Molecular Orbital Studies of Electron Donor-Acceptor Complexes. II. Carbonyl Cyanide-Benzene Complex and Dispersion Energy Contribution

William A. Lathan, George R. Pack, and Keiji Morokuma*

Contribution from the Department of Chemistry, The University of Rochester, Rochester, New York 14627. *Received March 31, 1975*

Abstract: An ab initio SCF calculation is carried out for the carbonyl cyanide-benzene complex, a $\pi\pi$-type electron donor-acceptor complex. The results suggest the necessity of inclusion of the dispersion energy. The dispersion energy is calculated by the use of the sum-of-states second-order perturbation expression for this system, as well as the carbonyl cyanide-water complex, the $H_2CO \cdots C_2H_4$, and two hydrogen-bonded systems, $H_2CO \cdots H_2O$ and $(H_2O)_2$. The dispersion energy changes drastically some characteristics of the intermolecular potential curve for the carbonyl cyanide-benzene complex.

I. Introduction

Ab initio SCF calculations have been quite successful in predicting geometries and interaction energies of hydrogen-bonded molecular complexes.[1-3] The energy decomposition scheme within the SCF framework[4] enables one to compute the electrostatic E_{es}, polarization E_{pl}, exchange repulsion E_{ex}, and charge transfer E_{ct} energies separately. At the equilibrium geometry of hydrogen-bonded complexes, each of two attractions, E_{es} and E_{ct}, is usually of comparable magnitude with the repulsion E_{ex}, but the electrostatic energy E_{es} often controls the direction of approach of interacting molecules.[1b,2,4]

Recently we have reported a successful application of the ab initio SCF method to two $n\pi$-type "electron donor-acceptor" complexes, i.e., the carbonyl cyanide-water $OC(CN)_2-H_2O$ and tetracyanoethylene-water $(NC)_2C{=}C(CN)_2-H_2O$ systems.[5,2] The stabilization of energies and some characteristics of the potential-energy curves of ground and excited state complexes are in good agreement with experiment. The energy decomposition analysis shows that for these weak complexes between polar molecules, the electrostatic energy E_{es} is the dominant contributor at the equilibrium geometry and determines the relative orientation of interacting molecules.

The existence of many complexes involving aromatic hydrocarbons,[6] the presence of vertical stacking interaction between certain drugs and the nucleotide bases of DNA,[7] and various similar phenomena prompted us to study the interaction energies of $\pi\pi$-type electron donor-acceptor complexes. The carbonyl cyanide-benzene complex is our first choice, with the following justifications. This is one of the smallest $\pi\pi$ complexes of practical interest. Although this complex has not been studied experimentally, charge-transfer spectra of complexes between carbonyl cyanide and other aromatic hydrocarbons such as toluene have been recorded.[8] A comparison of the present results with our previous calculations for the carbonyl cyanide-H_2O complex would also contribute to a better understanding of the origin of stabilization of electron donor-acceptor complexes. Since the former electron donor, C_6H_6, is less polar, if at all, than the latter, H_2O, the pattern of contribution of various energy components could be quite different between the two complexes.

As will be shown later, the ab initio SCF calculation for the carbonyl cyanide-benzene complex gives the equilibrium distance of 3.8 Å between two molecular planes with a stabilization energy of 0.7 kcal/mol. This energy is much smaller than an experimental estimate of 5 kcal/mol for the carbonyl cyanide-toluene complex,[8] and this interplane distance is substantially larger than 3.4 Å, a standard experimental interplane distance for aromatic hydrocarbon complexes in crystals.[6] It is recognized immediately that in a complex between two conjugated molecules the dispersion energy E_{disp} which is not included in the SCF calculation[9] would make an important contribution to the stabilization.

The dispersion energy is essentially due to the intermolecular electron correlation. It can be calculated, together with other energy components, by correlated wave functions such as CI (configuration interaction) and MC (multiconfiguration) SCF wave functions.[10] Or it can be calculated by the second-order perturbation expression.[11] The dispersion energy has been neglected in most ab initio calculations for intermolecular interactions. It has been estimated semiempirically for $(H_2O)_2$,[12] and the sum-of-states perturbation calculation has been carried out with a minimal STO basis set for H_2O-NH_3 and $(H_2O)_2$.[13] Most elaborate are calculations by Lischka for both intra- and intermolecular correlation energies using various localized MO CI methods for He or H_2 complexed with HF or H_2O and for $(HF)_2$.[14] For complexes between small polar molecules the dispersion energy makes small and relatively unimportant contributions. On the other hand, in electron donor-acceptor complexes between relatively large, sometimes less polar molecules the dispersion energy would be of critical importance and its ab initio calculation is desired.

In the following section we first present the results of SCF calculations for the carbonyl cyanide-benzene complex. In the subsequent sections we discuss a method to calculate the dispersion energy and actually carry out calculation of E_{disp}, as well as SCF contributions (E_{es}, E_{ex}, E_{pl}, and E_{ct}), for a simple model $\pi\pi$ donor-acceptor complex, $H_2CO \cdots C_2H_4$, and the carbonyl cyanide-benzene complexes. The same method will be also applied to the carbonyl cyanide-H_2O complex as well as two hydrogen-bonded complexes, $(H_2O)_2$ and $H_2CO \cdots H_2O$. The last section is a discussion on the dispersion energy.

II. Electrostatic, Polarization, Exchange, and Charge Transfer Energy for the Carbonyl Cyanide-Benzene Complex

Ab initio SCF calculations were carried out for the carbonyl cyanide-benzene complex in order to obtain the total SCF stabilization energy E_{SCF} and its energy components, electrostatic E_{es}, polarization E_{pl}, exchange E_{ex}, and charge-transfer E_{ct} energies, by the energy decomposition analysis. The minimal basis set, STO-3G with recommended exponents and scale factors,[15] was used because such a small set usually gives a good geometry estimate and a qualitative measure of the stabilization energy in molecular complex calculations.[5,2] The energy decomposition analysis was performed by the method proposed and used by the authors.[4,5,2] The monomer geometry of carbonyl cyanide was assumed to be that of our previous studies,[5] and a standard geometry (CC = 1.39 Å, CH = 1.09 Å) was assumed for benzene. Throughout the paper the individual monomer geometries were fixed and it is further assumed, based on experiments on complexes between aromatic hydrocarbons and planar electron acceptors,[6] that the two molecular planes are parallel to each other, with one molecule stacked on the other. A limited search for the equilibrium geometry was carried out by changing the interplanar distance R and by moving the center of the benzene molecule along the C=O axis and its extension: above the oxygen atom (R_A = 1.203 Å), above the C=O midpoint (R_A = 0.6015 Å), above a point 0.1 Å from the central carbon atom on the C=O axis (R_A = 0.1 Å), and above a point 0.3 Å from the central C on the extension of the C=O axis (R_A = −0.3 Å). The results are shown in Table I. The SCF energy minimum is found at R = 3.8 Å with the center of the benzene atom around the carbonyl carbon atom ($R_A \sim 0$). The major contributor to the stabilization is the electrostatic energy as is expected for this large intermolecular distance R. Since carbonyl cyanide has a large accumulation of the positive charge in the CCC triangle[5] and the C–H bonds of benzene are weakly polar with a negative charge on the carbon atoms, the approach found is quite reasonable.

It is recognized, however, that the calculated interplanar distance, 3.8 Å, is substantially larger than experimental distances, 3.1–3.5 Å, observed for varieties of $\pi\pi$-type complexes[6] in the solid including the probably comparable tetracyanoethylene-naphthalene complex.[16] The calculated stabilization energy, 0.7 kcal/mol, is much smaller than the experimental estimate, ~5 kcal, for the carbonyl cyanide-toluene complex.[8a] Even though the benzene complex is expected to be weaker than the toluene complex because of its smaller polarity, the SCF-calculated stabilization energy appears to be a substantial underestimate.

The disagreement may be attributed to (a) the size of the basis set, (b) the lack of geometry optimization, and (c) the failure of the SCF procedure for calculating the stabilization energy. Past experience[1-5] suggests that, though the first two factors will change the quantitative picture, they are not likely to account for the drastic disagreement. The SCF stabilization energy includes all important energy components but the dispersion energy, which is essentially the intermolecular correlation energy.[9,10,5] In a complex between two conjugated molecules the dispersion energy is expected to make an important contribution to the stabilization. In the following sections, we will show that in fact the dispersion energy is the most important contribution in the present complex.

III. Method of Dispersion Energy Calculation

Of various possible methods of calculating the dispersion energy, we chose the second-order sum-of-state perturbation method for its simplicity and easy applicability to complexes between large molecules. The dispersion energy (positive for stabilization), in this approximation, is given by[11]

$$E_{\text{disp}} = \sum_{i}^{\text{occ}} \sum_{k}^{\text{vac}} \sum_{\mu}^{\text{occ}} \sum_{\nu}^{\text{vac}} \frac{|\langle A_0 B_0 | H' | A_{i\to k} B_{\mu\to\nu} \rangle|^2}{E_{i_A\to k_A,\mu_B\to\nu_B} - E_0} \qquad (1)$$

$$= 4\sum_{i}^{\text{occ}} \sum_{k}^{\text{vac}} \sum_{\mu}^{\text{occ}} \sum_{\nu}^{\text{vac}} \frac{|\langle i_A k_A | \mu_B \nu_B \rangle|^2}{E_{i\to k}{}^{A} + E_{\mu\to\nu}{}^{B} - E_0{}^{A} - E_0{}^{B}} \qquad (2)$$

where A_0B_0 is the Hartree product of the Hartree-Fock wave functions for the ground states of the molecule A and B, $A_{i\to k}B_{\mu\to\nu}$ is the Hartree product of the wave functions for the singly excited states of A and B, H' is the molecular interaction part of the Hamiltonian, and $\langle i_A k_A | \mu_B \nu_B \rangle$ is a two-electron integral over the Hartree-Fock MO's of isolated molecules. Terms in the denominators such as $E_0{}^A$ and $E_{\mu\to\nu}{}^B$ are the unperturbed energies of isolated molecules in the ground and singly excited states. The value of eq 1 usually depends on the choice of excited state wave functions, $A_{i\to k}$ and $B_{\mu\to\nu}$.

Table I. Ground State Energy Decomposition Analysis for the Carbonyl Cyanide–Benzene Complex in kcal/mol (STO-3G Basis)

R,[a] Å	R_A,[b] Å	E_{es}	E_{ex}	E_{pl}	E_{ct}	E_{SCF}
2.8	0.1	2.95	−15.42	0.67	3.25	−8.54
3.0	0.1	2.09	−6.87	0.13	1.55	−3.10
3.2	0.1	1.47	−2.98	0.09	0.73	−0.69
3.6	0.1	0.95	−0.51	0.05	0.15	0.65
3.8	0.1	0.81	−0.22	0.04	0.06	0.70
4.0	0.1	0.70	−0.08	0.03	0.03	0.68
3.8	−0.3	0.82	−0.22	0.04	0.06	0.70
3.6	0.6015	0.88	−0.43	0.05	0.16	0.66
3.8	0.6015	0.76	−0.17	0.04	0.07	0.69
3.8	1.203	0.62	−0.13	0.04	0.05	0.59

[a] The distance between two molecular planes. [b] The position of the center of the benzene molecule along the C=O axis and its extension. The positive direction is toward the oxygen atom, with the carbonyl carbon as the origin. Details in the text.

Nakatsuji recently showed for an intramolecular perturbation that, if the perturbed wave function is assumed to be a linear combination of the Hartree-Fock ground and single excited wave functions, the sum-of-state perturbated energy expression is not valid unless one uses as the excited states the wave functions obtained by the configuration interaction of all the singly excited configurations.[17] One can easily extend his theorem to the intermolecular perturbation such as dispersion energy to conclude that the excited state wave functions, $A_{i\to k}$ and $B_{\mu\to\nu}$, have to be those of the full single excitation CI of isolated molecules.[18] However, Kochanski used successfully the single excitations from Hartree-Fock canonical occupied orbitals to virtual orbitals as the basis for the Ne–Ne and He–He interactions.[19] This prompts us to use canonical orbitals in eq 2 for the present systems.

Evaluation of eq 2 requires the following MO integrals. For evaluation of excitation energy in the isolated molecule, say, $E_{i\to k}{}^A - E_0{}^A$, one needs $\langle ii|kk\rangle$ and $\langle ik|ik\rangle$ for i = 1, 2, . . . , $n_A{}^o$ (the number of occupied MO's of A) and k = 1, 2, . . . , $n_A{}^v$ (the number of vacant MO's of A). This evaluation is relatively inexpensive even for large molecules. [If one wants to use CI wave functions mentioned above, one needs $\langle ij|kl\rangle$ and $\langle ik|jl\rangle$ for i,j = 1, 2, . . . , $n_A{}^o$ and k,l = 1, 2, . . . , $n_A{}^v$.] The most expensive part of the dispersion energy calculation is evaluation of $n_A{}^o n_A{}^v n_B{}^o n_B{}^v$ integrals: $\langle i_A k_A | \mu_B \nu_B \rangle$ for i_A = 1, 2, . . . , $n_A{}^o$; k_A = 1, 2, . . . , $n_A{}^v$; μ_B = 1, 2, . . . , $n_B{}^o$, and ν_B = 1, 2, . . . , $n_B{}^v$. But this evaluation is substantially less expensive than the complete transformation of two-electron integrals, which is required if one evaluates all the energy components in the perturbation expansion.[1] This expense consideration, as well as the programming simplicity, justifies our scheme that E_{es}, E_{ex}, E_{pl}, and E_{ct} are evaluated with the Hartree-Fock procedure,[4,5] and only E_{disp} is calculated with the perturbation expansion.

IV. Dispersion Energy Results

A. A Simple Model System. $H_2CO\cdots C_2H_4$. In order to examine the basis set dependency and general characteristics

Table II. Energy Components for the Formaldehyde–Ethylene $\pi\pi$ Electron Donor–Acceptor Complex in kcal/mol[a]

R, Å	E_{es}	E_{ex}	E_{pl}	E_{ct}	E_{SCF}	E_{disp}	E_T
			$H_2CO \cdots C_2H_4$ (STO-3G basis)				
2.5					−12.50	0.97	−11.53
3.0					−1.54	0.38	−1.16
3.5					−0.01	0.17	0.16
3.75					0.09	0.12	0.21
4.0					0.09	0.08	0.17
			$H_2CO \cdots C_2H_4$ (4-31G basis)				
2.5	11.1	−29.9	0.8	4.1	−13.90	3.44	−10.46
3.0	2.2	−5.5	0.2	1.2	−1.89	1.36	−0.53
3.5	0.7	−0.9	0.1	0.7	0.55	0.57	1.12
3.75	0.5	−0.4	0.1	0.5	0.68	0.38	1.06
4.0	0.4	−0.1	0.0	0.3	0.57	0.26	0.83

[a] Positive energy means the attraction, where repulsive energy is negative.

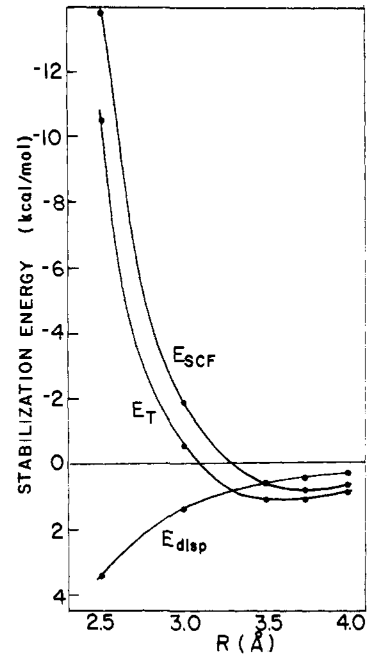

Figure 1. The SCF stabilization energy E_{SCF}, the dispersion energy E_{disp}, and their sum E_T as the function of the vertical distance R between CH_2O and C_2H_4 in their complex. 4-31G basis set.

Table III. Energy Components for the Carbonyl Cyanide–Water $n\pi$ Electron Donor–Acceptor Complex in kcal/mol[a]

R, Å	E_{es}	E_{ex}	E_{pl}	E_{ct}	E_{SCF}	E_{disp}	E_T
			$(CN)_2CO \cdots H_2O$ (STO-3G basis)				
2.0					−9.57	1.73	−7.84
2.4					2.44	0.76	3.20
2.7					3.53	0.43	3.96
3.0					3.07	0.25	3.32
			$(CN)_2CO \cdots H_2O$ (4-31G basis)				
2.4	16.2	−14.1	1.8	3.2	7.01	2.01	9.02
2.7	9.7	−4.4	1.0	1.8	8.02	1.15	9.17
3.0	6.6	−1.3	0.6	1.2	7.00	0.68	7.68
3.3	4.8	−0.4	0.3	0.7	5.52	0.41	5.93

[a] Positive energy means the attraction, where repulsive energy is negative.

Table IV. Energy Components for the Carbonyl Cyanide–Benzene $\pi\pi$ Electron Donor–Acceptor Complex in kcal/mol[a]

R, Å	E_{SCF}	E_{disp}	E_T
	$(CN)_2CO \cdots C_6H_6$ (STO-3G basis)		
2.8	−8.54		
3.0	−3.10	2.14	−0.96
3.2	−0.69	1.57	0.88
3.6	0.65	0.89	1.54
3.8	0.70	0.69	1.39
4.0	0.68		

[a] Positive energy means the attraction, where repulsive energy is negative.

of the dispersion energy, we have chosen a system consisting of formaldehyde and ethylene as a model to represent a weak $\pi\pi$ electron donor-acceptor complex. The planes of the two component molecules are assumed to be parallel, with the CC axis of ethylene perpendicular to the CO axis of formaldehyde. Furthermore, the midpoint of the ethylene CC bond is above the carbon atom of formaldehyde. The monomer geometries were fixed at the experimental ones;[20] the parameter of interest is the vertical distance R between planes (the distance from the formaldehyde carbon to the midpoint of the ethylene CC bond). This system was studied as a function of R with both the STO-3G and 4-31G[21] bases and results are displayed in Table II. Included also in Table II are the stabilization energy E_{SCF} within the Hartree-Fock scheme and, for the 4-31G basis, its components, electrostatic (E_{es}), exchange (E_{ex}), polarization (E_{pl}), and charge transfer (E_{ct}), resulting from the energy decomposition analysis.[4] The total stabilization energy E_T is the sum of E_{SCF} and E_{disp}. All positive quantities denote attraction whereas repulsive energies are negative. The importance of the dispersion energy's contribution to the total stabilization energy at the 4-31G basis set level may be seen more clearly in Figure 1. Although the SCF results predict the most stable configuration to be at R = 3.76 Å with a stabilization of 0.68 kcal/mol (interpolated), the addition of dispersion energy causes a shift in the equilibrium distance to 3.54 Å with the stabilization energy of 1.12 kcal/mol. Thus, dispersion energy is an important factor in the preferred equilibrium distance and stability of this model system. Other items of interest which will be seen to occur for other complexes as well are (1) the general tendency of the 4-31G basis to predict larger SCF stabilization energies than STO-3G due to overestimation of charge effects[3,1b] and (2) greater dispersion energies at a given R with 4-31G than with STO-3G. These findings will be discussed more fully below.

B. $CO(CN)_2 \cdots H_2O$. Table III shows results for the ground state of the carbonyl cyanide$\cdots H_2O$ $n\pi$ electron donor-acceptor complex. The distance R is the distance between the carbonyl cyanide plane and the oxygen of water and the water molecule is assumed to be approaching a point within the triangle of carbon atoms from above the plane, an approach found to be most favored in the SCF study. A report of an SCF study of both the ground and charge-transfer states of this system has appeared elsewhere and should be consulted if more geometrical details are desired.[5] Although the dispersion contribution gives 1 kcal/mol to the total stabilization, no pronounced effect is made on the potential curve.

C. $CO(CN)_2 \cdots C_6H_6$. Table IV lists results for the STO-3G study of the carbonyl cyanide-benzene $\pi\pi$ electron donor-acceptor complex, the system which provided the impetus for this entire dispersion energy study. The geometry of the complex is what was used and found to be most stable in the SCF calculation in section II, i.e., R_A = 0.1 Å. The SCF results predict at most a stabilization of 0.7 kcal/mol at the interplane distance R = 3.8$_1$ Å while experimental estimate of the stabilization based on other systems is in the neighborhood of 5 kcal/mol at R = 3.1–3.5 Å. Clearly the dispersion term is needed to predict a reasonable stabilization energy. With dispersion we predict a distance of 3.6$_0$ Å and a stabilization of 1.5 kcal/mol. Comparative studies for H_2CO-C_2H_4 and $CO(CN)_2$-H_2O suggest that a study with

Table V. Energy Components for the Linear Water Dimer[a] in kcal/mol[b]

R_{oo}, Å	E_{es}	E_{ex}	E_{pl}	E_{ct}	E_{SCF}	E_{disp}	E_T
			$(H_2O)_2$ (STO-3G basis)				
2.5					4.43	0.49	4.92
2.6					5.94	0.38	6.32
2.7					6.35	0.29	6.64
2.8					6.14	0.22	6.36
2.9					5.62	0.17	5.79
3.0					4.97	0.14	5.11
			$(H_2O)_2$ (4-31G basis)				
2.5					3.23	1.01	4.24
2.6	18.8	−19.2	1.2	4.9	5.71	0.80	6.51
2.7					7.06	0.64	7.70
2.8	12.4	−8.7	0.7	3.3	7.66	0.51	8.17
2.9	10.3	−5.8	0.5	2.8	7.79	0.41	8.20
3.0	8.6	−3.9	0.4	2.4	7.63	0.33	7.96

[a] Monomer geometries are from K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, 36, 2460 (1962). The dimer orientation is from T. R. Dyke and J. S. Muenter, *ibid.*, 60, 2929 (1974). [b] Positive energy means the attraction, where repulsive energy is negative.

Table VI. Energy Components for the $H_2CO \cdots H_2O$ Hydrogen-Bonded System[a] in kcal/mol[b]

R_{oo}, Å	E_{es}	E_{ex}	E_{pl}	E_{ct}	E_{SCF}	E_{disp}	E_T
			$H_2CO \cdots H_2O$ (STO-3G basis)				
2.55					0.87	0.94	1.81
2.75					3.30	0.58	3.88
2.85					3.47	0.46	3.93
2.95					3.34	0.37	3.71
3.15					2.71	0.24	2.95
			$H_2CO \cdots H_2O$ (4-31G basis)				
2.55	17.7	−22.6	2.0	5.2	2.30	1.71	4.01
3.75	11.4	−10.2	1.0	3.3	5.57	1.12	6.69
2.85	9.4	−6.8	0.8	2.8	6.12	0.91	7.03
2.95	7.9	−4.5	0.6	2.3	6.28	0.74	7.02
3.05					6.19	0.61	6.80
3.15	5.8	−2.0	0.4	1.8	5.95	0.50	6.45
3.35					5.27	0.34	5.61

[a] Monomer geometries from K. Takagi and T. Oka, *J. Phys. Soc. Jpn.*, 18, 1174 (1963); K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, 36, 2460 (1962). The complex orientation is the most stable one found in SCF calculation. Reference 4. [b] Positive energy means the attraction, where repulsive energy is negative.

the 4-31G basis would push this stabilization beyond 4 kcal/mol.

D. $(H_2O)_2$ and $H_2CO \cdots H_2O$. Results also are given for two hydrogen-bonded systems, the linear water dimer and $H_2CO \cdots H_2O$, in Tables V and VI, respectively. Although dispersion energy of course adds to the stabilization, no pronounced effects are evident. Hankins, Moskowitz, and Stillinger have estimated a dispersion energy for the linear water dimer at R_{OO} = 2.76 Å as 0.9 kcal/mol.[12] (After this paper was submitted, a paper appeared,[22] which carried out extensive SCF CI calculations for small hydrogen-bonded systems including $(H_2O)_2$. They used a large GTO basis set with polarization functions and performed CI including all possible single and double excitations. The correlation energy contribution, which include the intramolecular correlation as well as intermolecular correlation (i.e., dispersion energy), to the stabilization energy for $(H_2O)_2$ is 1.48, 1.22, 1.03, 0.87, and 0.75 kcal/mol at R_{OO} = 2.7, 2.8, 2.9, 3.0, and 3.1 Å, respectively. Our dispersion energy recovered about half of their values.)

V. Discussion

We have presented SCF and dispersion energy results for several electron donor-acceptor and hydrogen-bonded complexes. As mentioned above, the greater SCF stabilization energies with the 4-31G basis compared to STO-3G can be explained by 4-31G's general tendency to overestimate charge effects. This tendency of extended sp bases has been discussed by many workers and it is generally accepted that in order to bring the charge distribution back into agreement with experiment, it is necessary to include d functions in the basis.[3] Thus the addition of d functions in our study would be expected to move the SCF stabilization energies downward from the 4-31G values toward the STO-3G results.

The effect of inclusion of polarization functions in the basis on the dispersion energy is more difficult to assess. Extending a basis leads to additional attractive dispersion energy as a result of interaction of the occupied orbitals with additional vacant molecular orbitals. Thus, addition of d functions would lead to a greater dispersion energy because more atomic orbitals would be in the basis and consequently more vacant molecular orbitals would be available for excitations. Kochanski has found that d functions are necessary for a good description of the "Hartree-Fock dispersion energy" for the neon-neon interaction.[19] However, in her system the d functions resulted in new MO's of different symmetry. No new MO symmetries would appear in most systems we have studied if d functions were to be included. Thus d functions are not expected to have a pronounced effect because of their symmetry. But, of course, additional functions must be included in the basis before convergence in the dispersion energy can be expected. As mentioned above, our 4-31G estimate of dispersion energy for the water dimer is a factor of 2 too low in comparison with an estimate based on the neon dispersion attraction modified by the water-to-neon polarizability ratio.[12]

Although only the STO-3G basis was used, dispersion energies for the carbonyl cyanide-benzene complex are the largest calculated of any of the systems for a given R. This is reasonable since benzene and carbonyl cyanide are more polarizable (have more low-lying excited states) than the other component molecules.

It is instructive at this stage to compare calculated dispersion energy with an estimate from London's dispersion equation:[9]

$$E_{disp} = \frac{3}{2} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{r_{AB}^6} \tag{3}$$

which is based on the dipole-dipole interaction between point molecules. Here I_A and α_A are the ionization potential and the polarizability of the molecule A, and r_{AB} is the distance between the molecules A and B. The best calculated value 1.443×10^{-24} cm^3 of α for H_2O agrees with an experimental value of 1.45×10^{-24} cm^3.[23] Therefore, the above calculated value for H_2O, together with the calculated value for H_2CO, $\alpha_{23} = 3.292 \times 10^{-24}$ cm^3 (no experimental value),[23] will be used in eq 3. With I_{H_2O} = 12.62 eV and I_{H_2CO} = 10.88 eV,[24] one obtains

$$E_{disp}(H_2O\text{-}H_2O) = 454 \text{ kcal}/(r_{AB}\ \text{Å})^6$$

$$E_{disp}(H_2CO\text{-}H_2O) = 960 \text{ kcal}/(r_{AB}\ \text{Å})^6$$

For r_{AB} = 2.61, 2.7, 2.8, 2.9, 3.0, and 3.1 Å, $E_{disp}(H_2O\text{-}H_2O)$ = 1.47, 1.17, 0.94, 0.76, 0.62, and 0.51 kcal/mol and $E_{disp}(H_2O\text{-}H_2CO)$ = 3.11, 2.48, 1.99, 1.61, 1.32, and 1.08 kcal/mol, respectively. If one assumes that the AB distance r_{AB} is equal to the OO distance in ab initio calculations, one can compare these values with those in Tables V and VI and other ab initio results. The present 4-31G calculations are found to recover about a half of the estimate of the London equation. One also notes that a good CI calculation of ref 22 gives a correlation energy contribution (intramolecular plus dispersion) in good agreement with the London result for $(H_2O)_2$.

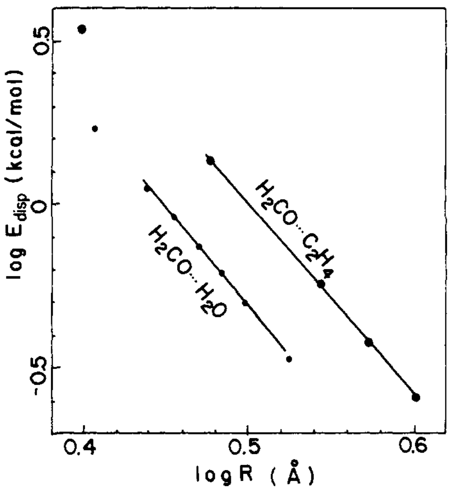

Figure 2. Plot of log E_{disp} vs. log R for $H_2CO\cdots C_2H_4$ and $H_2CO\cdots H_2O$ complexes to determine n, the inverse power of R dependency of the dispersion energy. 4-31G basis set.

The R dependence of the 4-31G dispersion energy for $H_2CO\cdots C_2H_4$ and $H_2CO\cdots H_2O$ is shown in Figure 2. These plots of log E_{disp} vs. log R yield curves whose tangents have slopes equal to $-n$ in the relation

$$E_{\text{disp}} = CR^{-n} \tag{4}$$

For the approximate middle (near the equilibrium geometry) of these curves we find an $R^{-6.0}$ dependence in the $H_2CO\cdots H_2O$ system and a $R^{-5.7}$ dependence for $H_2CO\cdots C_2H_4$. These curves show the general feature found in the 4-31G dispersion energies: the value of n in eq 4 increases slightly with R for the systems considered (n ranges from approximately 5.7 to 6.2 for $H_2CO\cdots H_2O$). A value of n equals 6 is expected for a dipole-dipole contribution between point molecules (eq 3). Higher interaction terms such as dipole-quadrupole cause n to increase beyond 6, whereas introducing a molecule with finite size rather than a point tends to decrease n. For instance, if a molecule is assumed to be a disk of radius r and the other molecules is a point placed at a distance R above the center of the disk and if one further assumes that there is a uniform dipole contribution from the disk, the dispersion energy would be of the form of

$$E_{\text{disp}} = A\left(\frac{1}{r^2R} - \frac{1}{r^2(R^2 + r^2)^{1/2}}\right)^2 \tag{5}$$

For a unit radius $r = 1$, the inverse power n of the standard dispersion equation, eq 4, would be given by

$$n = \frac{\mathrm{d}\log E_{\text{disp}}}{\mathrm{d}\log R} = \frac{2[2R^2 + 1 + R(R^2 + 1)^{1/2}]}{R^2 + 1} \tag{6}$$

which gives n ranging from 2 ($R = 0$) to 6 ($R = \infty$) including 4.41, 5.39, and 5.70 for R = 1, 2, and 3, respectively. The reduced value of $n = 5.7$ calculated for $H_2CO\cdots C_2H_4$ seems to be consistent with this model discussion.

Besides a choice of basis set which is necessary at the SCF level, calculation of dispersion energy using a sum-of-state perturbation expansion necessitates a further choice: excited state wave functions. Following Nakatsuji's argument[17] it can be shown that the best choice is wave functions from a complete CI of singly excited configurations. Another choice is the use of single configuration wave functions based on molecular orbitals which optimize the energy of such configurations under certain restrictions, as obtained by such methods as Huzinaga's hole potential method[25] and Morokuma and Iwata's electron-hole potential method.[26] Such methods definitely improve excitation energies over the method using SCF canonical occupied and vacant orbitals, but have no guarantee that the off-diagonal term neglected in the sum-of-state expression, eq 1, is actually small.[17] Though effects of various choices of excited state wave functions in the sum-of-state expressions should be examined more carefully, Kochanski's results on atom-atom dispersion calculation and our present results suggest that the use of canonical orbitals would be acceptable, at least for qualitative purposes.

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