponding ab initio results. As a means of measuring the goodness of the fit of the model to ab initio calculations we have computed the ratio

$$\rho = \sum di^2 / \sum Ei$$

where the Ei are the ab initio energies for a particular component, summed over all systems, and $\sum di^2$ is the sum of differences between the model and the ab initio calculation for that component. For hydrogen bonds the values of ρ are electrostatic energy, 0.04; polarization energy, 0.08; charge-transfer energy, 0.11; exchange repulsion energy, 0.14; total energy, 0.09. The electrostatic energy is reproduced very well by the model. Although the other components show more scatter, most of the trends are reproduced quite well. The comparison of the total energies as calculated by the model and by the ab initio method is shown in Figure 1. The stronger binding cases are somewhat overestimated and the weaker ones are somewhat underestimated. Nevertheless the deviations are not large, most trends are reproduced, and we believe that the useful predictive power of the model is apparent.

The model was also applied to the 16 hydride hydrogen bond cases which include the combinations of the six proton donors and acceptors treated in ref 23 and 38 for which the ab initio calculations were not done in that work. The results of these calculations are in Table IV (ρ for comparison of 4-31G calculated total energies and model calculations is 0.10).

The H bonds most poorly represented by the model are those involving H_3N as a proton acceptor. It is also instructive to focus on a comparison of $\text{H}_3\text{N}\cdots\text{HF}$ and $\text{H}_2\text{O}\cdots\text{HF}$, whose relative energies of interaction are reversed by the model (in comparison with the ab initio calculations). We see that the relative size of the various energy components for the two complexes is qualitatively correct, but that the model electrostatic energy for $\text{NH}_3\cdots\text{HF}$ is not enough greater than that for $\text{H}_2\text{O}\cdots\text{FH}$ to compensate for the larger exchange repulsion in $\text{NH}_3\cdots\text{HF}$.

Proton Affinities. Kollman⁹ has reported ab initio calculations, with component analyses, on the proton affinities of a variety of bases. We have applied the model to these cases and show the results in Table V. We have measured the goodness of fit of the individual terms by calculating the quantity ρ as described above for the hydrogen-bond case. The values are polarization energy, 0.12; charge-transfer energy, 0.06; total proton affinity, 0.02. Figure 2 shows a plot of the energies calculated from the model vs. the 4-31G results. Experimental proton affinities, for comparison, may be found in ref 9. The

Table III. Comparison of *ab Initio* and Model Calculated Energy Components for H-Bonded Complexes (kcal/mol)

Complex	E_{ES}		E_{PL}		E_{CT}		E_{EX}		E_{TOT}	
	MOD	4-31G ^a	MOD	4-31G ^a	MOD	4-31G ^a	MOD	4-31G ^a	MOD	4-31G ^a
HF-HF	-10.3	-8.8	-0.6	-0.5	-2.5	-3.1	3.3	4.6	-10.1	-7.8
H ₂ O-HF	-16.9	-16.7	-1.0	-1.3	-4.2	-2.9	7.7	7.7	-14.5	-13.2
H ₃ N-HF	-21.5	-25.0	-1.5	-1.9	-6.2	-4.6	15.2	15.2	-14.0	-16.3
HCl-HF	-3.3	-3.2	-0.2	-0.2	-1.2	-1.8	2.3	1.7	-2.5	-3.4
H ₂ S-HF	-5.4	-5.7	-0.4	-0.3	-1.8	-2.7	4.3	2.9	-3.2	-5.8
H ₃ P-HF	-6.0	-6.7	-0.4	-0.6	-1.9	-3.3	4.8	3.6	-3.4	-6.9
Hf-HCl	-8.0	-6.4	-0.5	-0.3	-1.0	-2.8	1.3	5.1	-8.2	-4.5
H ₂ O-HCl	-13.1	-11.7	-1.0	-1.0	-1.7	-3.2	2.9	7.7	-12.9	-8.2
H ₃ N-HCl	-16.6	-17.6	-1.3	-1.7	-2.4	-5.2	5.7	13.7	-14.7	-10.8
HCl-HCl	-2.0	-1.8	-0.1	-0.1	-0.3	-1.3	0.6	1.1	-1.9	-2.0
H ₂ S-HCl	-3.3	-3.1	-0.2	-0.2	-0.5	-2.0	1.0	1.8	-3.0	-3.5
H ₃ P-HCl	-3.6	-3.7	-0.2	-0.3	-0.5	-2.6	1.1	2.2	-3.3	-4.3
HF-HOH	-4.4	-5.5	-0.4	-0.2	-1.4	-2.5	1.5	2.8	-4.7	-5.4
HCl-HOH	-1.5	-2.0	-0.1	-0.1	-0.6	-1.3	0.8	0.9	-1.3	-2.5
HF-HNH ₂	-1.6	-2.9	-0.3	-0.1	-0.7	-2.1	0.7	1.5	-1.8	-3.5
HCl-HNH ₂	-0.5	-1.1	-0.0	-0.0	-0.2	-0.7	0.3	0.3	-0.5	-1.6
HF-HSH	-1.3	-2.3	-0.2	-0.2	-0.3	-1.3	0.3	1.3	-1.6	-2.4
HCl-HSH	-0.6	-0.9	-0.1	-0.0	-0.1	-0.1	0.2	0.5	-0.6	-1.1
HF-HPH ₂	-0.2	-0.5	-0.1	-0.1	-0.1	-1.0	0.1	0.6	-0.3	-1.0
HCl-HPH ₂	-0.1	-0.2	-0.0	-0.0	-0.0	-0.4	0.1	0.2	-0.1	-0.4

^a Reference 23 contains the minimum energy geometries used; see ref 12 also for the 4-31G component calculations.

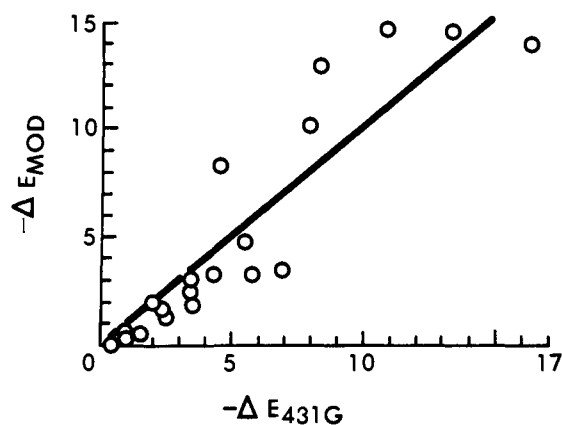


Figure 1. Comparison of the model calculated H-bond energies ($-\Delta E_{MOD}$) with the quantum mechanically calculated ones ($-\Delta E_{4-31G}$) (kcal/mol). The line is of unit slope and represents perfect agreement between the model and the quantum-mechanical calculations.

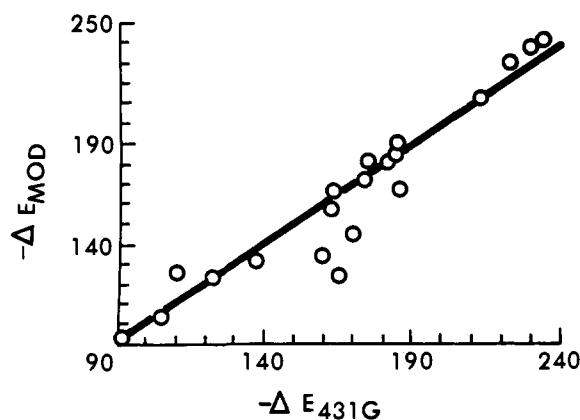


Figure 2. Comparison of the model calculated proton affinities ($-\Delta E_{MOD}$) with the quantum mechanically calculated ones ($-\Delta E_{4-31G}$) (kcal/mol). The line is of unit slope and represents perfect agreement between the model and the quantum-mechanical calculations.

data show that the model will reproduce not only most of the qualitative trends, both experimental and *ab initio*, but also

Table IV. Model Calculated Energy Components for H-Bonded Complexes (kcal/mol)

complex	model calculation					4-31G ^a
	E_{ES}	E_{PL}	E_{CT}	E_{EX}	E_{TOT}	E_{TOT}
H ₂ O-HOH	-11.6	-0.8	-2.9	4.7	-10.6	-8.1
H ₃ N-HOH	-14.6	-0.9	-3.6	7.0	-12.1	-8.9
H ₂ S-HOH	-5.1	-0.5	-1.0	1.9	-4.8	-3.9
H ₃ P-HOH	-5.7	-0.2	-0.8	1.5	-5.1	-4.0
H ₂ O-HNH ₂	-6.5	-0.4	-1.1	1.5	-6.6	-4.1
H ₃ N-HNH ₂	-8.3	-0.5	-1.5	2.5	-7.8	-4.1
H ₂ S-HNH ₂	-2.9	-0.1	-0.4	0.7	-2.7	-2.2
H ₃ P-HNH ₂	-3.2	-0.0	-0.4	0.6	-3.0	-2.2
H ₂ O-H ₂ S	-3.5	-0.5	-0.6	0.9	-3.7	-3.8
H ₃ N-H ₂ S	-9.3	-0.7	-1.1	2.2	-8.9	-4.4
H ₂ S-H ₂ S	-3.2	-0.1	-0.2	0.4	-3.2	-1.8
H ₃ P-H ₂ S	-3.0	-0.1	-0.2	0.4	-3.5	-2.1
H ₂ O-H ₃ P	-1.9	-0.2	-0.1	0.2	-2.1	-1.1
H ₃ N-H ₃ P	-2.4	-0.2	-0.1	0.2	-2.6	-1.2
H ₂ S-H ₃ P	-0.8	-0.0	-0.9	0.2	-0.8	-0.6
H ₃ P-H ₃ P	-0.9	-0.0	-0.8	0.1	-0.9	-0.8

^a Reference 23 contains the minimum energy geometries used in these calculations; see ref 12 for the 4-31G calculations.

reproduces the effect of *methyl substitution* on the various hydrides.

The largest deviation of the model from the *ab initio* calculations occurs in the case of ethylene, where the model predicts a much too low proton affinity. Another difference between *ab initio* and the model is the larger contribution of charge transfer compared to polarization effects in the model. In fact, the methyl substituent effect was shown by Umeyama and Morokuma to be predominantly due to the polarization energy term in 4-31G *ab initio* calculations (STO-3G *ab initio* calculations found an increase in proton affinity upon methyl substitution in the amines due mainly to charge-transfer terms).

Other Complexes. We now extend the model to other "charge-transfer" systems which we had studied by *ab initio* methods.²⁰ In the *ab initio* calculations we wished to span a variety of representative molecular types, while also being limited by the method to small molecules. As one way of obtaining a broad variety of systems we chose some molecules

Table V. Comparison of ab Initio and Model Calculated Energy Components for Proton Affinities (kcal/mol)

base	E_{ES}^a	E_{PL}		E_{CT}		E_{TOT}	
		model	4-31G ^b	model	4-31G ^b	model	4-31G ^b
HF	-45.5	-8.9	-16.0	-49.3	-44.1	-103.7	-105.4
H ₂ O	-85.6	-14.6	-27.3	-66.0	-50.5	-166.3	-163.4
H ₃ N	-110.0	-23.4	-23.4	-78.8	-79.4	-212.3	-212.9
HCl	-17.7	-10.0	-9.9	-65.3	-64.9	-93.0	-92.5
H ₂ S	-34.4	-14.7	-13.8	-82.4	-89.7	-131.5	-137.9
H ₃ P	-36.4	-16.7	-22.8	-81.2	-100.3	-134.2	-159.4
CH ₃ H ₂ N	-106.4	-25.7	-34.0	-97.9	-82.2	-230.1	-222.6
(CH ₃) ₂ HN	-102.4	-28.1	-44.9	-107.3	-82.0	-237.8	-229.3
(CH ₃) ₃ N	-97.2	-30.4	-55.2	-113.4	-81.3	-241.1	-233.7
CH ₃ F	-47.0	-10.3	-26.2	-66.8	-49.7	-124.1	-122.9
CH ₃ OH	-84.0	-17.3	-34.9	-79.1	-56.1	-180.4	-175.0
(CH ₃) ₂ O	-83.1	-19.7	-41.8	-86.6	-59.7	-189.4	-184.6
CH ₃ Cl	-20.2	-30.6	-17.3	-75.5	-73.0	-126.3	-110.5
H ₂ CO	-61.1	-17.3	-42.8	-78.7	-58.6	-157.1	-162.5
HCN	-56.7	-28.7	-54.9	-59.1	-58.2	-144.4	-169.8
CH ₃ CN	-67.0	-31.0	-59.4	-68.6	-59.2	-166.5	-185.6
CH ₃ CHO	-67.8	-18.8	-46.2	-84.9	-56.9	-171.5	-173.9
(CH ₃) ₂ CO	-70.6	-20.3	-50.2	-90.2	-60.6	-181.1	-181.4
H(NH ₂)CO	-78.7	-18.6	-46.5	-87.1	-58.9	-184.3	-184.1
C ₂ H ₄	-9.1	-25.0	-41.4	-90.2	-114.6	-124.3	-165.1

^a Ab initio and model values are the same; see text. ^b Reference 9; geometry used is given in this paper.

Table VI. Comparison of ab initio and Model Calculated Energy Components for Selected Donor-Acceptor Complexes (kcal/mol)

complex	$R, \text{\AA}^a$	E_{ES}		E_{POL}		E_{CT}		E_{EX}		E_{TOT}	
		model	4-31G ^b	model	4-31G ^b	model	4-31G ^b	model	4-31G ^b	model	4-31G ^b
NH ₃ -SO ₂	2.70	-18.6	-18.6	-1.8	-1.9	-5.3	-5.2	13.9	14.3	-11.8	-11.4
NH ₃ -SO ₂	2.63	-21.2	-22.2	-2.1	-2.1	-6.2	-6.1	17.9	18.7	-11.7	-11.7
NH ₃ -SO ₂	2.45	-30.0	-33.4	-3.3	-3.4	-9.6	-10.1	34.2	35.7	-8.1	-11.3
MA ^c -SO ₂	2.63	-20.5	-21.1	-2.1	-2.1	-6.9	-6.9	17.9	17.9	-11.6	-11.6
MA-SO ₂	2.45	-29.2	-33.1	-3.2	-4.0	-10.6	-12.3	34.2	35.7	-8.0	-13.7
DMA ^c -SO ₂	2.63	-19.7	-20.3	-2.1	-2.1	-7.4	-7.4	17.9	17.9	-11.1	-11.1
DMA-SO ₂	2.45	-28.0	-32.5	-3.2	-4.5	-11.3	-13.3	34.2	36.0	-7.5	-14.3
DMA-SO ₂	2.40	-31.8	-36.3	-3.6	-4.5	-12.7	-13.3	41.0	36.0	-7.1	-14.5
TMA ^c -SO ₂	2.63	-18.5	-19.1	-2.0	-2.0	-7.0	-7.0	17.9	17.9	-10.3	-10.3
TMA-SO ₂	2.45	-26.6	-31.8	-3.1	-4.9	-11.8	-14.0	34.2	36.0	-6.5	-14.8
TMA-SO ₂	2.36	-32.2	-40.0	-3.9	-6.6	-14.9	-17.8	47.3	49.5	-3.6	-15.0
PH ₃ SO ₂	3.51	-4.5	-4.4	-0.0	-0.0	-1.2	-2.6	3.1	3.2	-2.6	-3.8
H ₂ S-SO ₂	3.42	-4.6	-5.1	-0.2	-0.4	-1.5	-11.8	3.8	3.2	-2.5	-4.1
NH ₃ -SO ₃	2.55	-41.0	-33.7	-3.1	-3.6	-4.3	-11.9	16.7	19.7	-31.7	-29.5
NH ₃ HNCO	1.88	-15.7	-19.1	-1.2	-1.8	-3.8	-3.7	10.5	12.0	-10.9	-12.1
H ₂ S-HNCO	2.59	-4.2	-4.7	-0.7	-0.3	-0.5	-2.3	2.7	2.5	-2.7	-4.8
H ₂ S-H ₂ S	3.1	-0.9	-1.2	-0.2	-0.1	-0.3	-1.1	0.5	0.8	-0.9	-1.6

^a Distance between "central atoms" of monomers. ^b Reference 20, except for NH₃-SO₂, 2.70 Å, which is from ref 12. ^c MA ≡ methylamine; DMA ≡ dimethylamine; TMA ≡ trimethylamine.

that are commonly considered "hard" and others that are "soft". We used Drago's¹⁸ E and C parameters as one guide to selecting a variety of system types. We have also done many calculations on SO₂, which is a small, nonprotonic Lewis acid, amenable to ab initio methods. Also we investigated the ability of the model to treat methyl substitution in these complexes.

The results are in Table VI. It can be seen that the model does treat a variety of complexes quite well. The principal weakness of the model is in the treatment of the methylated amines with SO₂ at the minimum energy distance. Although the 4-31G calculations show a moderate increase in binding strength upon successive methylation, the model shows a drastically reduced strength. Although all the attractive terms are somewhat low, the major problem lies in the electrostatic term. For the NH₃...SO₂ complex the model result for this term is quite close (about 1 kcal/mol), while for trimethylamine-SO₂ the model result is about 8 kcal/mol. The problem here is with the power of the electrostatic distance dependence. We have taken this as proportional to the inverse fifth power, which fits most other systems. But the data in Table II shows that for

ammonia and the amines with SO₂ the dependence is steeper, about the inverse sixth power. If the energies are compared at a common distance of 2.45 Å, we find that the energies from the model are all far too low, because of the electrostatic term. Also, at 2.45 Å the trend in model-calculated energies for the series of methylated amines reverses that of the 4-31G calculation. Part of this problem is the electrostatic energy, which for the model decreases by 3.6 kcal from ammonia to trimethylamine, while the 4-31G calculation shows only a 1.6-kcal decrease. In addition the increase in charge-transfer energy calculated from the model for this series is only 2.6 kcal while the 4-31G calculation shows a 3.9-kcal increase.

Lithium and Potassium Ion Affinities. The model was applied to some of the lithium ion affinities for which ab initio calculations have been reported.^{9,39} The results are shown in Table VII and a comparison of the total energies from the two methods is shown in Figure 3. The general overall fit is good. It is interesting to note, furthermore, how well the model reflects some of the more subtle trends. The Li⁺-NH₃ and -amine total energies from the model reproduce the trend in the 4-31G results which show a decrease in the energy with in-

Table VII. Model Calculated Energy Components for Li⁺-Base Affinities (kcal/mol)

base	model					E_{TOT}^a (4-31G)
	E_{ES}	E_{PL}	E_{CT}	E_{EX}	E_{TOT}	
NH ₃	62.12 (60.46) ^b	7.04	9.43	27.92	50.67 (49.01) ^b	50.67 (49.40) ^b
MA	58.99	7.73	11.78	27.92	50.58	50.17
DMA	56.48	8.44	13.03	27.92	50.03	49.96
TMA	53.33	9.15	13.88	27.92	48.44	49.16
H ₂ O	47.06	6.04	11.35	24.17	40.28	47.90
MeOH	45.81	7.17	13.45	24.17	42.26	49.61
(CH ₃) ₂ O	44.55	8.29	14.70	24.17	43.37	49.99
HF	27.61	4.19	10.02	13.11	28.71	34.48
MeF	28.87	4.86	13.21	13.11	33.83	39.31
HCl	12.55	3.79	9.52	10.56	15.30	17.68
MeCl	14.43	6.69	10.93	10.56	21.49	22.63
CH ₂ O	37.65	7.98	15.04	13.38	45.53	47.34
CH ₃ MeO	45.11	8.68	16.19	13.38	54.84	52.30
Me ₂ CO	47.00	9.39	17.17	13.38	58.42	56.22
CH(NH ₂)O	52.40	8.59	16.09	13.38	61.94	59.78

^a Reference 9 contains geometries used in these calculations. ^b Values in parentheses are for H₃N with $\theta(\text{HNH}) = 109.5^\circ$, which is the angle used in the 4-31G calculations for methyl-, dimethyl-, and trimethylamine.

Table VIII. Comparison of ab Initio and Model Calculation Energy Components for Li⁺ and K⁺ with NH₃ and H₂S (kcal/mol)

system	E_{ES}		E_{PL}		E_{CT}		E_{EX}		E_{TOT}	
	model	4-31G	model	4-31G ^a	model	4-31G	model	4-31G	model	4-31G
Li ⁺ -NH ₃ ^b	-62.12	-56.9	-7.1	-7.0	-9.4	-1.9	27.9	15.1	-50.7	-50.7
Li ⁺ -H ₂ S ^b	-19.1	-20.6	-4.9	-4.9	-12.2	-6.7	20.9	6.3	-15.2	-25.9
K ⁺ -NH ₃ ^b	-23.5	-26.7	-1.7	-1.9	-1.3	-1.2	14.1	5.6	-12.3	-24.2
K ⁺ -H ₂ S ^b	-9.42	-10.0	-1.6	-2.5	-1.4	-0.1	8.5	1.5	-3.9	-11.8

^a 4-31G energies from ref 9. ^b 4-31G energies from ref 20.

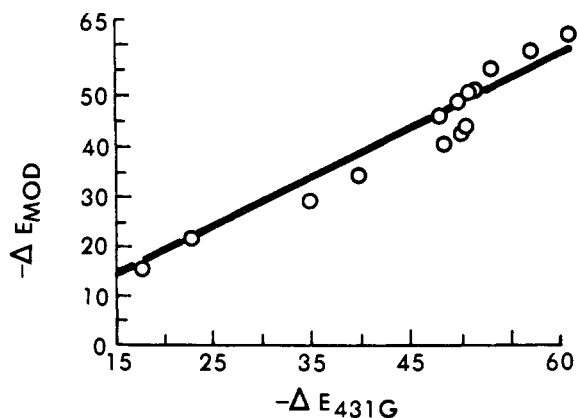


Figure 3. Comparison of the model calculated Li⁺ affinities ($-\Delta E_{MOD}$) with the quantum mechanically calculated ones ($-\Delta E_{4-31G}$) (kcal/mol). The line is of unit slope and represents perfect agreement between the model and the quantum-mechanical calculations.

creasing methylation. As mentioned above in connection with the choice of parametrization, some of the terms in the ab initio component analysis may be in error because of mixing, and this appears to be especially so in the case of the lithium and potassium ion affinities. In particular the ab initio charge transfer energy may be too low, at the expense of the exchange energy. Our choice of parametrization, relating charge transfer to that for proton affinities and exchange repulsion to the total energy, may well provide a better assessment of these terms than the ab initio component analysis.

For the series water, methanol, dimethyl ether the effects of methylation are correctly reproduced, although the model gives total energies which are too low by about 7 kcal/mol relative to the amines (experimentally, H₂O also has a Li⁺ affinity about 3 kcal/mol less than NH₃). These results can be compared with the component analysis for Li⁺...H₂O reported by Kollman.¹² Although the mixing problem compli-

cates the analysis, most of the difference can be accounted for in the electrostatic energy. This arises from the fact that we calculate the electrostatic energy as the electrostatic energy of the base at the Li⁺...base distance, i.e., treating the Li⁺ ion as a point charge.

It is also interesting to note that the model produces a greater lithium ion and a lower proton affinity for formamide than for the amines in agreement with the 4-31G results and experiment.

In Table VIII are given lithium and potassium ion affinities for NH₃ and H₂S along with the 4-31G component analysis results. The model calculations reproduce the relationship between these systems as given by ab initio calculations but the interaction energies are too high. This is due primarily to the exchange repulsion energy, which is greatly overestimated. This may be due in part to the choice of the distance-dependence parameter, γ_{EX} , in eq 8.

While we have used γ_{EX} universally as 3.6, our distance-dependence analysis in Table II shows that a larger γ , about 4.5, is more appropriate for lithium and potassium ion affinities. This accounts for about 4 kcal of the differences.

IV. Conclusions and Directions for Improvement of the Model

As indicated above, we have attempted to develop a model both simple and general enough to be applied by any chemist to a variety of intermolecular interactions (see Appendix for a concise recipe). We think we have succeeded in this goal, but there are still definite needs for improvement in the predictive ability of the model.

As noted in the comparison of H₃N...HF and H₂O...HF and in the comparison of Li⁺...NH₃ and Li⁺...OH₂, a more sophisticated representation of the electrostatic energy and its distance dependence is one of the more important directions for the model. We have proposed a simple method for describing the charge distribution of monomers²¹ and hope that a simple multipole expansion using such charge distributions

(see ref 40) will enable a more accurate description of the electrostatic energy (the estimation of "penetration" effects may prove elusive in this regard).

It is instructive to focus for a moment on $(\text{H}_2\text{O})_2$, $(\text{HF})_2$, and $(\text{NH}_3)_2$, since these are among the most studied H-bonded systems. The 4-31G ab initio dimerization energies are -8.1 , -7.8 , and -4.3 kcal/mol; the model finds -10.6 , -10.1 , and -7.8 kcal/mol. The overestimate of the electrostatic energy with this level of ab initio basis set is well documented. If we simply scale down the electrostatic energies in these dimers by 50%, the adjusted model dimerization energies, -4.82 , -4.98 , and -3.65 kcal/mol, are in much better agreement with the best available calculations at a consistent basis set level (6-31G*)⁴¹ (-5.6 , -5.9 , and -2.9 kcal/mol) and in good agreement with Hartree-Fock limit estimated of these quantities⁴² (-3.9 , -4.2 , and -2.1 kcal/mol). The experimental values for $(\text{H}_2\text{O})_2$ and $(\text{HF})_2$ dimerization energies are -5.5 ± 0.5 and -6.0 ± 1.0 kcal/mol, very close to the 6-31G* calculations. Although this correction factor is very crude, it is encouraging for further more sophisticated approaches in which each monomer is separately analyzed. As noted before,¹⁵ we have not added dispersion energies to the model as yet, because we have few calibration points and the errors in the dimerization energies due to our calibration to 4-31G ab initio are still too large to make such addition meaningful. It should be emphasized, however, that the errors in Li^+ and H^+ affinities at the 4-31G level are mainly a consistent overestimate of the complexation energy and the relative affinities are well reproduced.^{9,12} Thus, we feel that the model can eventually be reliable directly to experimental interaction energies.

Another area in which further development is required is the need for a more sophisticated representation of the distance dependencies of the energy terms, so one can more adequately predict intermolecular geometries. This may require an abandonment of our goal of a simple, algebraic equation for intermolecular energies. To apply the model, one is required to use a reasonable geometry, based on experimental or theoretical knowledge of related intermolecular complexes.

Finally, we should put these studies in perspective by a comparison with the Drago equation¹⁸ noted in the Introduction. For example, the relative magnitude of our electrostatic energies (Table V) and the Drago E parameters¹⁸ for some N, O, S, and P bases are quite similar. The Drago equation is based on empirical enthalpies of intermolecular complex formation in inert solutions and is a useful predictive equation for molecules for which one has experimental values for its enthalpy of association with two other molecules. Our equation can be used for a somewhat broader range of gas-phase complexes (from proton affinities to weak H bonds), but suffers at this point from being quantitatively less accurate. Part of this inaccuracy can be traced to our calibration to 4-31G ab initio and can be remedied by correcting the electrostatic energies as described above for the H-bonded cases. However, it is not likely that our simpler equation will ever be as accurate as the Drago equation. The usefulness of our equation will be in assessing Lewis basicity or acidity for compounds prior to experimental study and for those compounds which may be difficult to study experimentally.

Appendix. Recipe for Using the Model Equation

The model equation is $E = E_{\text{ES}} + E_{\text{PL}} + E_{\text{CT}} + E_{\text{EX}}$ with energies in kcal/mol.

Electrostatic Energy. The equation is

$$E_{\text{ES}} = K_{\text{ES}} \times (\text{POTA}) \times (\text{POTB}) \times (R_0/R_0 + \Delta R)^{n_{\text{ES}}}$$

K_{ES} is 6530 kcal mol⁻¹ au⁻²; n_{ES} is 5 for neutral-neutral complexes and 2.5 for ion-neutral complexes. POTA and POTB are electrostatic potentials at the reference position (R_0)

for the Lewis acid (POTA) and Lewis base (POTB) in atomic units. Some published values of electrostatic potentials may be found in ref 9, 12, and 23. For H^+ , Li^+ , and K^+ affinities (POTA) is omitted.

R_0 . The reference distance for the electrostatic potentials follows those established in ref 9, 12, and 23: first row base atoms, 2.12 Å; second row base atoms, 2.65 Å; for H^+ affinities, at energy minimum near the base molecule; H-bonding electrophiles, 2 Å from H-bonding proton; all other electrophiles, 2.7 Å. ΔR (Å) is the difference between the distance used in the calculation and the reference distance.

Polarization Energy. The equation is

$$E_{\text{PL}} = K_{\text{PL}} \times (\text{POTA} \times \alpha_{\text{B}} + \text{POTB} \times \alpha_{\text{A}}) / R_{\text{AB}}^{n_{\text{PL}}}$$

K_{PL}	neutral-neutral	470.9 kcal mol ⁻¹ au ⁻¹ Å ³
	H^+ affinities	4.43 kcal mol ⁻¹ au ⁻¹ Å
	Li^+ and K^+ affinities	19.68 kcal mol ⁻¹ au ⁻¹ Å

α are polarizabilities in Å³ calculated from atom and group refractions,²⁸ corrected by an inverse fourth power distance dependence for substituent groups; for example, the α used for trimethylamine as a base can be related to that used for NH_3 by $\alpha_{\text{NMe}_3} = \alpha_{\text{NH}_3} + 3 \times \alpha_{\text{Me}} \times (1/R^4)$, where Me is the difference in polarizability of a methyl group and a hydrogen atom and $R = (1 + R(\text{N-C}))/2$. $R(\text{N-C})$ is the N-C bond distance. This form for R is chosen so that, as $R(\text{N-C}) \rightarrow \infty$, the contribution goes to zero. As $R(\text{N-C}) \rightarrow 0$, the entire contribution from the substituent is included. n_{PL} for neutral-neutral = 6; for ion-neutral = 4. R_{AB} is the intermolecular distance in Å. For H bonds this is measured from the base to the midpoint of the A-H bond.

Charge-Transfer Energy. The equation is

$$E_{\text{CT}} = -\sqrt{\Delta^2 + 4\beta^2}$$

where $\beta = \beta^0 e^{-b_{\text{CT}}R}$ and $\Delta = (\text{ionization potential})_{\text{base}} - (\text{electron affinity})_{\text{acid}}$.

Ionization Potentials. Literature values were used.

Electron Affinities. Experimental values were used, except for positive ions. For H^+ it is considered a parameter of the model and taken as 5 eV (115 kcal), compared to the experimental value of 13.6 eV. For Li^+ and K^+ affinities the same fraction, $5/13.6$, of the experimental value is used. $\beta^0 = 83$ kcal/mol; $b_{\text{CT}} = 1.2 \text{ Å}^{-1}$.

R is the distance between the modeled position of electron pairs on donor and acceptor. For H-bonded cases, bonding electron pairs are positioned based on relative electronegativities following the method in ref 21. Lone pairs are positioned at the lone-pair extents of Allen.²² For other systems R must be established in a manner appropriate to the system while retaining this fundamental approach. See text for specific examples.

Exchange Repulsion Energy. The equation is

$$E_{\text{EX}} = K_{\text{EX}} e^{-\gamma_{\text{EX}}R}$$

$K_{\text{EX}} = 132.1$ except for Li^+ and K^+ affinities where 55.33 is used; $\gamma_{\text{EX}} = 3.6 \text{ Å}^{-1}$. R is the distance between electron pairs modeled as in the case of the charge transfer energy calculations. For specific cases see text.

Example Calculation

$$\text{NH}_3\text{-HF}, R(\text{N-F}) = 2.69 \text{ Å}$$

$$E_{\text{ES}} = K_{\text{ES}} \times (\text{POTA}) \times (\text{POTB}) \times \left(\frac{R_0}{R_0 + \Delta R} \right)^{n_{\text{ES}}}$$

$$= (6530) \times (-0.075) \times (0.044) \times (1)^5 = -21.5 \text{ kcal/mol}$$

$$E_{\text{PL}} = -K_{\text{PL}} \times (\text{POTA} \times \alpha_{\text{B}} + |\text{POTB}| \times \alpha_{\text{A}}) / R_{\text{AB}}^{n_{\text{PL}}}$$

$$= -470.9 [(+0.036 \times 5.28)$$

$$+ (-0.75 \times 2.0)] / \left(2.69 \times \frac{0.917}{2} \right)^6 = -1.5 \text{ kcal/mol}$$

$$E_{CT} = \Delta - \sqrt{\Delta^2 + 4\beta^2}$$

where $\beta = \beta^0 e^{-b_{CT}R}$ where $R = R_{AB} - (LP/2) - ELPR^* - R_0$

$$E_{CT} = 250.9 \times \sqrt{250.9^2 + 4 \times 27.95^2} = -6.2 \text{ kcal/mol}$$

$$\beta = 83e^{-1.2 \times 0.907} = 27.95$$

$$R = 2.69 - 0.885 - 0.598 - 0.3 = 0.907$$

$$E_{EX} = K_{EX} e^{-\gamma_{EX}R}$$

$$E_{EX} = 132.1e^{-3.6 \times 0.60} = 15.2 \text{ kcal/mol}$$

$$R = 2.69 - 1.77 - 0.32 = 0.60$$

$$= R_{NF} - LP - BP$$

where LP = lone-pair length on N and BP = bond-pair distance from F.

References and Notes

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- For all SO_2 complexes, R_0 is 2.7 as chosen based on the H_3N-SO_2 interaction. Since the position for the reference potential for second-row bases was initially chosen at 0.53 Å longer than that for first-row bases, R , which refers to the S \cdots base distance for SO_2 -base complexes involving second-row bases, is reduced by this amount in eq 2. For interaction of the singly charged species H^+ , Li^+ , and K^+ with Lewis bases the base potential is scaled using an inverse 2.5 power, consistent with the usage above for two uncharged species and in the electrostatic equation $K_{ES}^* POT_A = 1$.
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- R was taken as 1.0 Å for all first-row bases and 1.3 Å for all second-row bases, reflecting the mean value of $R(B \cdots H^+)$ for those respective cases. The inverse fourth power dependence on the distance is the expected classical value and is reasonable in light of the ab initio distance dependence given in Table II. For lithium and potassium ion affinities a similar expression was used, referencing the calculation to the Li^+-NH_3 case at 1.96 Å.
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