

Model $\text{CaH}_2(\text{L})$ and $\text{CaF}_2(\text{L})$ Complexes ($\text{L} = \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}, \text{CO}, \text{N}_2$): Consequences of Interactions between “Inert-Gas” Ligands and Floppy Molecules

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The model complexes $\text{CaX}_2(\text{L})$ ($\text{X} = \text{H}, \text{F}$; $\text{L} = \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}, \text{CO}, \text{N}_2$) exhibit chemically significant interactions between the CaX_2 fragment and the “inert-gas” ligand L . This is shown by *ab initio* calculations at the MP2 and CEPA 1 levels of theory using extended basis sets. Interaction energies of up to ca. 4–8 kcal/mol for $\text{L} = \text{CO}, \text{N}_2$ and of ca. 1–3 kcal/mol for $\text{L} = \text{Kr}, \text{Xe}$ have been calculated, and both the $\text{X}-\text{Ca}-\text{X}$ angles and the $\text{Ca}-\text{X}$ distances are affected by interaction with the ligand L . These results indicate that the interactions of floppy molecules like CaF_2 and inert-gas matrices composed of CO, N_2 , or noble gases like Kr or Xe are nonnegligible, and the structures of the guest molecules may well differ from those of the free species.

Introduction

The isolation and characterization of high-temperature molecules frequently is achieved by trapping them at low temperature in so-called “inert-gas matrices”, which usually consist of N_2 , CO , or, very often, noble gases.¹ The characterization is performed by various methods, e.g. by IR, Raman, or photoelectron spectroscopy. The term inert-gas matrix implies that no significant interactions between the trapped molecule and the matrix environment occur, and thus the spectroscopic characteristics pertain to the isolated gas-phase species (with possibly different populations of vibrational levels than at higher temperatures in the gas phase). This assumption is certainly fulfilled for relatively rigid molecules.

However, for molecules with low-energy bending or out-of-plane modes, small but significant interactions with the matrix might change the molecular structure and vibrational spectra. Differences in vibrational frequencies for molecules isolated in different matrices have been observed for a number of alkaline earth dihalides,^{2–9} as well as for various transition metal complexes.¹⁰ CaF_2 is one of the most extensively studied floppy molecules (at least in the area of inorganic chemistry¹¹), both experimentally^{5–9,12} and computationally.^{13–15} High-level *ab initio* calculations agree that CaF_2 has a very shallow potential energy surface for the bending motions.^{13–15} However, the equilibrium structure (bent or linear) has not been characterized unambiguously, although most of the more recent calculations give bending angles slightly below 160° .^{13d,f,g,14,15} Calculated bending frequencies^{13–15} are considerably smaller than those obtained by matrix isolation techniques.^{5–8}

Isotopic shift experiments (using ⁴⁰Ca and ⁴⁴Ca) concerning the antisymmetric stretching mode (ν_3) of CaF_2 have been performed in inert-gas matrix environments to provide estimates of the bending angle.^{5–9} These studies usually give angles around 140 – 150° , about 10° – 15° smaller than most of the calculated angles.^{13–15} Snelson noted that the isotopic shifts for heavy central atoms like Ca are not very sensitive functions of the bending angle.⁵ Interestingly, studies in different matrices yielded successively smaller ν_3 -frequencies for matrices with presumably increased host-guest interactions.⁹ Thus, even the stretching modes are affected by the host matrix.

Knowledge of how the internal motions and even structural characteristics of floppy molecules or ions are influenced by interaction with inert-gas matrices would be very useful for the interpretation of spectroscopic observations. The host-guest binding energies involved are equally interesting. *Ab initio* calculations on model systems might provide at least order-of-

magnitude estimates of the effects involved. In an unpublished manuscript, DeKock and co-workers have performed model studies on the complexes of CaH_2 and CaF_2 with CO .¹⁶ Due to limitations of computational facilities at that time, these studies had to be restricted to the Hartree-Fock level of theory. However, it is well-known that for weak complexes (with significant contributions from van der Waals type interactions) electron correlation is extremely important.¹⁷ Modern hard- and software now allows geometry optimizations of these systems at correlated levels. The use of pseudopotentials¹⁸ permits the extension of the study to the highly interesting complexes involving heavy noble gas atoms (e.g. Kr, Xe).

The comparison of CaH_2 and CaF_2 complexes is particularly interesting: Both CaX_2 species may be characterized as “quasilinear” with shallow bending potentials. However, CaH_2 has been found linear^{13f,19} (except for one study^{13b}), whereas most results on CaF_2 indicate it to be bent as an isolated molecule.^{12–15} This distinction also holds true at the theoretical levels employed in this study. We will follow the approach of DeKock et al.¹⁶ and simulate the host-guest interaction by calculating complexes with one inert-gas atom (or molecule) connected to Ca (head-on for CO and N_2), with resulting C_{2v} symmetry (see Figure 1). This is admittedly a crude model. However, we expect to obtain an approximate lower bound to the effects in real systems, provided the basis set superposition errors may be kept small.

We will focus on the structural and energetic characteristics of the model complexes, particularly on the ligand-induced bending of the CaX_2 fragment. Vibrational frequencies and intensities would also be highly interesting. However, to reflect the CaX_2 - L interaction correctly, such data need to be obtained at correlated levels, employing rather large basis sets. These calculations are beyond the scope of the present study. Nevertheless, the calculated structural and energetic results should aid the interpretation of matrix-isolation experiments involving floppy molecules.

Computational Details

Quasirelativistic multielectron fit (MEFIT) pseudopotentials, treating Ca as a 10-valence-electron system,¹⁹ the noble gas atoms as 8-valence-electron systems,²⁰ and fluorine as a 7-valence-electron system,²¹ have been used. For C, N, and O, we also employed pseudopotentials to replace the [1s]-core.²² The valence basis sets used for the SCF-optimizations are 6s6p5d on Ca,¹⁹ (6s6p1d)/[4s4p1d] on Ar, Kr, and Xe,²⁰ and (7s7p1d)/[4s4p1d] on Ne.²⁰ For C, N, and O, a diffuse sp-set²³ and one d-polarization function²⁴ have been added to (4s4p)/[2s2p] sets,²⁵ giving 3s3p1d-valence bases similar to that employed on F.^{15a} The basis

TABLE I: Geometries and Binding Energies for $\text{CaH}_2(\text{Ng})$ Complexes^a

Ng	$r(\text{CaNg})$	$r(\text{CaH})$	HCaH	$\Delta E_{\text{complex}}$		
				MP2	CEPA1/B2//B1 ^b	+CPC ^d
Ne B1	3.309	2.044	173.9	-0.20	-0.42	-0.22
B1	3.415	2.044	linear ^c	-0.18	-0.38	-0.17
B2 ^b	2.849	2.042	167.4	-0.60		
B2 ^b	2.962	2.044	linear ^c	-0.50		
Ar B1	3.182	2.042	164.7	-1.21	-1.40	-0.87
B1	3.272	2.045	linear ^c	-1.01	-1.13	-0.50
Kr B1	3.335	2.041	162.0	-1.56	-1.52	-1.04
B1	3.438	2.045	linear ^c	-1.27	-1.21	-0.62
Xe B1	3.537	2.042	161.2	-2.04	-2.03	-1.32
B1	3.635	2.046	linear ^c	-1.71	-1.72	-0.80
B2 ^b	3.517	2.043	160.5	-2.30		
B2 ^b	3.614	2.047	linear ^c	-1.94		
free CaH_2		2.045	linear			

^aDistances in angstroms, angles in degrees, energies in kilocalories per mole; MP2 geometries. ^bB2: 4s4p3d1f Ng basis. B1: 4s4p1d Ng basis. ^cLinear CaH_2 fragment enforced. ^dCEPA 1 results with counterpoise correction.

TABLE II: Geometries and Binding Energies for $\text{CaF}_2(\text{Ng})$ Complexes^a

Ng	$r(\text{CaNg})$	$r(\text{CaF})$	FCaF	$\Delta E_{\text{complex}}$		
				MP2	CEPA1/B2//B1 ^b	+CPC ^d
Ne	2.840	2.026	156.2	-0.88	-1.54	-0.95
	2.879	2.035	linear ^c	-0.56	-1.22	-0.79
Ar	3.015	2.026	154.2	-2.75	-2.68	-1.85
	3.051	2.036	linear ^c	-2.06	-2.22	-1.51
Kr	3.176	2.026	153.2	-3.16	-3.04	-2.16
	3.220	2.037	linear ^c	-2.35	-2.35	-1.62
Xe	3.386	2.027	151.8	-3.68	-3.56	-2.53
	3.439	2.038	linear ^c	-2.67	-2.72	-1.85
free CaF_2		2.025	155.6			
		2.034	linear ^c			

^aDistances in angstroms, angles in degrees, energies in kilocalories per mole. ^b4s4p3d1f Ng basis. ^cLinear CaF_2 fragment enforced. ^dCEPA 1 results with counterpoise correction.

sets and pseudopotentials on Ca and F are the same as those used in our previous studies on alkaline earth hydrides¹⁹ and dihalides.¹⁵ Dunning and Hay's hydrogen (4s1p)/[2s1p] set²⁶ was employed.

For MP2²⁷ optimizations, one f-function on Ca¹⁹ was added to help better describe core-valence correlation effects. This is also true for the CEPA 1²⁸ single point calculations of the binding energies at the MP2-optimized geometries. For these single point calculations the d-function on the noble gas atoms has been replaced by a 3d1f-set²⁰ (we denote this extended basis as B2, the smaller as B1). In two cases ($\text{CaH}_2(\text{Ne})$ and $\text{CaH}_2(\text{Xe})$), additional MP2 optimizations with the extended basis set (B2) have been carried out.

To obtain the linearization energies of the XCax fragment, we also have performed partial MP2 optimizations with the XCax angle fixed at 180°. The use of size-consistent methods like MP2²⁷ or CEPA 1²⁸ is mandatory for the calculation of binding energies in these weak complexes. Hartree-Fock gradient geometry optimizations and numerical MP2-optimizations have been performed with the Gaussian 88 program,²⁹ whereas CEPA 1²⁸ single point calculations employed the MOLPRO program.³⁰

Results

A. Geometries. Tables I-IV summarize the optimized geometries and binding energies ($\text{CaX}_2 + \text{L} \rightarrow \text{CaX}_2(\text{L})$) for the model systems. As Hartree-Fock calculations cannot describe faithfully the weak intermolecular interactions with large dispersion contributions present in the $\text{CaX}_2(\text{Ng})$ complexes, only MP2 geometries are given in Tables I and II. SCF and correlated results are given for $\text{L} = \text{CO}, \text{N}_2$ (Tables III and IV). However, even for these relatively strong complexes, correlation shortens the bonds considerably (compare the SCF and MP2 M-L distances). The contraction of the Ca-F and Ca-H bond lengths due to core-valence correlation for the complexes is similar to that for the free molecules.^{15a,19}

The performance of the 4s4p1d noble gas basis sets used in most of the MP2 optimizations may be judged by comparing results

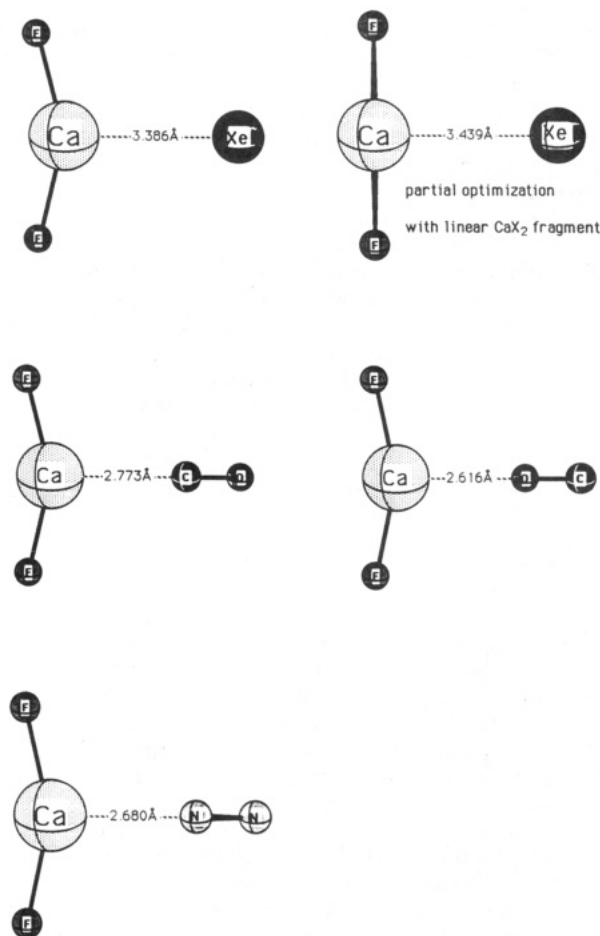


Figure 1. Structures for some of the model complexes studied.

TABLE III: Geometries and Binding Energies for CaH₂(L) Complexes (L = CO, N₂)^a

(a) SCF Geometries and Energies											
L	r(CaL)	r(CaH)	r(CO(NN))	HCaH	ΔE _{complex}	L	r(CaL)	r(CaH)	r(CO(NN))	HCaH	ΔE _{complex}
CO	2.944	2.086	1.097	164.9	-4.72	free CaH ₂		2.082		~linear	
OC	2.668	2.084	1.108	159.0	-4.32	free CO			1.102		
N ₂	2.837	2.083	1.071	162.8	-3.45	free N ₂			1.072		

(b) MP2 Optimizations and CEPA 1 Energies								
L	r(CaL)	r(CaH)	r(CO(NN))	HCaH	ΔE _{complex}			
					MP2	CEPA1	+CPC ^c	
CO	2.817	2.047	1.136	163.0	-7.53	-6.62	-5.40	
	2.796	2.050	1.137	linear ^b	-7.13	-6.35	-4.87	
OC	2.682	2.044	1.144	161.4	-3.78	-4.56	-3.52	
	2.709	2.047	1.143	linear ^b	-3.37	-4.00	-2.74	
N ₂	2.732	2.046	1.124	163.2	-5.64	-5.29	-4.02	
	2.731	2.048	1.124	linear ^b	-5.21	-4.93	-3.42	
free CaH ₂		2.045		~linear				
free CO			1.141					
free N ₂			1.125					

^a Distances in angstroms, angles in degrees, energies in kilocalories per mole. ^b Linear CaH₂ fragment enforced. ^c CEPA 1 results with counterpoise correction.

TABLE IV: Geometries and Binding Energies for CaF₂(L) Complexes (L = CO, N₂)^a

(a) SCF Geometries and Energies											
L	r(CaL)	r(CaF)	r(CO(NN))	FCaF	ΔE _{complex}	L	r(CaL)	r(CaF)	r(CO(NN))	FCaF	ΔE _{complex}
CO	2.883	2.037	1.096	158.8	-6.42	free CaF ₂		2.033		162.8	
OC	2.615	2.035	1.109	154.7	-6.08	free CO			1.102		
N ₂	2.766	2.035	1.071	157.6	-5.12	free N ₂			1.072		

(b) MP2 Optimizations and CEPA 1 Energies								
L	r(CaL)	r(CaF)	r(CO(NN))	FCaF	ΔE _{complex}			
					MP2	CEPA1	+CPC ^c	
CO	2.773	2.033	1.135	153.0	-9.40	-8.64	-7.21	
	2.754	2.044	1.136	linear ^b	-8.41	-7.83	-6.52	
OC	2.616	2.030	1.144	155.3	-5.27	-6.47	-5.05	
	2.619	2.039	1.143	linear ^b	-4.62	-5.69	-4.35	
N ₂	2.680	2.031	1.123	154.7	-7.30	-7.28	-5.65	
	2.668	2.041	1.123	linear ^b	-6.61	-6.60	-5.02	
free CaF ₂		2.025		155.6				
free CO			1.141					
free N ₂			1.125					

^a Distances in angstroms, angles in degrees, energies in kilocalories per mole. ^b Linear CaF₂ fragment enforced. ^c CEPA 1 results with counterpoise correction.

for CaH₂(Ne) and CaH₂(Xe) obtained with the extended 4s4p3d1f Ne and Xe bases (cf. B2 in Table I). The significant Ca-Ne bond contraction observed with the extended basis (>0.4 Å) indicates that the description of the polarizability of the small and only weakly bound Ne atom probably is inadequate even at this level of theory (note the 6° change in the H-Ca-H angle). On the other hand, the difference of the Ca-Xe distance in CaH₂(Xe) at the two basis set levels is only ca. 0.02 Å. The angle changes by less than 1°. Thus, the smaller basis set already gives good results for the more polarizable and more strongly bound Xe. The behavior for Ar and Kr is expected to be intermediate. The CO and N₂ complexes are probably less basis set dependent than the noble gas systems. The qualitatively correct description of the binding in the model complexes by MP2 calculations is supported by the energies obtained at the CEPA 1 level (section B).

The Ca-Ng distances in the partially optimized structures with linear X-Ca-X fragments are significantly larger. This is more pronounced for X = H (ca. 0.1 Å) than for X = F (ca. 0.03-0.05 Å). The CO and N₂ complexes show either a small 0.03-Å Ca-L lengthening (CaH₂(OC)), no significant effect (CaH₂(N₂), CaF₂(OC)), or a small 0.01-0.02-Å contraction (CaX₂(CO), CaF₂(N₂)). These results indicate appreciable dipole/induced-dipole contributions to the binding in the noble gas complexes. No such contributions are possible for linear CaX₂ fragments. In general, the Ca-X distances in the linear fragments are slightly longer than for the fully optimized systems, in agreement with the behavior of free MX₂ species (M = Ca, Sr, Ba).^{14,15,19,31} This

is mostly due to the improved covalent bonding contributions involving metal d-orbitals in the bent structures. Comparison of the Ca-X distances in the partially optimized complexes and that in linear CaX₂ indicates a slight lengthening due to complexation (Tables I-IV). These two effects, Ca-X bond lengthening due to CaX₂-L binding and shortening due to the decreased X-Ca-X angles, partially cancel for the fully optimized complexes.

The decrease of the X-Ca-X angles upon complexation shows that indeed structural changes are induced by the interactions with the inert-gas particles. CaH₂, which is calculated linear as a free molecule, bends even upon interaction with the extremely weakly complexing Ne atom. While the F-Ca-F angle in CaF₂(Ne) is slightly larger than that in CaF₂, this is probably due to the small Ne basis (cf. the B2 optimization data for CaH₂(Ne) in Table I). In all other cases, the F-Ca-F angles in the complexes are slightly smaller than those in CaF₂ (Tables II and IV). Obviously, the structural changes due to complexation are larger in CaH₂ than in CaF₂, indicating an even more floppy behavior of the former.^{15,19}

While the angles in the CaX₂(Ng) complexes decrease approximately with increasing binding energy (Tables I and II, cf. section B), the behavior is less straightforward with L = CO: For example, the angles in CaX₂(CO) are larger than those in CaX₂(Xe), in spite of the larger binding energies of the CO complexes. Moreover, the angle in CaF₂(CO) is smaller than that in CaF₂(OC), whereas the behavior is reverse in the corresponding CaH₂ derivatives. However, in view of the relatively small angle

TABLE V: XC_2X Linearization Energies (kcal/mol) for $\text{CaX}_2(\text{L})$ Complexes^a

complex	MP2	CEPA 1	LILE-(MP2) ^b	LILE-(CEPA1) ^b
free CaH_2	-0.18	-0.18		
$\text{CaH}_2(\text{Ne})$	0.02	0.04	0.20	0.22
$\text{CaH}_2(\text{Ar})$	0.20	0.27	0.38	0.43
$\text{CaH}_2(\text{Kr})$	0.29	0.31	0.47	0.49
$\text{CaH}_2(\text{Xe})$	0.33	0.31	0.51	0.49
$\text{CaH}_2(\text{CO})$	0.40	0.27	0.58	0.45
$\text{CaH}_2(\text{OC})$	0.41	0.56	0.59	0.74
$\text{CaH}_2(\text{N}_2)$	0.43	0.68	0.61	0.84
free CaF_2	0.24	0.22		
$\text{CaF}_2(\text{Ne})$	0.32	0.32	0.08	0.10
$\text{CaF}_2(\text{Ar})$	0.69	0.46	0.35	0.24
$\text{CaF}_2(\text{Kr})$	0.81	0.69	0.49	0.47
$\text{CaF}_2(\text{Xe})$	1.01	0.84	0.69	0.62
$\text{CaF}_2(\text{CO})$	0.99	0.81	0.67	0.59
$\text{CaF}_2(\text{OC})$	0.65	0.78	0.33	0.56
$\text{CaF}_2(\text{N}_2)$	0.69	0.68	0.45	0.46

^aEnergies without counterpoise corrections (CPC) were employed. CPC slightly changes all values (cf. Table I-IV). ^b"Ligand-induced linearization energies" obtained after subtracting the free CaF_2 linearization energy or the energy needed to bend CaH_2 to 160° , respectively.

changes ($<2^\circ$) not too much emphasis should be placed on these differences.

The N-N distances in the N_2 complexes do not deviate significantly from that in free N_2 . Slightly larger effects are observed with CO: While the C-O distances in the $\text{CaX}_2(\text{CO})$ complexes are ca. 0.005 Å shorter than that in carbon monoxide (in agreement with the small antibonding character of the HOMO in CO),³² the O-bound species exhibit somewhat larger C-O distances.

B. Energies. In all cases, the agreement between MP2/B1 and CEPA 1/B2//MP2/B1 energies is reasonable. Obviously, the shorter distances obtained with the extended Ng basis sets, (MP2/B2) for $\text{CaH}_2(\text{Ne})$ and $\text{CaH}_2(\text{Xe})$ (Table I), lead to somewhat larger binding energies, particularly for Ne.

A reasonably accurate description of the dipole moment of CO (well-known to have the wrong sign at the HF level³³) is critical for the $\text{CaX}_2(\text{CO})$ and $\text{CaX}_2(\text{OC})$ species (cf. Tables III, IV). Thus, the preference for C-binding is considerably underestimated at the HF level.¹⁶ As judged by the CEPA 1 energies, MP2 to some extent overestimates the binding energies for $\text{CaX}_2(\text{CO})$ but underestimates those for $\text{CaX}_2(\text{OC})$. In contrast, the agreement between CEPA 1 and MP2 energies is excellent for $\text{CaX}_2(\text{N}_2)$. The fact that significant binding energies with $\text{L} = \text{CO}, \text{N}_2$ are obtained already at the HF level indicates orbital-controlled contributions to the binding in these species.

To estimate the magnitude of basis set superposition errors (BSSE) of the binding energies, we have applied the counterpoise correction^{34a} to the CEPA 1 calculations (cf. last column in Tables I-IV). The relative contributions of the BSSE to the CEPA 1 binding energies range from ca. 17% in $\text{CaF}_2(\text{CO})$ to ca. 48% in $\text{CaH}_2(\text{Ne})$; i.e. BSSE is most critical for the weakest bonds. As the counterpoise correction tends to overestimate the BSSE (however, note ref 34b), the energies in the last two columns should provide reasonable upper and lower bounds of the binding energies.

The order of magnitude and the trends of the interactions should thus be reproduced satisfactorily by our calculations. The "inertness" trend of the "host" particles, $\text{Ne} \gg \text{Ar} > \text{Kr} > \text{Xe} > (\text{OC}) > \text{N}_2 > \text{CO}$, is in agreement with chemical experience.³⁵ The binding energies for CO, for N_2 , and for the heavier noble gases Kr and Xe are indeed chemically significant. Interactions at least of this magnitude can be expected in matrices comprised of these gases.

Tables I-IV show that the binding energies for the complexes optimized with the linear X-Ca-X fragment constraint are generally reduced compared to the unrestricted geometries. The linearization energies of the CaX_2 fragments within the complex are compared in Table V. While bending of free CaH_2 to ca.

160° costs ca. 0.2 kcal/mol, linearization of the bent CaH_2 fragments in the $\text{CaH}_2(\text{L})$ complexes (with $\text{L} = \text{CO}, \text{N}_2$) requires ca. 0.5 kcal/mol. The linearization energies for the heavier noble gas complexes are ca. 0.3 kcal/mol.

The F-Ca-F linearization energies in $\text{CaF}_2(\text{L})$ ($\text{L} = \text{Xe}, \text{CO}, \text{N}_2$) are comparable and increase slightly from $\text{L} = \text{Ne}$ to $\text{L} = \text{Xe}$. To compare the results for CaH_2 and CaF_2 , Table V (last column) also gives the values obtained after subtracting the linearization energy in free CaF_2 (for the $\text{CaF}_2(\text{L})$ complexes) or the energy required to bend CaH_2 to 160° (for the $\text{CaH}_2(\text{L})$ species). We term this measure the "ligand-induced linearization energy" (LILE). Except for $\text{CaX}_2(\text{Ne})$ and $\text{CaX}_2(\text{Ar})$ (where the electron correlation contributions probably have not been considered adequately), the LILEs range from ca. 0.4 kcal/mol to 0.9 kcal/mol. There is a rough increase with increased binding energy, but the trend is not monotonous. As the energies involved are very small, some scattering of the data is to be expected (the linearization energies for the $\text{CaH}_2(\text{L})$ species slightly increase when the counterpoise correction is applied, while those in the $\text{CaF}_2(\text{L})$ derivatives slightly decrease; cf. binding energies in Tables I-IV). However, the values are significant, and the extra linearization energies induced by complexation are usually larger than the linearization energy of free CaF_2 .

Conclusions

From ab initio pseudopotential calculations on the simple model complexes $\text{CaX}_2(\text{L})$ ($\text{X} = \text{H}, \text{F}; \text{L} = \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}, \text{CO}, \text{N}_2$), order-of-magnitude estimates of interactions expected for floppy molecules in inert-gas matrices have been obtained. Chemically significant interaction energies of ca. 4-8 kcal/mol for $\text{L} = \text{CO}, \text{N}_2$ and still appreciable binding energies of ca. 1-3 kcal/mol for $\text{L} = \text{Kr}, \text{Xe}$ warrant care when data obtained for floppy molecules isolated in inert-gas matrices are interpreted. The model employed is too simple to make specific predictions for the structural changes induced by the matrix. Other coordination modes, e.g. cyclic structures for CO or N_2 complexes³⁶ or coordination to F or H, may have to be considered. However, it is clear from the present study that both angles and bond distances may be affected by the environment.

Electron correlation and extended basis sets are extremely important for reliable predictions on the species studied. An extension of these investigations to the calculation of vibrational frequencies would be interesting. More realistic model systems have to be studied before definitive conclusions for inert-gas matrices can be drawn. Ever faster computers and more efficient programs will make this possible eventually.

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Diffusion Effects on Pyrene Excimer Kinetics: Determination of the Excimer Formation Rate Coefficient Time Dependence¹

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A numerical method is presented to recover the excimer formation rate coefficient from the experimental monomer and excimer decay curves. This method was applied to study pyrene monomer-excimer kinetics in cyclohexanol from 25 °C up to 85 °C. We observed that the time evolution of the rate coefficient deviates from the Smoluchowski equation, showing a minimum at high temperatures and concentrations, when the reversibility effects are more pronounced.

I. Introduction

Since the earliest days of this century there has been special interest in the rate of reactions that are influenced by the diffusive motion of the reactants. Many types of processes fall within this category: aggregation phenomena, enzyme-substrate binding, reassociation of photodissociated pairs, relaxation phenomena following pH or temperature jump, and fluorescence and phosphorescence quenching reactions. The feature that distinguishes these processes is the early time behavior, in which the redistribution of the reactants competes with the intrinsic chemical reaction step.

With the recent developments in picosecond lasers and improved fluorescence quenching measurements, it is now possible to study these transient effects with greater precision. The forward reaction

rate for diffusion-influenced processes²⁻⁵ is normally described in terms of a time-dependent rate coefficient $k_f(t)$. For irreversible reactions, $k_f(t)$ decays from its initial value at $t = 0$ to a steady-state value k_f^s . At times not too close to zero, the decay takes the form

$$k_f(t) = 4\pi N'_A D \sigma'_{\text{eff}} \left[1 + \frac{\sigma'_{\text{eff}}}{(\pi D t)^{1/2}} \right] \quad (1)$$

where N'_A is Avogadro's number per millimole, σ'_{eff} is an effective reaction radius, and D is the mutual diffusion coefficient of the reactants. In recent years, good experimental evidence has been provided in support of this behavior from fluorescence quenching measurements.⁶⁻⁹

For reversible reactions, the description of the reaction kinetics is much more complex.¹⁰⁻¹⁴ Conceptually, one imagines that the reverse reaction generates reactants at different times in close

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