THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2006, *110,* 2−4
Published on Web 12/13/2005

Blue Shift in X−H Stretching Frequency of Molecules Due to Confinement

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Received: October 21, 2005; In Final Form: November 21, 2005

The effect of spatial confinement on the properties of isoelectronic molecules HF, H_2O, NH_3, and CH_4 has been studied by encapsulating them in a C_{60} fullerene cage. Second-order Møller−Plesset perturbation theoretical (MP2) calculations suggest that all the guest species are stable inside the fullerene cage. This stabilization arises from the dispersion interaction between the guest and the host. It is shown that the excitation energy ($E_{\sigma^*} - E_\sigma$) for the X−H bond increases and that there is a blue shift in the stretching frequencies due to confinement.

1. Introduction

Spatial confinement can influence the physical and chemical properties of the trapped species to a large extent, if the size of the confining cavity is comparable to that of the quantum object. The problem of a particle in a box remains a classic example of confinement leading to quantization. With the developments in nanoscience and nanotechnology, properties of atoms and molecules under the confines of nanotubes and nanocages acquire special significance. We show in this Letter that molecules such as HF, NH_3, H_2O, and CH_4 confined to the inner space of a fullerene cage exhibit a blue shift in their stretching frequencies.

Confinement of atoms, ions and molecules under spherical potentials has been studied in the earlier literature. For a recent review on the subject, see ref 1. Bond properties and chemical reactivities of molecules trapped inside a cavity change dramatically. Auluck and Kothari[2] considered a model for a confined harmonic oscillator and proposed that the effect of confining the oscillator is to displace its energy levels toward higher energies, resulting in a blue shift of its stretching frequency. Singh[3] studied the problem of H_2^+ in a spheroidal box and reported the increase of total energy of the system due to confinement. Structure and spectral properties of an H_2 molecule confined in a spherically symmetric harmonic oscillator potential were studied using the configuration interaction method by Waz et al.[4] They reported a shortening of bond length and a blue shift in the absorption and emission bands with an increase in confining strength.

The electronic structure of a Li_2 molecule confined in an anisotropic harmonic oscillator potential has been studied for different confining strengths by Sako et al.[5] They have reported that the electron density of the confined Li_2 molecule is squeezed when compared to that of the free molecule. As a result, the equilibrium bond length is decreased with increase in confinement strength.

Cruz and Soullard[6] have studied recently the effect of pressure on the ground-state energies and molecular conformations of methane, ammonia and water molecules. They found that the rise in the ground-state energy for these confined molecules depends on the confinement radius. The bond compressibility due to confinement varied in the order $CH_4 > NH_3 > H_2O$.

The effect of confining atoms, ions and molecules to the inner space of a fullerene cage was examined by Cioslowski and coworkers.[7,8] Using Hartree−Fock method and 4-31G basis set for the host cage and double-ζ basis set for the guest species, they found that the cage remained intact in all the cases and that the endohedral complexes containing ions and polar molecules were stabilized and the ones containing nonpolar molecules or neutral atoms were destabilized relative to the separated host and guest species. In a majority of endohedral complexes containing diatomic molecules, they found that the bond length of the guest species decreased and the stretching frequency increased due to the confinement.

Rubin et al.[9] have shown that it is possible to prepare He@C_{60} and that the insertion of He inside a fullerene cage occurs possibly through the opening of one of the C−C bonds. Encapsulation of H_2 inside the fullerene cage by the molecular surgery method, that is, opening of the cage, insertion of the guest species and subsequent cage closure, has been reported recently by Komatsu et al.[10] Insertion of H_2O inside a fullerene derivative has also been reported by Iwamatsu et al.[11]

In a recent study, Ramachandran and Sathyamurthy[12] have reported the effect of nonpolar confinement on water clusters by encapsulating them in a fullerene cage by their MP2/6-31G calculation and have shown that the cage containing water molecules was intact and that the water clusters assumed structures drastically different from those in the gas phase. The hydrogen bonds were no longer intact due to the pressure exerted by the cage. For details of other studies on endohedral fullerene systems, see the references provided therein.

To study further the properties of molecules in such a confined environment, we have undertaken an ab initio investigation of HF, H_2O, NH_3, and CH_4 inside the C_{60} cage. The details of the methodology and the results follow.

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10.1021/jp056027s CCC: $33.50

TABLE 1: Stabilization Energies and Other Results for Certain Endohedral Fullerenes

	ΔE_{stab} (kcal/mol)		X−H bond length (Å)	X−H stretching frequencies[b] and the blue shifts ($\Delta\nu$) (cm^{-1})				X−H force constant[b] (N/m)	dipole moment (Debye)	$\Delta E^{c,d}$ (kcal/mol)
system	HF/6-31G	MP2/6-31G[a]		symm	$\Delta\nu$	asym	$\Delta\nu$			
HF			0.9209	3692				850	2.3	1108
$HF@C_{60}$	−2.50	−7.5	0.9214	3693	1			850	0.54	1129
H_2O			0.9497	3560		3701		775	2.5	1103
$H_2O@C_{60}$[e]	−0.40	−10.6	0.9485	3601	41	3731	30	793	0.5	1124
NH_3			0.9912	3376		3559		680	1.4	1047
$NH_3@C_{60}$	+6.25	−10.8	0.9900	3414	38	3596	37	695	0.3	1062
CH_4			1.0821	2841		2943		479	0.0	877
$CH_4@C_{60}$	+17.6	−7.84	1.0690	2979	138	3100	157	527	0.0	907

[a] Single point calculation on HF/6-31G optimized geometry. [b] Scale factor of 0.8929 has been used for the frequency values and 0.7972 for the force constants.[16] [c] $\Delta E = E_{\sigma^*(\text{X-H})} - E_{\sigma(\text{X-H})}$. [d] Obtained from NBO analysis by MP2/6-31G//HF/6-31G calculations. [e] Some of the entries in this row differ slightly from those reported in ref 12, because of the slightly different orientation of H_2O inside the cage in the present study.

2. Methodology

Geometry optimization for all systems under investigation was carried out using the Gaussian 03 suite of programs.[13] The Hartree−Fock (HF) method with the 6-31G basis set was used for geometry optimization and frequency calculations. Single point energy calculations using second-order Møller−Plesset perturbation (MP2) theory with 6-31G basis set were carried out for the HF/6-31G optimized geometries. Natural bond orbital analysis (NBO) has also been performed in this level of calculation.

3. Results and Discussion

In the case of guest species of XH_n type, the X (X = F, O, N, C) atom is found to be located slightly off center, inside the fullerene cage. The O atom is displaced by 0.11 Å from the center of the cage. The displacements for N and C atoms from the cage centers are 0.06 and 0.0001 Å, respectively, for $NH_3@C_{60}$ and $CH_4@C_{60}$.

After encapsulation, the bond parameters of the C_{60} cage remain essentially unaltered. The radius of the C_{60} cage (3.53 Å) obtained by HF/6-31G optimization remains nearly the same (within ±0.001 Å), indicating that the guest molecules are situated almost freely inside the cage.

The stabilization energy (ΔE_{stab}) of the endohedral complexes is calculated as

$$\Delta E_{\text{stab}} = E_{\text{complex}} - (E_{\text{cage}} + E_{\text{guest}})$$

The Hartree−Fock calculations predict ΔE_{stab} to be −2.50, −0.40, +6.25, and +17.6 kcal/mol for $HF@C_{60}$, $H_2O@C_{60}$, $NH_3@C_{60}$, and $CH_4@C_{60}$, respectively, as listed in Table 1. After zero point correction is applied, the stabilization energies become −2.15 kcal/mol for $HF@C_{60}$, +0.49 kcal/mol for $H_2O@C_{60}$, +7.90 kcal/mol for $NH_3@C_{60}$, and +19.54 kcal/mol for $CH_4@C_{60}$.

Single point MP2/6-31G calculations for HF/6-31G optimized structures predict that all the guest species get stabilized inside the C_{60} cage showing the importance of electron correlation in these systems. The stabilization energies are −7.5, −10.6, −10.8, and −7.84 kcal/mol for $HF@C_{60}$, $H_2O@C_{60}$, $NH_3@C_{60}$, and $CH_4@C_{60}$, respectively. Thus the encapsulation of a guest species by the C_{60} cage leads to a lowering of total energy and this stabilization arises from the dispersive interaction between the guest molecule and the fullerene cage.

A careful examination of the HOMO−LUMO gap of fullerene shows that it is only slightly perturbed on encapsulation, indicating a weak interaction between the host and the guest and the absence of any charge transfer between them. The natural bond orbital analysis suggests that the energy gap between σ(X−H) and σ^*(X−H) of the guest molecules increases on encapsulation as illustrated in Table 1.

In the HF/6-31G optimized geometry of the complexes, the O−H, N−H, and C−H bond lengths are found to be decreased slightly from those of the free molecules as shown in Table 1. The decrease is found to be 0.001 Å for the O−H and N−H bonds. For C−H bond the decrease is 0.0131 Å. The H−F bond length increases by 0.0005 Å on encapsulation.

The H−X−H bond angles of the guest molecules are not affected much on encapsulation. In the HF optimized structure, the distance between the H atom of the guest molecule and the cage falls in the range 2.4−2.7 Å, close to the kind of distances observed in weak hydrogen bonds.[14] The average hybridization of carbon atoms[15] in C_{60} is known to be $sp^{2.27}$. This indicates that the p orbital is more diffused outward than inside and decreases the probability of hydrogen bonding with the inner π cloud of the cage. The absence of hydrogen bonding in the system is indicated by the absence of any red shift in the X−H stretching frequencies (see below).

The dipole moment of a bare C_{60} cage is zero. However, the encapsulation of a polar guest species polarizes the cage in such a way that the carbon atoms of the cage pointing toward the positively charged atoms of the guest species become negatively charged and those near the negatively charged atoms of the guest species become positively charged. As a result, there is a drop in the net dipole moment for these systems.

Frequency analysis of the encapsulated species was carried out using the HF method and 6-31G basis set for the HF/6-31G optimized structure. The resulting frequencies were found to be real, indicating that the geometries obtained correspond to real minima. They were scaled by a factor of 0.8929 following the standard practice.[16] For all the endohedral complexes studied, the X−H stretching frequency of the guest molecule *increases* on encapsulation. The blue shift due to encapsulation is the lowest for HF and highest for CH_4. It varies in the order $CH_4 > NH_3 \sim H_2O > HF$. The force constant of the corresponding bonds varies in the order H−F > O−H > N−H > C−H. That is, lower the force constant, the more vulnerable is the bond to confinement and higher is the blue shift in stretching frequency as illustrated in Table 1. This is also in keeping with the increased bond length and hence increased steric repulsion with the cage, in going from HF to CH_4.

Cioslowski had already predicted a blue shift in the stretching frequencies of H_2, N_2, CO, and LiH encapsulated inside the fullerene.[8] Interestingly, there was a slight blue shift or a slight red shift in the stretching frequency of FH, depending on its orientation. Using density functional theoretic calculations, Charkin et al.[17] had also predicted a blue shift in the stretching frequencies of MX_4 type species inside $C_{60}H_{36}$ and related cages.

Molecular clathrates are known to acquire fullerene like structures.[18] For $CH_4@(H_2O)_{20}$, the vibrational frequencies have been computed by us at the HF/6-31G* level and it is found that the symmetric and asymmetric stretching frequencies of CH_4 undergo a blue shift of 26 and 33 cm^{-1}, respectively, due to the confinement arising from the $(H_2O)_{20}$ cage.[19]

A blue shift in C−H stretching frequencies of molecules involved in hydrogen bonds has been discussed in detail by Li et al.[20] Results reported in the present study are different from their results in that there is no indication of hydrogen bond between the guest molecule and the host cage. Therefore, it is reasonable to conclude that the blue-shift arises from confinement.

4. Conclusion

In summary, our calculations show that the isoelectronic species HF, H_2O, NH_3, and CH_4 are stabilized inside the C_{60} cage. Although the HOMO−LUMO gap of C_{60} is not affected much by encapsulation, the $\sigma-\sigma^*$ energy gap of the X−H bond increases significantly. There is a noticeable blue shift in the X−H stretching frequencies of the trapped molecules due to confinement.

Acknowledgment. O.S. thanks the Indian Academy of Sciences, Bangalore, for a summer fellowship. C.N.R. thanks the University Grants Commission, New Delhi for a fellowship. This study was supported in part by a grant from the Council of Scientific and Industrial Research, New Delhi.

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